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The Carbon Dioxide Adsorption Behaviour of Geological Samples of the South-Eastern Main Karoo Basin, South Africa

By

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of
MAGISTER SCIENTAE
in
GEOLOGY

to the
FACULTY OF SCIENCE
at the
UNIVERSITY OF JOHANNESBURG

SUPERVISOR: DR. NICOLA WAGNER
Declaration

I, Rowen Caleb Abraham, hereby declare that this dissertation submitted for the degree of Magister Scientiae in Geology at the University of Johannesburg, with exception of all other people's ideas gracefully acknowledged, is my own work. I recognise the help I have received from my supervisor Dr Nicola Wagner. I also declare that this research has not been submitted for any degree or examination in any other university or institute of higher education.

Rowen Caleb Abraham

Date
Dedication

The field of Earth Science

My Family & Friends

Dr. Nikki Wagner
Abstract

Carbon dioxide capture and geological storage has been recognised as an essential technique used to reduce CO₂ emissions into the atmosphere. The potential storage basin should consist of enough vacant space in the form of pore-spaces, and supercritical CO₂ must remain stable within the reservoir rock for storage to be feasible. This study considers the porosity and CO₂ adsorption capacity of potential seal or reservoir rock types with a depth of > 800 m, taken from the Willowvale area, South-Eastern Karoo Basin, South Africa. Samples were extracted from a borehole core drilled as part of the Karin project. The samples were selected at depths between ~ 800 – 2100 m, and the borehole intercepted most of the Main Karoo Basin stratigraphy. The samples consisted of typical rocks identified throughout the Karoo Basin: sandstones, shales, and dolerites. A variety of analytical techniques were used to predict storage or seal potential, including microscopy, X-Ray Diffraction (XRD), Brunauer-Emmet-Teller (BET), and High Pressure Volumetric Analysis (HPVA).

The mineralogy was determined using thin section petrography and confirmed by XRD. The sandstone samples consisted of: quartz; albite; chlorite; orthoclase, and muscovite; one sandstone sample (KWV-6) contained carbonates (dolomite). Typically, the shale samples consisted of: quartz; albite; chlorite; muscovite. The carbonaceous samples (KWV-14 and KWV-16) have clay (illite) and carbonate (calcite) compositions. The dolerites samples generally consist of: albite; anorthite, quartz, and diopside, dominated by plagioclase.

Porosity was determined both in thin section, through the microscopic assessment of dyed epoxy resin, and by BET. Microscopically, visible porosity was only found in sandstone samples KWV-2 and KWV-6 as isolated spaces within the rock. BET porosity was found to be very low, ranging between 0.995 – 1.5 % (vol. %) and 0.0032 – 0.0.0045 cm³/g pore volumes.

The CO₂ adsorption assessment by a High Pressure Volumetric Analyser conducted at the Illinois State Geological Survey, was problematic. Quantities of CO₂ adsorbed onto the rock samples were exaggerated, but the isothermal trends generated were usable. The isothermal trends and shapes of the graphs are comparable to literature in relation to their corresponding lithotypes. Excess adsorption ranges between 1.7 – 0.001 mol/g. Inflection points on isotherms were found with pressure ranges of ~5 – 10 MPa, where maximum adsorption was observed.

The results show that the rock samples of the South-Eastern Main Karoo Basin have the potential to adsorb CO₂, some more so than others. Dolerites were found to be the least adsorptive and the carbonaceous shale of the Whitehill Formation was found to adsorb the most CO₂. Hence, the dolerite could be considered as a suitable seal, and the Whitehill Formation as both a storage reservoir or seal.
Acknowledgements

I would first like to thank my supervisor Dr. Nikki Wagner of the Department of Geology at the University of Johannesburg. The door to Dr. Wagner’s office was always open whenever I ran into a tough spot or had a question about my research or writing. She consistently allowed this project to be my own work, but guided me in the right the direction whenever she thought I needed it. Not only did she assist with my research, she also found a means of funding for bursaries and covered the overseas travel expenses to the International Energy Agency for Greenhouse Gas (IEAGHG) Summer School held in Canada; for this I am eternally grateful.

To the South African Centre for Carbon Capture and Storage (SACCCS), I would like to extend my gratitude for funding this project, with special thanks to Ms. Evelyn Nyandoro for her attention to all my bursary needs. Additionally, a special mention to CIMERA for supplementing running cost to project.

I would also like to thank the experts who were involved in the analyses carried out for this research project: Dr. Gregory Okolo from the North-West University who assisted with BET analysis as well as his essential advice on the project; Mr. Baldwin in the SPECTRAU laboratory housed at the University of Johannesburg who made thin sections according to uncommon specifications; and Mr. Peter Berger of ISGS Illinois for running the HPVA experiments. Without their passionate participation and input, the critical analysis of this study could not have been successfully conducted.

Finally, I must express my very profound gratitude to my parents, Raymond and Beverley Abraham, for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this dissertation. This accomplishment would not have been possible without them. Thank you.

Author: Rowen Abraham.
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Acronyms

**BET**: Brunauer–Emmett–Teller

**CCGS**: Carbon Capture and Geological Storage

**CCS**: Carbon Capture and Storage

**CIMERA**: The Centre of Excellence and Integrated Energy and Mineral Resource Analysis

**EGR**: Enhanced Gas Recovery

**EOH**: End of Hole

**EOR**: Enhanced Oil Recovery

**GHG**: Greenhouse Gas

**GWF**: Global Warming Factor

**HPVA**: High Pressure Volumetric Analyser/Analysis

**KARIN**: Karoo Research Initiative

**KWV**: Karoo Willowvale area

**MKB**: Main Karoo Basin

**PSD**: Pore Size Distribution

**SAfECCS**: South-Africa Europe Cooperation in Carbon Capture and Storage

**STP**: Standard Temperature and Pressure

**UNFCCC**: United Nations Framework Convention on Climate Change

**WTO**: World Trade Organisation

**XRD**: X-Ray Diffraction
Chapter 1 Introduction

1.1 Background

The increase in anthropogenic CO\textsubscript{2} emissions, which have risen drastically over recent years, has impacted our environment negatively by their contribution to global climate change. Carbon dioxide is believed to contribute approximately 64\% to the enhanced ‘greenhouse effect’ (Bryant, 1997). CO\textsubscript{2} emissions from the combustion of fossil fuels for heat and electricity generation, accounts for 42\% of all global Co2 emissions, and emissions from other industrial sources accounting for 19\% (IEA, 2017).

Approximately 90\% of South Africa’s primary energy is derived from fossil fuels, with coal providing 92\% of electricity generated for the country’s energy requirements (South African Department of Environmental Affairs, 2010). An estimated amount of 85\% (119 Mt) of the total CO\textsubscript{2} emissions in South Africa recorded in 2008 were derived from fossil-fuel CO\textsubscript{2} emissions (Boden and Andres, 2011), which is mostly as a result of coal-fired power stations. South Africa is ranked 14th highest in terms of CO\textsubscript{2} emissions globally, having emitted more than 367 Mt of CO\textsubscript{2} in 2011 (IEA, 2013). There is, therefore, a serious need for South Africa to reduce its CO\textsubscript{2} emissions to keep up with global standards. South Africa has committed to reduce its CO\textsubscript{2} emissions in the order of 34\% by 2020 and 42\% by 2025 (Department of Environmental Affairs and Tourism, 2011). CCS has the potential to reduce overall CO\textsubscript{2} mitigation costs as well as increasing flexibility in attaining reduced Greenhouse Gas (GHG) emissions (IPCC, 2005), making it a viable option for South Africa’s requirements for CO\textsubscript{2} emission reform.

CCGS is a technique which includes processes consisting of the separation of CO\textsubscript{2} from industrial and energy related sources for transport to a geological storage site, where long term sequestration from the atmosphere takes place (IPCC, 2005). The current study is focused on the potential of geological storage where captured CO\textsubscript{2} would be confined within specific geological horizons. One of the primary aspects when assessing the suitability of a CO\textsubscript{2} storage site is the adsorption potential of the rock material in which sequestration is to take place.

High pressure adsorption techniques are used to link the adsorption potential of CO\textsubscript{2} on a rock substrate at specified high pressure intervals, recreating subsurface pressure regimes. The migration towards these high-pressure applications have created new challenges with regards to experimentally obtained adsorption data and their interpretations. The traditional protocols in calculating CO\textsubscript{2} adsorption when applied to measure and denote supercritical adsorption isotherms are presently being revisited, as they are considered to be less accurate according
to new knowledge (Gumma and Talu, 2010). Despite the significant developments which have been made regarding the accuracy of commonly used CO\textsubscript{2} adsorption techniques, as well as the expanding data pool knowledge, the actual mechanism of adsorption at high pressures in microporous material is still poorly understood (Pini, 2014).

This study focused on the CO\textsubscript{2} adsorption potential of shales, sandstones, and dolerites at conditions representative of deep sedimentary reservoirs. The CO\textsubscript{2} adsorption isotherms obtained for various shale, sandstone and dolerite lithologies found in the south-eastern South African Karoo Basin were assessed and compared to reference literature relating to similar rock types. This was done in conjunction with characterisation analyses pertaining to the pore space volume of the geological material, as well as the petrology.

1.2 What is Carbon-Dioxide Capture and Geological Storage?

CCGS is a mitigation technique used to restrict large amounts of CO\textsubscript{2} from being expelled into the atmosphere in response to global climate change interventions. The technology involves capturing CO\textsubscript{2}, produced from large scale industrial plants, and compressing it into a supercritical phase for transport, followed by an injection process which entails injecting this compressed supercritical CO\textsubscript{2} into a deep geological formation at carefully selected sites for permanent sequestration (Global Carbon Capture and Storage Institute, 2015).

The information of the density/volume of the adsorbed fluid is essential to define gas-reserves and potential capacity evaluations for CO\textsubscript{2} storage (Gumma and Talu, 2010). Within deep seated subsurface formations, the fluid pore pressure is fairly high (within the range of 10-30 MPa) where most gases are in a supercritical phase (Pini, 2014). Carbon dioxide needs to be stored in a supercritical phase as it acts like a gas in that it can diffuse readily through pore spaces of solids, and like a liquid, and that it takes up less space than the gas phase (Halland et al., 2012). As a supercritical fluid, CO\textsubscript{2} is 500 to 600 times denser than at surface conditions (Halland et al., 2012); this ensures a higher volume of CO\textsubscript{2} of which can be stored, as well as reducing buoyancy which would restrict upward migration.

The sequestration of CO\textsubscript{2} in rock formations is not an unfamiliar or unproven science as it has been used for years to enhance the recovery of hydrocarbons in oil and gas fields, known as enhanced oil or gas recovery (EOR/EGR). Also, natural CO\textsubscript{2} gas and other substances have been stored in geological reservoirs at a commercial scale for decades (Cloete, 2010). It is well known that specific geological formations have the capacity to store and preserve hydrocarbons for millions of years under certain conditions as these reservoirs are currently being economically exploited by the oil and gas industries globally. Using this as a model, it can therefore be implied, with a great amount of certainty, that the same or similar geological
conditions which meet the general criteria for storing hydrocarbons over geological time can therefore be used as a storage reservoir for CO₂.

1.3 Problem Statement

Due to the lack of conventional CO₂ storage capacity for the implementation of CO₂ sequestration in South Africa, there is a need to explore for unconventional storage mechanisms (Cloete, 2010). The South African Centre for Carbon Capture and Storage (SACCCS) have identified the on-shore Zululand Basin as a possible storage reservoir (Cloete, 2010). SACCCS have not yet considered the Main Karoo Basin (MKB) as a possible CO₂ storage reservoir.

The large, deep onshore Karoo Basin may also be possible storage target area, but it has not been studied for its CO₂ storage potential in terms of CO₂ adsorption. Research conducted in the Karoo Basin pertained to oil and gas exploration during the 1970’s to 1980’s and the CO₂ adsorption potential of the residing lithologies was not considered. The pore volume, fracture system and diffusivity of CO₂ within the rock horizons are not understood in this area. This study expects to address these uncertainties in the south-eastern area of the Main Karoo Basin with regards to CO₂ storage potential regarding 3 main factors: mineralogy, porosity and CO₂ adsorption potential.

1.4 Aim, Objectives & Research Questions

The aim of this study is to determine whether the rocks found in the south-eastern part of the Main Karoo Basin fit the criteria for CO₂ sequestration focusing on certain key aspects.

Under the umbrella of the given aim, a multitude of objectives were set out. The main objectives were:

a) use of routine analytical techniques including, thin section petrography and X-Ray Diffraction (XRD) to classify the geological samples according to their composition;

b) identify whether these rocks have available pore space to store CO₂ using BET;

c) to determine whether the sampled rock types found in the Willowvale area have the potential to adsorb CO₂ using HPVA; and finally

d) using the experimental results obtained from the different analyses to determine whether the sampled rocks are suitable for CO₂ storage in terms of their adsorption potential by comparing these results with published data.
The key research questions this study addresses are:

a) Do these rock samples have the capacity to adsorb CO₂?

b) Does the rock composition have an affect CO₂ adsorption?

c) Are the mineralogical compositions of the various rock types sampled conducive for CO₂ storage?

d) Are the sampled rocks of the various stratigraphic units consist of the porosity required to store large amounts of supercritical CO₂?

e) Are constructed CO₂ adsorption isotherms comparable with literature?

f) Is it conclusive (in terms of aspects assessed in this study) that the rock types found in this area of the Karoo Basin are suitable for CO₂ storage?

1.5 Scope

As part of the Centre of Excellence for Integrated Mineral and Energy Resources (CIMERA) shale gas exploration project in the Karoo Basin (known as the KARIN project), freshly drilled core was available for research. Geological material from the KWV-01 Willowvale borehole core drilled in the South-Eastern Karoo Basin, South Africa has been assessed by de Kock et al. (2016) in terms of shale gas potential. Comparable core material was assessed in the current study for its suitability for CO₂ sequestration, in terms of reservoir and seal rock. The samples were taken from depths required for supercritical CO₂ to remain stable, that is. The pore space volume and surface area of the potential reservoir rock ideally need to consist of an amount suitable to store large amounts of CO₂.

This study encompasses an array of aspects regarding the determination of CO₂ adsorption capacity of geological samples from the KWV-01 core, co-ordinates: S32°14’41’’ E28°35’08’’. The samples include sandstones, shales and dolerites, lithologies common in the Karoo Basin. The analytical aspects include mineralogical and physical characterisation as preliminary assessments leading to the adsorption capacity of the geological material.

By use of a combination of analytical techniques such as routine petrography and Brunauer-Emmett-Teller (BET), the pore space volume can be estimated in terms of supercritical CO₂ storage. Results obtained from the High Pressure Volumetric Analyser were expected to show positive adsorption potential of supercritical CO₂ for the samples obtained, thus supporting long term storage of both shale and sandstone lithologies. This is done to observe ability of these rock samples to adsorb CO₂ under specific temperature and pressure conditions, which allow supercritical CO₂ to remain stable. This would provide insight to how much CO₂ could be adsorbed under these conditions. Ultimately, adsorption capacity could be used to define the role of various lithologies in a CO₂ storage basin in terms of a potential reservoir for storing CO₂ or a seal/cap rock to contain stored CO₂. Just like in the oil/gas deposits, a reservoir and
a cap rock are two required aspects when exploring for a suitable CO₂ storage site for CCS and are routine assessments for oil/gas exploration (Bachu, 2000).

Mineralogical characterization is achieved by use of routine analytical techniques such as transmitted light petrography and XRD. This was done firstly to identify the mineralogy and major mineral phases in each sample in order to observe the difference in adsorption potentials of the various rock types.

The physical characterization aspect of this study involves identifying, classifying and quantifying pore spaces within the geological material. This was achieved by using a combination of techniques including thin section observations and the Brunauer-Emmitt-Teller (BET) experimental technique, to quantify pore space surface area and volume, essential in estimating storage capacity in terms of quantity of CO₂ which can be stored.

The key focus of the research pertained to the adsorption potential of these geological samples which were assessed in order to quantify the adsorption. A graphical approach (isotherms) was implemented to observe resulting volume changes due to CO₂ adsorption onto the geological material and quantified in excess adsorption isotherms. The experimental results were compared to case studies (Busch et al., 2008; Fujii et al., 2009; Fujii et al., 2010; Heller and Zoback, 2014) to determine whether the geological samples have indeed adsorbed CO₂. This research study essentially follows the works of Busch et al. (2008) and Fujii et al. (2009) in terms of experimental approach in assessing CO₂ storage potential of geological materials.

1.6 Regional Geology of the Study Area

The study area is located in the Willowvale region of the Eastern Cape province, South Africa (Fig. 1.1 and 1.2). This region represents the south-eastern part of the Main Karoo Basin. The succession of rocks found in this part of the basin consist of the Beaufort, Ecca and Dwyka Groups of the Karoo Supergroup, all of which were intercepted by the CIMERA-KARIN drilling project and recorded within the drillcore.

It is generally accepted that the Karoo sedimentation initiated during the Late Carboniferous period, at approximately 300 Ma, following a substantial tectonic event which occurred on the southern margin of the supercontinent (Gondwana) giving rise to the amalgamation of Pangea (Catuneanu et al., 2005; Johnson et al. 2006). Both the Cape and Karoo Basins are interpreted to have been developed under two large scale episodes of recurrent subsidence and sedimentation within Gondwana's interior (Tankard et al., 2009). Sedimentation of the Karoo continued across Gondwana until the breakup of the supercontinent during the Middle Jurassic at around 183 Ma, when sedimentation was terminated and replaced by the emplacement of
a Large Igneous Province (LIP) defined as the Drakensburg Group (Catuneanu et al., 2005; Duncan, et al., 1997).

The Main Karoo Basin’s sedimentary succession makes up a combined thickness of 12 km along its the southern margin preserved as a large erosional remnant of the Karoo Supergroup, encompassing in the order of two-thirds of the South African landscape (Fig. 1.1) (de Kock et al., 2016). In this region, the basin is confined by the Cape Fold Belt in the south, defined by a narrow region of crustal shortening and thickening, which had been developed as a result of the Late Paleozoic and Mesozoic subduction along this margin of Gondwanaland (Hansma et al., 2016; Tankard et al., 2009). The basin thins drastically northward forming an asymmetrical basin with variable thicknesses (de Kock et al., 2016).

The migration of Gondwana from high latitudes towards the equator changed environmental climatic conditions. This part of the Main Karoo Basin reflects the sequence of rock successions (Johnson et al., 1996; Tankard et al., 2009). The Dwyka Group is the lowermost stratigraphic unit (Fig. 1.3) and preserved within this succession are glacial deposits which marks the beginning of the Karoo sedimentation. The Main Karoo Basin then transitions into carbonaceous marine conditions (at around 290 Ma (Rubidge, 2005), developing deep submarine fans in the south and producing fluvio-deltaic systems to develop during equatorial migration, all of which is preserved in the Ecca Group (de Kock et al., 2016). As increasing arid conditions continued, the basin became more terrestrial, developing into a fluvial-lauacustrine environment which is preserved in the Beaufort Group (Smith, 1990, 1993). This was followed by dominant sedimentary fill comprising fluvial and aeolian sandstones of the Molteno, Elliot and Clarens Formations (Fig. 1.3) of the Stormberg Group (Smith, 1990, 1993). These successions represent an increase in arid conditions, where the final stages of sedimentation of the Main Karoo Basin, represented by the Elliot and Clarens Formations, show evidence to this within its aolian deposits, transitioning from playa lake and wadi-type environments, to dune sand dominated system (Smith, 1990). Sedimentation terminated basinwide at roughly 183 Ma given by the emplacement of the Karoo Large Igneous Province (LIP), where large amounts of basaltic lava outpoured onto the surface in the order of at least 1400 m thickness, known as the Drakensberg Group (Fig. 1.5) from a large feeder complex of dolerite sills and dykes (Jourdan et al., 2005; Svensen et al., 2012).

The main stratigraphic units intercepted by the Willowvale borehole consist of the Beaufort and Ecca Groups. The Balfour-Koonap Formations of the lower Beaufort Group were intercepted, marking the top of the hole at around an interval of 10 – 250 m, consisting of mudstone, sandstone, conglomerate, and dolerite lithologies. Following this, the interval 230 – > 2300 m spans the Ecca Group, making up the bulk of the borehole core. The first formation
of the Ecca Group observed here is the Waterford Formation, which consists of sandstone with minor shale laminations. Thereafter, the Fort Brown Formation (between 250 – 750 m interval of the KWV drillcore) consists of clay-pebble conglomerate, shale, sandstone and dolerite lithologies. Following the Fort Brown Formation is the Ripon Formation, which ranges from 750 – 2100 m (Fig. 1.4a), consisting of stratigraphic units of the Trumpeters, Wonderfontein and Pluto’s Vale Members. These units consist of an array of lithologies comprising sandstone, mudstone (or shale), dolerite and gabbro (Fig. 1.4b). Sedimentary successions found here display well-formed sedimentary structures and have been intruded by dolerites at specific intervals throughout the entire formation. The base of the borehole intercepted the lower units of the Ecca group, namely the Collingham, Whitehill and Prince Albert Formations consisting of sandstone, shale (including organic-rich shales) and dolerite. The End of Hole (EOH) of the KWV borehole occurred at a depth of 2352.39 m; marking the base of the borehole is the Dwyka Group consisting of glacial diamictites.
Fig. 1.1 - Simplified geological map and cross-section of the Karoo Basin, showing dolerite dykes and sills of the southern part of the basin compiled by de Kock et al. (2016). The KWV-01 Willowvale drill-site is highlighted in a blue box in cross section (borehole co-ordinates: S32°14’41’’ E28°35’08’’ at elevation 263m).

Fig. 1.2 - Regional geology of the study area. The circled red star indicates the location of the drill site co-ordinates: S32°14’41’’ E28°35’08’’. This image was modified by de Kock et al. (2016) from the 1:250 000 scale 3228 Kei Mouth map-sheet of the Council for Geoscience.
Figure 1.3 – Lithostratigraphic subdivisions of the Karoo Supergroup within the Main Karoo Basin compiled by Catuneanu et al. (2005) based on the time scale of Palmer (1983) and information from Rubidge (2005). Highlighted in red are the stratigraphic units from which samples were acquired for this study, although the thickness of these units differ to those intercepted in KWV-01.
<table>
<thead>
<tr>
<th>Depth</th>
<th>Lithology</th>
<th>Sample</th>
<th>Structures</th>
<th>Description</th>
<th>Stratigraphy</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>Grey to black shale</td>
<td>KWV-1, KWV-2</td>
<td>Rh</td>
<td>Sandstone with silt + shale interbeds</td>
<td>Trumpeters Member</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rh</td>
<td>Clay clasts</td>
<td>Wonderfontein Member</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rh</td>
<td>Shale</td>
<td>Ecca Group</td>
</tr>
<tr>
<td>900</td>
<td>Grey to black shale</td>
<td></td>
<td>Rh</td>
<td>Wavy + lenticular sandstone + shale</td>
<td>Pluto’s Vale Member</td>
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<td></td>
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<td></td>
<td>Dolerite</td>
<td>Ripon Formation</td>
</tr>
<tr>
<td>1000</td>
<td>Grey to black shale</td>
<td></td>
<td>Rh</td>
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<td></td>
<td>+ silt beds (rhythmite)</td>
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<td>1100</td>
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<td>Rh</td>
<td></td>
<td>Dark grey very fine</td>
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<td>+ shale</td>
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<td>Dolerite</td>
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<tr>
<td>1200</td>
<td>Grey to black shale</td>
<td>Rh</td>
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<td>Dark grey to black shale</td>
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<td>Rhythmite with minor silts</td>
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<tr>
<td>1300</td>
<td>Grey</td>
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<td></td>
<td>Calcite veins</td>
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<td></td>
<td>Massive silty shale</td>
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<td>Massive silty mudstone</td>
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<td>massive silty</td>
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<td>mudstone beds</td>
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<td>Massive silty mudstone with minor sandstone</td>
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<td>Rhythmite</td>
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<td>1500</td>
<td>Grey</td>
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<td>Siltstone + sandstone</td>
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<td>Coarse-grained dolerite</td>
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<td>Massive fine sandstone + silts</td>
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<td>Massive silty mudstone + fine sandstone + silts</td>
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<td>Fine sandstone</td>
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<td>Sandstone dyke</td>
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<td>Massive mudstone + rhythmite</td>
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<td>Black rhythmite</td>
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<td>Mudstone</td>
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<td>Rhythmite + minor mudstone and sandstone</td>
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<td>Dolerite</td>
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<td>Rhythmite + fine sandstone</td>
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Figure 1.4a - Graphic log of various lithologies from depths 800 - 1500 m, found in borehole core KWV-01 as described by de Kock et al. (2016). Samples were sampled as indicated on the log.
<table>
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<th>Sample</th>
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<td>Rhyolite + rhythmite</td>
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<td>2000</td>
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<td>Whitehill Formation</td>
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Figure 1.4b – Graphic log of various lithologies from depths 1500 – 2300 m, found in borehole core KVV-01 as described by de Kock et al. (2016). Samples were sampled as indicated on the log.
### Legend

<table>
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<tr>
<th>Symbol</th>
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<td>Convoluted Bed</td>
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### Table 1.1 – Samples that were targeted as indicated on Figs. 1.4a and 1.4b

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<th>Depth (m)</th>
<th>Formation/Member</th>
<th>Lithology</th>
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<td>~ 812</td>
<td>Trumpeters Member</td>
<td>Massive Siltstone</td>
</tr>
<tr>
<td>KWV-2</td>
<td>~ 813</td>
<td></td>
<td>Sandstone</td>
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<td>KWV-5</td>
<td>~ 840</td>
<td>Wonderfontein Member</td>
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<td>Sandstone</td>
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<td>KWV-9</td>
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<td>Silty Shale</td>
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<td>~ 1500</td>
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<td>KWV-14</td>
<td>~ 2296</td>
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<td>KWV-16</td>
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<td>Carbonaceous Shale</td>
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<td>Karoo Dolerites (intruded Whitehill Formation)</td>
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<td>~ 2300</td>
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Chapter 2 – Literature Review

In order to provide a compelling argument for this study, a body of knowledge needs to be considered. This chapter provides insight into concepts of CCS with regards to its approach towards combating climate change, methods of storing CO$_2$, commencing with trends in fossil fuel usage. With these concepts in mind, this chapter will zone in on the primary focus of this research by considering previous studies concerning adsorption effects of CO$_2$ on geological materials, specifically pertaining to shales, sandstones and granites, the closest proxy to dolerites studied in this project.

2.1 Trends in Fossil Fuel Production & Consumption

As the human population increases and becomes more modernized as a society, energy needs have risen radically, even as energy intensive processes decline due to technological developments (Lewis and Nocera, 2006). Throughout history, specifically since the post-industrial revolution, fossil fuels have been the main source of energy globally. Although a fair amount of fossil fuel energy has been subsidized by renewable energy (wind, solar, hydro, and geothermal energy), especially since the early 2000’s, the world is still highly dependent on fossil fuels such as oil, gas, and coal to cater for its energy requirements.

The global trend in terms of energy consumption produced from primary sources of the energy mix indicates that there remains an increased need for fossil fuels. As per the British Petroleum Company (2016) statistical review data (Table. 2.1), the global energy requirements are still heavily dependent on fossil fuels. From 2013 to 2015, there has been a steady increase in fossil fuel consumption. The growing need for coal supply is driven by the fact that around half of the electricity generated globally is derived from coal, despite the growing implementation and deployment of renewable energy (World Energy Council, 2013). Shifting the perspective to the African continent, South Africa holds the highest energy consumption on the continent, consuming in the order of 124 Mt oil equivalent worth of energy annually (British Petroleum Company, 2016).
Table 2.1 – Global and South African consumption of primary energy by fuel

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<th>Natural Gas</th>
<th>Coal</th>
<th>Total Fossil Fuels</th>
<th>Nuclear Energy</th>
<th>Hydro electric</th>
<th>Renewables</th>
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<td>3081.5</td>
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Values are calculated using millions of metric tons of oil equivalents. Data sourced from: British Petroleum Company (2016).

Worldwide, coal production essentially owes most of its growth to China which holds the highest production of coal globally. The USA still stands strong in second place, followed by India and Australia (World Energy Council, 2013). The total estimated coal resources found worldwide amounts to around 869 billion tons, which is said to sustain current coal production rates for approximately 115 years, overshadowing current oil and gas resource estimates (World Energy Council, 2013), thus making it a dependable future energy resource. In terms
of amount of resource utilized, coal has shown significant growth as within this century coal has equalled the total consumption of oil and gas, nuclear and renewables combined.

Coal has played a critical part in South Africa’s energy mix as well as being one of its key exports. In recent statistics, South Africa is ranked as the 6th largest coal producer globally, producing over 252 Mt of coal in 2015 (IEA, 2016), where most of its minable coal comes from the Volksrust and Vryheid Formations found in the north-eastern regions of the country. Over 30 billion tons of coal resources are estimated to be found in South Africa alone, where 95% of the total coal produced on the African continent is derived (EIA, 2015).

When compared to global trends in consumption of energy by fuel (Fig. 2.1), South Africa is more reliant on fossil fuels as a primary energy resource than most countries, mostly due to its adolescent renewable energy industry. In terms of utilization of these resources, South Africa makes use of an approximate 2.4% of the total world coal energy consumption, derived from data collected over the period between 2013 and 2015 by British Petroleum Company (2016). plant accounts for close to 33% of the total utilization of coal within South Africa (Eskom, 2016). South Africa currently makes use of 36% of the total world consumption of coal used for the purpose of electricity production (Eskom, 2016), making it one of the leading countries to currently depend heavily on this resource in this regard. Furthermore, on a local scale, the increased amount of coal utilization is a result of its primary industrial purpose for electricity generation, where over 72% of the country’s energy requirements is derived from coal (Eskom, 2016). In terms of growth in consumption, South Africa has seen a slight, but noticeable increase in the use of fossil fuels in recent years, where most of its energy requirements is derived from coal (Table. 2.1).

Coal is also extensively used in the petrochemical industry, to produce petrol, diesel and chemical products. The Sasol Secunda plant accounts for close to 33% of the total utilization of coal within South Africa (Eskom, 2016).

The global oil and gas industry are still booming to this day, while the world still relies on the resources for petroleum and electricity respectively. Oil contributes to over 32% of the total energy consumption as recorded in 2010 (World Energy Council, 2013) and has still overall shown significant growth in recent years. According to the British Petroleum Company (2016), over 4 330 million tons of oil was consumed in 2015 alone. The total proven oil reserves amount to 1697 billion barrels as recorded in 2015 (British Petroleum Company, 2016). Although there has been a high increase in global consumption of oil, reserves have shown an increase of 60% over 1991 to 2011 (World Energy Council, 2013).

The natural gas industry has shown substantial growth over recent years and has surpassed coal demands in 2012 (World Energy Council, 2013). The role of natural gas’ contribution to
the primary energy supply mix is projected to rise from 22% in 2010 to 25% in 2030 (World Energy Council, 2013). It is said that the significant growth of the gas industry would be as a result of the increasing utilization of natural gas for electricity production, which could contribute to 40% of the gas market in 2030 (World Energy Council, 2013).

South Africa’s relatively discrete oil and gas industry is eclipsed by its coal industry due to coal’s sizeable contribution towards the country’s energy requirements (Yamaguchi, 2016). Although oil and gas are not a primary source of energy in South Africa, it is still an essential part of its energy mix and therefore it cannot be disregarded. South Africa began to explore for oil and gas resources during the 1940’s under The Geological Survey of South Africa (Yamaguchi, 2016). According to the Oil and Gas Journal ‘Worldwide Report’ South Africa has an estimated reserve of 15 million bbls (2,385,000,000 litres) making up a meagre 0.12% of Africa’s total crude oil reserves (Yamaguchi, 2016). South Africa is currently listed with no economical natural gas reserves, although the country manufactures it through gas to liquid (GTL) processes (Yamaguchi, 2016). South Africa’s oil and gas reserves are found predominantly offshore in the southern region within the Bredasdorp Basin close to the border of Namibia (Yamaguchi, 2016). The Orange Basin contains a considerable amount of hydrocarbons but has not yet been fully prospected or exploited (ARI, 2013; Yamaguchi, 2016). South Africa produced 41 billion cubic feet (Bcf) of natural gas in 2013 and had made use of 173 Bcf, where the remaining fraction was imported from Mozambique through a pipeline (EIA, 2015).

According to the Energy Information Administration (EIA) South Africa was classified in 2013 as holding the 8th largest technically recoverable shale gas resource in the world at approximately 390 Trillion cubic feet (Tcf) (ARI, 2013); this is still not yet a proven resource. Most of the South Africa’s shale gas resources are found in the MKB, mostly in the Whitehill (211 Tcf), Prince Albert (96 tcf) and the Collingham (82 tcf) Formations (EIA, 2015). Currently, a few research initiatives have been introduced by organisations such as the CIMERA housed at the University of Johannesburg, Shell and the Council for Geoscience (CGS) on the MKB to prove these shale gas reserves actually exist. However, research efforts conducted by the KARIN reported that natural shale gas in the South-Eastern Karoo Basin situated within the Eastern Cape of South Africa has little to none available natural gas.

One of the most shale gas discoveries in 2014, Well Chaiye 1 in South China, reported a desorption gas content of between 2 – 5 m³/t (Wang, 2018). In comparison, findings from the KARIN project (borehole KWV-01) disclosed that the highest desorbed gas content recorded from the samples analysed was that of ~0.2 m³/t. Whitehill shales found at lower depths to the ones showing “high” desorbed gas had notably lower to no desorbed gas content (de Kock et
al., 2016), showing that in this region of the MKB, there is no economically exploitable shale gas resources. Other research initiatives in this section of the MKB have been scheduled by the CGS in the shale gas exploration realm.

2.2 CO$_2$ and Climate Change - A Global and Local Perspective

Climate change has become a concerning issue with regards to increasing global temperatures attributed to increasing anthropogenic GHG emissions. With the global trend in mass consumption of CO$_2$ producing resources, as a result, climate change has become a major factor. This has to be taken into consideration in both a global and local scale.

Many countries have identified climate change to be a major issue in recent years. In order to control and mitigate increasing GHG emissions, specifically CO$_2$, all major CO$_2$ emitting countries need to first fully understand their contribution to global GHG emissions, and to find a suitable solution to lower their emissions accordingly. There has been a boom in cleaner energy demands across the globe, with great incentive brought on by the 2015 COP21 Conference held in Paris. The Conference placed pressure on countries to mitigate their CO$_2$ emissions so that global temperature does not exceed the 2°C threshold. Moving beyond this threshold value has major environmental implications, as stated by many scientists and politicians globally. These environmental implications include sea-level rise, increasingly erratic and violent weather patterns, desertification, famine, water scarcities, and conflict as a secondary effect (Council on Foreign Relations, 2013).

Following a decade of increasing global CO$_2$ emissions in the order of 4% per annum, there was a substantial decrease to 1% increase per annum of CO$_2$ emission growth during 2012 – 2013 (Olivier et al., 2015). Thereafter, the rate of increase in CO$_2$ emissions have slowed, with an increase of only 0.5% recorded in 2014(Olivier et al., 2015). The highest emitting countries/regions, which account for approximately 2/3rds (61%) of the total global CO$_2$ emissions, include: China (30%), the United States (15%), the European Union (EU-28) (10%) and India (6.5%) (Olivier, et al., 2015).

China’s fast-tracked industrialization, which boomed after joining the World Trade Organization (WTO) in 2003, has resulted in tremendous growth in the CO$_2$ emissions since then (Olivier et al., 2015). China, in 1990, produced half the CO$_2$ emissions comparison to the USA in that year (Olivier et al., 2015). Since 2007, China has overtaken the USA as the leading CO$_2$ emitter, with emissions of 2461 Mt of CO$_2$ in 1990 increased to 8241 Mt in 2010; thus, almost tripling the emissions in two decades (Hao et al., 2016). Furthermore, China’s emissions signified an increase of 68% of the total global CO$_2$ emissions recorded from 2000 to 2010 (Hao, et al., 2016; Nandi, 2013). China saw no growth demand for coal resources in 2014 and its emissions increased by a mere 0.9% in relation to 2013 recorded emissions,
making it the lowest annual increase the country experienced in the last decade (Olivier et al., 2015). There is a clear indication of the high impact of fossil fuel combustion in China (especially coal combustion) to global CO₂ emissions.

The USA had an increase of 50 million metric tons (MMt) of CO₂ emissions in 2014 due to total energy production, of which a 19 MMt increase was a result of energy related to the commercial sector (EIA, 2015). CO₂ emitted as a result of fossil fuel combustion contributed 76% of the total global warming potential (GWP) weighted emissions in 2014 (EPA, 2016). This is a substantial contribution to the weighted GWP factor, making the USA one of the highest contributors of CO₂ emissions and leading impacting countries to climate change in the world today.

In terms of South Africa, although ranking nowhere close to the top two (U.S and China), the country still has a significant contributing role in global CO₂ emissions due to its energy consumption. In 2013, South Africa was positioned, globally, as the 14th largest CO₂ emitting country based on fossil fuel derived emissions (per capita) by emitting approximately 128 508 Mt of CO₂ per annum. South Africa is the largest CO₂ emitter in Africa in terms of per capita emission standards mainly due to its dependency on coal as its primary energy (Boden and Andres, 2013; Boden and Andres, 2011). From 2000 to 2010, South Africa saw an increase of approximately 24% in CO₂ emissions, of which the energy sector’s contribution was the largest source of these emissions, making up an average 89% of the total CO₂ emitted during the same time period (DEA, 2014); the remainder belonged to the transport, manufacturing, and construction industries. South Africa still has a long way to go regarding mitigation of CO₂ emissions and has to play its part in the global climate change arena.

Due to the mandate put out by a newly drafted global agreement known as the “Paris Agreement”, which was put in place on December 2015 in hopes to mitigate climate change (United Nations, 2016), many countries have taken measures in accordance with this agreement to lower GHG emissions. The Paris Agreement’s core efforts are to keep the global average temperature well below a 2°C increase in relation to pre-industrial levels. Participating nations agree that an increase of above 2°C would cause hazardous interference with the climate regime (Rogelj et al., 2016). It has been said that to limit the increasing global temperature, it requires that the total amount of CO₂ that could ever be released into the atmosphere is completely restricted (Rogelj et al. 2016; Flato et al. 2013). In order to obtain a constant global-mean temperature, anthropogenic emissions would need to be non-existent, although this is not feasible considering current emission trends and energy utilization. Any future emissions may cause irreversible increases in temperatures affecting climate system (Matthews and Caldeira, 2008). Achieving a net-zero increase in anthropogenic emissions is
currently unobtainable, but serious CO$_2$ mitigation needs to take place to defend against the rate of increasing global-mean temperatures.

Based on the current infrastructure of fossil fuel dependent industries, it is said that a cumulative estimate amount of 496 gigatonnes (Gt) will have been emitted into the atmosphere between 2010 and 2060 (Rogelj et al., 2016; Davis et al., 2010). The compounding nature of CO$_2$ emissions within the atmosphere would require initiatives consisting of carbon-neutral energy production advancements on par or greater than current energy production protocols to keep CO$_2$ levels to even two times their pre-anthropogenic levels by 2050 (Lewis and Nocera, 2006).

The United Nations (2016) reported that many countries have put in place strategic plans to combat high CO$_2$ emission levels. Over 100 countries have accepted a global warming limit of 2°C or below in relation to pre-industrial levels and have used this to drive change in terms of mitigation in hopes to lower climate change risks and effects (Meinshausen et al., 2009; United Nations, 2016). The two countries (USA and China) who are the primary contributors to global climate change have stepped up to mitigating GHG emissions, with South Africa following suite.

The USA has committed to lowering their emissions in the order of 17% by 2020 in relation to 2005 levels (United Nations, 2016). Proposed USA legislation called for a 30% reduction in emissions by 2025 and a total of 42% reduction by 2030 (UNFCCC, 2011). The constant projected CO$_2$ concentration decline seen by the U.S is due to the phasing out of unregulated fossil fuel energy production, whilst increasing energy derived from renewables, nuclear and CCS deployment, a trend which would be fast-tracked post 2030 (Williams et al., 2014).

China has made commitments toward CO$_2$ emission reduction. In the United Nation Framework Convention for Climate Change (UNFCCC) meeting held in 2013, China communicated to the secretariat that the country has set out to lower CO$_2$ emissions per unit of GDP by 40 – 45% by 2020 in relation to 2005 levels (UNFCCC, 2013). China attained a 21% reduction of CO$_2$ emissions from 2005 – 2010 and will need a further carbon intensity reduction of 3% per annum from 2016 – 2020 to reach commitment targets (Zhang et al., 2016). The National Bureau of Statistics of China (NBS) in February 2015 published that coal consumption dropped by 2.9% in 2014 in relation to 2013 levels, while seeing an increase of 2.2% of total energy consumption (Climate Action Tracker Partners, 2015).

South Africa communicated its intent to reduce CO$_2$ emissions to the UNFCCC secretariat in 2013. With regard to mitigation, South Africa has placed national priority towards actively engaging in international agreements under the UNFCCC and its Kyoto Protocol, which South Africa sanctioned in 1997 (DEA, 2011a). The country had committed to implement Nationally
Appropriate Mitigation Actions (NAMAs), which will allow for a 34% reduction in emission growth in relation to ‘business as usual’ by 2020 and a total of 42% reduction (UNFCCC, 2013). The way forward would entail financial, technological, and capacity building provisions which would allow South Africa’s GHG emissions to peak between 2020 – 2025 and stabilize for a decade, and thereafter decline (DEA, 2011a). Mitigation proceedings require companies and economic sectors to prepare and submit mitigation protocols that include how to attain emission reduction outcomes (DEA, 2011a). Current mitigation plans include:

1) migrating to low-carbon electricity generation;

2) upscaling energy efficiency at an industrial level as well as public, commercial and residential buildings and transport energy efficiency;

3) promoting transport related actions by implementing modes of transport changes (e.g. road to rail and private to public transport) as well as switching to low emission vehicles and low-carbon fuels;

4) carbon capture and storage implemented in the synthetic fuels industry (and later in other fossil fuel-based energy production industry);

5) opportunities for mitigating non-energy related emissions in agriculture and land-use;

6) and finally making the transition to more sustainable consumption and production routines (DEA, 2011a).

South Africa has also undertaken future plans for carbon tax policies which will allow for a fairly easy transition into a low-carbon economy, signaling to investors and customers the need for a more climate conscious investment strategy (National Treasury Republic of South Africa, 2013).

With emphasis on the current global condition regarding CO₂ emissions and climate change, more serious action needs to take place for an actual difference to be made. There is an underlying need to shift from current based energy production to low-carbon technologies. Due to the high dependency on fossil fuels to supply global energy requirements (world makes use of over 86% of energy derived from fossil fuel in total of all primary fuels (British Petroleum Company, 2016) and cannot immediately be substituted by renewable energy. The gradual change in clean energy needs new technological developments to allow time for the switch to clean renewable energy to achieve a constant plateau of carbon emissions globally, thereafter and ultimately to attain net-zero CO₂ emissions, as described by Matthews and Caldeira (2008), and Pacala and Socolow (2004). To see a quantifiable difference in CO₂ atmospheric concentrations by 2054 (560 ppm), technological interventions need to be implemented such
as: efficient vehicles; efficient buildings; efficient baseload coal plants; gas subsidies for coal baseload power; capture CO$_2$ at baseload power plants; H$_2$ plants and coal-to-synfuel plants with geological storage; nuclear and wind power in replacement of coal power; biomass fuel for fossil fuel to name a few examples (Pacala and Socolow, 2004). Pacala and Socolow (2004) discusses solving the climate change issues, and CCS is emphasized as one of the key technologies to be operational at an industrial level worldwide (in combination with several other mentioned methods of mitigation).

A technology currently available which can drastically reduce GHG emissions is CCS (Global CCS Institute, 2015). The need for CCS is highlighted as an important measure to reduce anthropogenic CO$_2$ emissions to avoid the 2°C increase in global climate change, where a 13% CCS deployment (Fig. 2.2), globally, is needed in the clean energy mix (IEA, 2015).

2.3 Carbon Capture and Storage – A Response to Climate Change

Due to global dependency on fossil fuels for energy and well-established associated industries, coal and other fossil fuels are unlikely to be replaced anytime soon. This being said, CO$_2$ emissions from combustion of fossil fuels and the consequent contribution they are believed to have on global climate change is a harsh reality. There is still hope for the future as clean-coal technologies such as CCGS are available as powerful mitigation tools for CO$_2$ reduction. Pacala and Socolow (2004) identifies various options (called wedges) to combat climate change for the next 50 years, and it was found that CCS is a major component for climate change remediation. In the International Panel on Climate Change 5th assessment
report it is stated that without CCS, long-term global climate goals may be unobtainable (IEA, 2015).

2.3.1 What is Carbon Capture and Geological Storage?

(CCf) is a series of techniques comprising separation of CO$_2$ from industrial and other energy related sources and transportation to a storage location where the pure, compressed CO$_2$, is isolated from the atmosphere for long periods of time (IPCC, 2005). There are three fundamental characteristics of CCS: 1) capture of CO$_2$ at large point sources; 2) compression and transportation of CO$_2$; and 3) storage of CO$_2$ in geological formations, in the ocean, in mineral carbonates or for use in industrial processes (IPCC, 2005).

2.3.2 Where can we capture CO$_2$?

Large-scale point sources of anthropogenic CO$_2$ consist of extensive fossil fuel or biomass energy production emitters, primary CO$_2$-emitting industries, natural gas production, and synfuel and hydrogen production plants (IPCC, 2005). While there are many sources to consider for CO$_2$ capture, only a few are actually viable candidates for capturing CO$_2$ as there are barriers which could restrict CCS implementation: cost of large-scale demonstration projects; running costs of plant; governmental policies and regulatory framework and; public acceptance (IEA, 2006). The power and industry sectors account for more than half of all CO$_2$ emissions globally, where large amounts of CO$_2$ emissions in these plants are produced by boilers and furnaces burning fossil fuels and released into the atmosphere through large exhaust stacks (IPCC, 2005). These large stack exhausts can be considered as point sources for CO$_2$ emissions and are prime examples for where capture plants can be established. Carbon dioxide needs to be of a relatively high purity when stored in geological formations as it could cause future complications like: leakages in pipelines – caused by corrosion; geochemical reactions which may cause reduced permeability and increase pore pressure (Anheden et al., 2005). One of the biggest costs CCS faces, in terms of financial and energy requirements, is capturing CO$_2$ from other contaminants found in flue gas (or other gas streams) produced by combustion of fossil due to industrial processes (IPCC, 2005). Although the recovery of CO$_2$ from other contaminants in a gas stream can be efficient due to current capturing techniques (80 – 95% CO$_2$ recoverable), it is a costly process, therefore CO$_2$ needs to be of a high proportion in relation to its contaminants within a gas stream for it to be feasible to capture (Anheden et al., 2005; IPCC, 2005).

Countries, such as South Africa, with a well establish large-scale synfuel plant, are in a unique position in terms of capture-ready emissions, where these industrial plants produce around 95% pure CO$_2$ due to their production process (Cloete et al., 2010). These emissions can be directly captured, transported and stored. These two types of point sources, namely the energy
and synfuel production plants, are of primary interest for CO₂ capture plants to be established as they produce high volumes of CO₂ at a single, fixed location.

2.3.3 How is CO₂ stored?

Once the CO₂ is captured, it is converted to a supercritical fluid before transport. The reason for this is that CO₂ in its gaseous phase is not viable for storage due to its large volume and buoyancy properties. With this in mind, CO₂ is stored in deep geological reservoirs as a supercritical fluid, which is more dense and efficient to store as supercritical CO₂ takes up less volume (therefore more CO₂ can be stored) under these conditions (Blunt, 2010). It also reduces the risk of upward migration due to its high density (Blunt, 2010). In order for supercritical CO₂ to remain stable, it has to be contained in a geological storage reservoir at a depth of > 800 m and at a minimum temperature of approximately 31.1 °C with consisting of a minimum pressure of 7.38 MPa (Fig. 2.3) (Bachu, 2000). Previous studies have noted that pressure distributed in sedimentary basins (like the MKB) possess a linear increase in pressure at a rate of 1 MPa per 100 m depth (Holloway and Savage, 1993). Therefore, assuming an average geothermal gradient of 25°/km, supercritical CO₂ will remain in this phase at depth of ≥800 m (Holloway and Savage, 1993; van der Meer, 1993).

![Figure 2.3 - Pressure-temperature diagram showing CO₂ stability fields (Vermeulen, 2011)](image)

Injection of CO₂ occurs below 800 m so that CO₂ remains as a supercritical fluid at that depth, allowing the fluid to diffuse through permeable porous sedimentary rock (reservoir rock) and utilising pore spaces as storage space in a variety of geological sites (IPCC, 2005). One of the most vital components of a potential geological storage basin is the impermeable cap rock layer which confines the CO₂ within the storage reservoir, preventing upward migration of injected CO₂ to the surface (Kaldi et al., 2013).
Carbon dioxide injection into geological horizons is not a new phenomenon; the technique has been used for many years by the oil and gas industry to extend the life of mine through EOR (IPCC, 2005). Borehole drilling, injection, computer modeling of storage reservoir and monitoring techniques established by the oil and gas industries can be repurposed for CCS (IPCC, 2005). This creates confidence in technique used for geological CO₂ sequestration and its practicability.

The concern of CO₂ leakage is one of the most important issues faced by the CCS industry. Subsurface buildup of CO₂ is a common geological phenomenon, where natural trapping of CO₂ occurs in some deep sedimentary reservoirs which contain CO₂ over geological time (IPCC, 2005). There are five main mechanisms of trapping CO₂ in a geological formation:

1) hydrodynamic/structural trapping – CO₂ trapped as a supercritical fluid/gas under a low permeable cap rock;
2) residual trapping – when CO₂ displaces and take the place of formation brine fluids;
3) solubility trapping – dissolution of CO₂ in brine fluids;
4) mineral trapping – when CO₂ is incorporated into a stable mineral phase due to the chemical reactions with mineral and organic matter in a formation; and

![Geological Storage Options for CO₂](image_url)

Figure 2.4 - Various well-established storage options after Cook (1999)
5) adsorption trapping – adsorption of CO₂ onto the surface of mineral or organic material (Cloete et al., 2010; Zhang and Song, 2014).

Therefore, potential storage basins need to studied to prove that natural processes like these occur so that CO₂ is restricted from leaking to the surface.

2.3.4 What are the Characteristics of a Suitable Geological Storage Basin?

Not all geological basins are suitable for CO₂ sequestration; environmental factors and geological settings needs to be taken into consideration. Bachu (2003) found that there are a set of 15 criterion to consider when exploring for CO₂ storage basins. These criteria include: tectonic setting; size; depth; geology; hydrology; geothermal gradient; hydrocarbon potential; maturity; coal and coal-bed methane; salts; on or offshore basin; climate; accessibility; infrastructure; and CO₂ sources (Bachu, 2003). Bachu (2000; 2002) broadly classified 3 characteristics with which a storage basin can be assessed for suitability:

1. Basin characteristics: tectonism, geology, geothermal gradients and hydrodynamic regimes are classified as “hard” criteria, as these aspects cannot be changed.

2. Basin resources such as oil, gas, coal and salt coupled with maturity and infrastructure are considered “semi-hard” criteria, as they are able to change with new findings, technological and economical improvements.

3. Societal factors such as level of development, economic and political standing are “soft” criteria, as it does not directly influence CO₂ storage capacity and can be changed.

Geological storage of CO₂ can occur in a variety of geological sites such as: oil fields; depleted gas reservoirs; deep un-minable coal seams; and saline aquifers (Fig. 2.4) (IPCC, 2005). These are considered to all be conventional ways of storing CO₂. New ways, or non-conventional ways of storing CO₂ in geological formations have been established for application if conventional storage is not available. A study by Khosrokhavar et al. (2014) found that gas shales (similar to the Whitehill Formation in the Karoo Supergroup) have the potential to store CO₂ in depleted gas reservoirs. Other unconventional geological storage options exist in basins which consist of porous, permeable sandstone or basalt as a reservoir, with a overlying impermeable caprock (Cloete et al., 2010; Matter et al., 2016).

2.3.5 Where has CCS worked before?

Although CCS has yet to be highly successful, there are a number of plants in operation, standing as global examples of its success in the following examples. Looking at the extent of deployment of CCS projects, there are 15 large-scale CCS projects in full swing across the globe, which possess the capacity to capture and potentially store 28 million tons of CO₂ per
annum (Global CCS Institute, 2015). According to the IEA (2015), CCS deployment needs to increase its capacity to 4 Gt by 2040 and 6 Gt by 2050, delivering a 13% cumulative emission reduction (Fig. 2.2) by the year 2050.

We are currently living in the landmark period for CCS projects, with the increasing deployment of projects and future CCS projects on the way (Fig. 2.5). There are a few pioneering projects which have seen great success in capturing and storing CO₂ currently operating today. In 2015, four specific CCS projects were classified as successful, namely the Quest project in Alberta, Canada; Uthmaniyah CO₂ –EOR project launched in Saudi Arabia; the Boundary Dam project in Saskatchewan, Canada and; the Sleipner project in Norway.

The Quest CCS project in Canada had been calculated to have the capacity to capture 1 Mtpa (million tons per annum) of CO₂ emissions from the production of synthetic crude oil (Global CCS Institute, 2015). The Quest project was the first large-scale CCS project in North America, storing the captured CO₂ in a deep saline formation. This was the first project to do so since the Norwegian Snøhvit CO₂ storage project established in 2008 (Global CCS Institute, 2015).

The Uthmaniyah CO₂ storage project in Saudi Arabia is also a very good example of an economically viable CCS project. The technique used by this project utilises the EOR method of recovering oil from this reservoir which allows for simultaneous oil recovery and storage of CO₂. This particular project capable of capturing an estimated 0.8 Mtpa of CO₂ (Global CCS Institute, 2015) from a natural gas liquids recovery plant for injection.

The Boundary Dam project in Canada was the first CCS operation to be implemented at a coal-fired power plant capable of capturing 1 Mtpa of CO₂ (Global CCS Institute, 2015).
The Sleipner Project in Norway has been one of the pioneering CCS projects which stores CO$_2$ beneath the North Sea in the Utsira Formation, where nearly 1 Mt of CO$_2$ is stored annually (Solomon, 2006).

In addition to the 15 large-scale CCS projects currently operating (Fig. 2.5), 7 more are to be operational by 2016/2017 and are currently in the execution stage (Global CCS Institute, 2015). 11 further planned projects to come online soon with the capacity to capture 15 Mtpa (Global CCS Institute, 2015). The expanding CCS industry has proven that this technology is much needed and is an effective tool for CO$_2$ emission reduction. With this in mind, there is still a much needed to “ramp up” in terms of getting more projects online before 2050 to stand a real chance of combating global climate change, and keeping below the 2°C threshold.

South Africa has implemented CCS into their clean energy plan, which is currently in its development stage. The SACCCS Roadmap for CCS has played a quintessential role for CCS implementation in South Africa (Cloete et al., 2010; Vincent et al., 2013). A pilot CCS test injection project underway (Surridge and Cloete, 2009; Vincent et al., 2013). Research has been done to identify possible storage basins in South Africa. The South-Africa Europe Cooperation in Carbon Capture and Storage (SAfECCS) are working together with the SACCCS to find sites for CO$_2$ sequestration (Surridge and Cloete, 2009). Basins of interest are the on-shore Algoa and Zululand geological basins (Vincent et al. 2013). A conducted by Vincent et al. (2013) took a close look at these sedimentary basins for CO$_2$ storage potential. The study found that the most suitable geological sites for storage reside in the Zululand Basin, where the test injection project site will most likely be developed. Laws and regulations regarding transport of CO$_2$ and site construction are still in negotiation, and are one of the hindering factors in development at the moment (Cloete et al., 2010; Vincent et al. 2013).

To predict the success of a CO$_2$ storage project, it is important to understand the storage materials. One of the most important aspects to study when looking for a suitable storage basin is the adsorption capacity of rocks in a potential storage basin.

2.4 CO$_2$ Adsorption and Geological Materials

Adsorption is the ability of a substance to adhere to the surface of a substrate without entering the bulk, or volume of another substance (Lohmann, 2017); and sorption is the act of doing so. This is clearly defined to add to the concluding findings of CO$_2$ adsorption and its value to the study to identify the “staying power” of CO$_2$ in subsequent geological layers under review at a molecular level.
To fully understand the CO\textsubscript{2} adsorption potential of the various rock samples used in this study, a base knowledge of previous results is required. The rock samples under question include: shale; sandstone and; dolerite of the South-Eastern Main Karoo Basin.

The adsorption potential of geological material (or for any adsorbate material) is measured by assessing the amount of surface uptake of an adsorbate over a set of pressures at a constant temperature (Heller and Zoback, 2014). There are two main techniques for measuring CO\textsubscript{2} adsorption: 1) gravimetric method and; 2) volumetric method (HPVA). A HPVA was used in the current study to quantify CO\textsubscript{2} adsorption on selected geological samples and results from both methods in literature are taken into consideration.

2.4.1 Shale – A Potential Seal or Storage Reservoir?

Conventionally, shales are described as sedimentary rocks which are stratified or laminated, break into fragile plates and are defined by their grain sizes between those of clay and silt sized particles (Nichols, 2013). The term shale can be applied to any mudrock, but it is more suitable to use the term shale for mudrocks that show fissility or lamination (Nichols, 2013). de Kock et al. (2016) described shales sampled in this study as shales as per general definition regarding lamination which these shales have and not primarily grain size. Shales have been studied in literature for their ability as both a seal and a possible CO\textsubscript{2} storage reservoir. The conventional utilisation of shale in potential CCS geological storage basins is driven by its low permeability and porosity, the function of which restricts the escape of supercritical CO\textsubscript{2} from the reservoir rock, hence, acting as a seal. Studies conducted, such as Busch et al. (2008) and Heller and Zoback (2014), have considered shales and gas shales as a possible geological storage reservoir for CO\textsubscript{2}. These studies are of relevance to SA, as there are gas shales in the Whitehill Formation which have resided in this unit over geological time and could be said to potentially have high adsorption capacity.

In the study conducted by Busch et al. (2008), CO\textsubscript{2} storage potential of the Muderong Shale from Australia was considered. Busch et al. (2008) described this shale to be fissile and clay-rich. High pressure volumetric adsorption and diffusion properties where tested on these samples. Using simulated reservoir conditions as experimental parameters, samples were exposed to single-gas adsorption experiments under temperatures of 45 and 50 °C in a temperature-controlled system. At these temperature conditions, CO\textsubscript{2} is either gaseous or, at pressures above 7.38 MPa, in a supercritical phase. The isotherms (Fig. 2.6a) show the results obtained by Busch et al. (2008), showing a comparison between CO\textsubscript{2} adsorption isotherms obtained for the Muderong Shale (properties of which are described in Table. 2.2), Ca-rich montmorillonite, Na-rich Montmorillonite, kaolinite, and illite. This was done to show a relationship between CO\textsubscript{2} adsorption in shales, and the effect clay minerals have on CO\textsubscript{2}
adsorption potential. The study found that inflection points showing maximum excess CO₂ adsorption for the Muderong Shale was achieved at 12 MPa pressure. The first experimental run of as-received (“a.r”) undried sample yielded ~ 1.0 nmol/g of excess adsorbed CO₂, and the second run yielded a lower 0.6 nmol/g (Fig. 2.6b). Thereafter, dried samples of the Muderong Shale yielded a much lower 0.4 nmol/g (Fig. 2.6b) excess adsorption. Of the Ca-rich montmorillonite, Na-rich montmorillonite, kaolinite and illite samples, the kaolinite samples showed a differently shaped isotherm. The dried kaolinite sample excess adsorption reached near zero when exposed to pressures above 10 MPa, and generally low excess adsorption in both dry and as received (a.r) samples. With the exception of kaolinite, all the other samples seemed to have reached their inflection point of maximum excess adsorption at around 8.5 MPa pressure. The study found that Ca-rich montmorillonite had the highest excess adsorption (1.6 mmol/g and 1.2 mmol/g for dried and moist samples respectively) followed by Na-rich montmorillonite (at ~0.65 mmol/g for both moist and dried samples), illite (at maximum excess adsorption values of 0.4 mmol/g and 0.2 mmol/g of both dried and a.r samples respectively) and the lowest being kaolinite with a maximum excess adsorption of ~ 0.18 mmol/g).

Overall, all isotherms produced in the Busch et al. (2008) study found a similar trend in adsorption isotherms. This means that there is a direct correlation between clay mineral content in shales, and the adsorption potential thereof. The study found that the CO₂ adsorption potential is attributed to various properties of shale consisting of: aqueous solubility; geochemical reactions and physical adsorption mainly onto clay minerals (Busch et al., 2008). Adsorption experience had shown that montmorillonite has the highest capacity for adsorption (Busch et al., 2008). Taking into account the high amount of shale found in sedimentary basins, there is a potential for CO₂ storage in such pelitic sedimentary lithologies (due to its inherent ability of minerals to trap large quantities of CO₂).
Table 2.2 - Physical and mineralogical properties of the Muderong Shale (Busch et al., 2008)

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Content (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain density (g/cm³)</td>
<td>2.7</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.33</td>
</tr>
<tr>
<td>Porosity (m³/m³)</td>
<td>0.2</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>25</td>
</tr>
<tr>
<td>Total organic carbon (%)</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Clay content (g/g)</td>
<td>0.66</td>
</tr>
<tr>
<td>Clay fraction (g/g)</td>
<td>0.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral composition Content (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite–smectite</td>
</tr>
<tr>
<td>Smectite in I-S</td>
</tr>
<tr>
<td>Mica/illite</td>
</tr>
<tr>
<td>Kaolinite</td>
</tr>
<tr>
<td>Chlorite</td>
</tr>
<tr>
<td>Quartz</td>
</tr>
<tr>
<td>Siderite</td>
</tr>
<tr>
<td>Orthoclase</td>
</tr>
<tr>
<td>Pyrite</td>
</tr>
</tbody>
</table>

In a similar study to Busch et al. (2008), gas shale samples were studied for adsorption potential of both CH₄ and CO₂ in a paper compiled by Heller and Zoback (2014). This study paid close attention to compositional differences between samples, including total organic content (TOC) and clay fractions (Table 2.3), and their role in adsorption behaviour. The study found that there is a strong relationship between the mineralogy and organic content of the samples and their capacity for adsorption. It was observed that the Barnett sample from the USA, which had the highest organic content (TOC 5.3%), had the largest adsorption capacity for both CH₄ and CO₂. Using the isotherm produced by Heller and Zoback (2014) (Fig. 2.7), it
was found that the Barnett Shale had an absolute CO₂ adsorption of ~ 65 scf/ton (standard cubic feet per ton) and ~30 scf/ton of CH₄. CO₂ had almost double the adsorption capacity to that of CH₄. Although not at the same capacity, the other shale samples have a similar adsorption trends between CO₂ vs. CH₄. The primary finding Heller and Zoback (2014) found was that CO₂ proved to be more adsorptive than CH₄, which is a good aspect to keep in mind when looking for storage basins. Gas shales (such as the Whitehill Formation carbonaceous shales) could have great potential for CO₂ storage as naturally occurring CH₄ could be displaced and replaced by CO₂. (assuming there is in fact gas in this formation).

Although there is a strong connection between TOC and CO₂ adsorption capacity of a rock sample, it is not always the case. In the same study by Heller and Zoback (2014), it was found that the Montney Shale (which has approx. half the TOC compared to the Barnett Shale) had a fairly high capacity for CO₂ in comparison to the Marcellus and Eagle Ford shale samples. The Marcellus sample, consisting of a high clay content (41%) had a higher adsorption capacity in comparison to the Eagle Ford sample, which comprised mostly of carbonates (80%). It was found (Fig. 2.7) that the Marcellus sample had adsorbed 25 scf/ton of CO₂ more than the Eagle Ford sample, meaning that there is a stronger capacity for adsorption in clay dominated rocks than in carbonate dominated ones. The general interpretation of the study done by Heller and Zoback (2014) was that the higher the TOC within the geological sample, the higher the adsorption capacity. Also, observations drawn from this study found that illite and kaolinite exhibited a relatively high adsorption capacity. The study concluded that a positive relation between the amount of clay content in shales and adsorption potential exists, in agreement with the Busch et al. (2008) study.

![Figure 2.7 - Isotherms of gas shales from the Barnett, Marcellus, Eagle Ford and Montney reservoirs showing absolute adsorption of CO2 and CH4. • represents CH4 and Δ represents CO2 (Heller and Zoback, 2014)](image)
Table 2.3 - Mineral, organic and water content of gas shale samples taken from the Barnett, Eagle Ford, Marcellus and Montney reservoirs (Heller and Zoback, 2014).

<table>
<thead>
<tr>
<th></th>
<th>Barnett 31</th>
<th>Eagle Ford 127</th>
<th>Marcellus</th>
<th>Montney</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>2633.7</td>
<td>3893.7</td>
<td>1920.73</td>
<td>2321.5</td>
</tr>
<tr>
<td>Water by Mass%</td>
<td>0.31</td>
<td>0.24</td>
<td>0.22</td>
<td>0.28</td>
</tr>
</tbody>
</table>

**Mineral and Organic Content**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (%)</td>
<td>5.3</td>
<td>1.8</td>
<td>1.2</td>
<td>2</td>
</tr>
<tr>
<td>Quartz (%)</td>
<td>51.3</td>
<td>7</td>
<td>38</td>
<td>42.3</td>
</tr>
<tr>
<td>Plagioclase/Feldspar (%)</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td>11.9</td>
</tr>
<tr>
<td>Calcite (%)</td>
<td>0</td>
<td>80</td>
<td>1</td>
<td>8.1</td>
</tr>
<tr>
<td>Dolomite (%)</td>
<td>0.4</td>
<td>1</td>
<td>1</td>
<td>9.9</td>
</tr>
<tr>
<td>Pyrite (%)</td>
<td>1.7</td>
<td>1</td>
<td>1</td>
<td>3.5</td>
</tr>
<tr>
<td>Apatite (%)</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Total Clay (%)</td>
<td>37.4</td>
<td>5</td>
<td>52</td>
<td>24.1</td>
</tr>
</tbody>
</table>

The mobilization of CO$_2$ in caprocks is a primary concern when considering a geological storage site. In terms of the effect of CO$_2$ on caprock/seal rocks, there has been an interesting outcome observed by Busch et al. (2009). Using a comprehensive experimental approach, Busch et al. (2009) found that some caprock lithologies could possess a substantial sink for CO$_2$ injected into a geological storage basin, thus reducing the threat of leakage to the surface. Busch et al. (2009) noted during analysis of adsorption capacity of the Muderong Shale, the resulting adsorption (at a constant temperature of 50 °C at a pressure of ~12 MPa and sample moisture content of 3.34%) obtained a maximum excess adsorption of ~43 kg/t (kilogram of CO$_2$ per ton of rock) for the first experimental run and 25 kg/ton for the second run. In comparing the Muderong sample with its untreated equivalent, Busch et al. (2009) found that the mineralogy of the treated (analysed) sample had changed significantly, which could be viewed as a mineral trapping mechanism attributed to shales of this kind. This provided preliminary, but reliable, evidence showing short-term reactions of CO$_2$. This is conducive for the ability for shale caprocks to take up large amounts of CO$_2$, which could inhibit mobilization of CO$_2$, and ultimately become a beneficial attribute towards containment. Therefore, shales can be viewed as both a seal, and a reservoir for CO$_2$ storage. Although there is strong evidence for immobilization of CO$_2$ in these shale lithotypes, there is still concern regarding swelling of the shale material which could cause instability in overlying caprock lithologies, therefore there is a need for further research on this topic (Busch et al., 2009).
2.4.2 Adsorption in CO₂ Reservoir Rocks

The typical rock type primarily used as a geological storage reservoir for CO₂ is sandstone. Sandstone is defined by being of sedimentary origin and consist of sand sized particles which are usually cemented together. Sandstones are composed of detrital particles which vary in maturity and sorting which could impact permeability and porosity, where a more mature sandstone could show low permeability (Nichols, 2013). Due to these properties, sandstone has high inherent porosity and permeability properties. Not all sandstones have the capacity to take up large quantities of CO₂; one of the discerning factors being the adsorption capacity. There have been many studies using volumetric analysis to prove the capability for CO₂ to be adsorbed onto sandstones to substantiate reservoir potential. Studies such as the ones by Fujii et al. (2010) and Fujii et al. (2009) have shown convincing evidence that certain sandstone lithotypes to have the ability to adsorb large amounts of CO₂.

In a study conducted by Fujii et al. (2009), Kimachi Sandstone (from Shimane Prefecture, Japan) and lidate Granite (from Fukashima, Japan) where analysed for their adsorption potential and suitability as CO₂ reservoir rocks. Granite was included in the study as the authors determined that that many areas within the vicinity of the potential storage site contained igneous intrusive rocks, similar to the Karoo Basin’s many dolerite dykes, which could affect reservoir capacity. Therefore, Fujii et al. (2009) set out to determine whether granite could lead to expansion of the storage reservoir by subjecting the lidate Granite to the same experimental analyses as the primary Kimachi Sandstone reservoir rock. Granite is a granular, crystalline igneous rock with comparable mineralogy to dolerites in terms of mica and feldspar aggregates.

The samples were analysed as whole rock, water-saturated and air-dried plug samples using a volumetric technique. Experimental parameters consisted of constant temperatures of 33, 40 and 50 °C and pressures up to 20 MPa. Excess CO₂ adsorption was measured and recorded Fujii et al. (2009).

Fujii et al. (2009) determined that for both rock types, the adsorption isotherms inflection points representing maximum excess adsorption were reached at 8, 9 and 10 MPa at constant temperatures of 33, 40 and 50 °C respectively. Temperature had a direct effect on adsorption potential, where the higher the temperature the lower the adsorption capacity, with a difference of ~0.25 mmol/g of CO₂ in 10 °C increments (Fig. 2.8). Water saturation played an important role in adsorption capacity (Fujii et al. 2009). The air-dried Kamachi Sandstone had a lower excess adsorption of ~ 1.25 mmol/g, while the water-saturated equivalent had a higher excess adsorption of ~ 1.5 mmol/g at a constant 40 °C temperature (Fig. 2.8). A similar trend was seen in the lidate (granite) isotherms.
Both the granite and sandstone samples showed potential for adsorption in both water-saturated and dried samples; therefore the study concluded that CO$_2$ can be adsorbed onto mineral surfaces with little concern for water-filled content. Finally, it was demonstrated by Fujii et al. (2009) that porosity has little to no effect on adsorption capacity, but rather the rock type plays a dominant role as the isotherms of both granite and sandstone showed an excess adsorption of 1.0 mmol/g and 1.8 mmol/g respectively at a constant temperature of 33 °C and 18 MPa (Fig. 2.8).

<table>
<thead>
<tr>
<th>Table 2.4 - Physical properties of Kimachi Sandstone and lidate Granite (Fujii et al., 2009)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Sample</strong></td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Kimachi Sandstone</td>
</tr>
<tr>
<td>Iidate Granite</td>
</tr>
</tbody>
</table>

Building on from the Fujii et al. (2009), Fujii et al. (2010) assessed these samples further at pressures up to 20 MPa at a constant temperature of 50 °C and 100 °C. The 4 samples of interest in that study were the Berea Sandstone, Kimachi Standstone, and two pure mineral samples of quartz and albite, the primary constituents in these sandstones. The Berea sandstone consisted predominantly of quartz (~90% vol.), whereas the Kimachi Sandstone consisted mainly of plagioclase (~90% vol.). The Berea Sandstone sample has a slightly lower porosity than the Kimachi Sandstone (Table. 2.5), yet reported a higher adsorption capacity.
The results obtained by Fujii et al. (2010) found that the maximum CO$_2$ adsorption capacity of the Berea Sandstone consisted of 3.7 mmol/cm$^3$ (equivalent to 1.75 mmol/g) and 2.8 mmol/cm$^3$ (1.3 mmol/g) at constant 50 °C and 100 °C observed at a 20 MPa pressure (Fig. 2.8). When compared with the feldspar-rich Kimachi sandstone, it had a far lower adsorption capacity (close to half of that of the Berea sandstone), with a maximum adsorption of 1.0 mmol/cm$^3$ (0.4 mmol/g) at 50 °C and 100 °C at pressures of 10 MPa and 15 MPa respectively. Between the two mineral samples (quartz and albite), quartz performed the best in terms of adsorption capacity, with a maximum excess adsorption of 1.0 mmol/cm$^3$ at a pressure of ~ 10 MPa, whereas the albite sample showed a 0.8 mmol/cm$^3$ at approximately the same pressure and constant 50 °C temperature.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Bulk density (g/cm$^3$)</th>
<th>Porosity (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kimachi sandstone</td>
<td>2.80</td>
<td>2.51</td>
<td>20.0</td>
</tr>
<tr>
<td>Berea sandstone</td>
<td>0.84</td>
<td>2.11</td>
<td>19.0</td>
</tr>
<tr>
<td>Quartz</td>
<td>-</td>
<td>2.60</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Albite</td>
<td>-</td>
<td>2.60</td>
<td>0.9</td>
</tr>
</tbody>
</table>

As with the Fujii et al. (2009) study, the Fujii et al. (2010) study, by use of the gravimetric method, found that an increased temperature had an adverse effect on adsorption potential of geological material. All the samples exposed to 100 °C had far less excess adsorption than at 50 °C. Another conclusion drawn from the results, showed that porosity does not directly affect the adsorption capacity for CO$_2$, as the Berea Sandstone which had a slightly lower porosity and displayed a far greater capacity for adsorption of CO$_2$ than the Kimachi Sandstone. The high level of adsorption potential found in the Berea Sandstone could also have been attributed to its high quartz content. From the results, the pure quartz sample outperformed the albite sample in terms of adsorption capacity in the order of ~ 0.2 mmol/cm$^3$ (Fig. 2.9). Fujii et al. (2010) concluded that, due to the peculiarly high excess adsorption found in the Berea Sandstone, that quartz arenitic sandstones (such as the Berea Sandstone) provides significant potential as a geological CO$_2$ storage reservoir than its arkosic counterparts (Fujii et al., 2010).
Chapter 2: Literature Review

2.5 Chapter Summary

- Fossil fuel is still an essential component in the world’s energy mix.
- Literature states there is a link between anthropogenic CO$_2$ emissions and climate change which needs to be addressed.
- CCS is a technology which consists of capturing CO$_2$ at the point source of emission, compressing the captured CO$_2$ in a supercritical state and transporting it to a geological storage site, where it is pumped to the subsurface for storage.
- CCS is a quintessential component for climate change remediation.
- CCS has worked in numerous sites around the world and has been implemented in many country’s clean energy plans globally.
- Understanding the CO$_2$ adsorption potential of a geological storage basin is crucial before attempting to inject CO$_2$. This due to leakage concerns if adsorption is too low or does not occur within geological material.
- Studies by Busch et al. (2008), Heller and Zoback (2014), Fujii et al. (2009), and Fujii et al. (2010) lay the foundation for the current study in determining CO$_2$ storage potential in terms of the CO$_2$ adsorption capacity of rocks found in the South-Eastern MKB. Findings from literature are summerised in Table 2.6.

Figure 2.9 - Adsorption isotherms (derived from the gravimetric method) of various rock and mineral samples at constant temperatures of 50 °C on the left and 100 °C on the right (Fujii et al., 2010).

![Adsorption isotherms](image-url)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Inflection Pressure</th>
<th>Max. CO₂ Adsorption Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Busch et al. (2008) CO₂ adsorption at constant 45°C – Volumetric Method</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muderong Shale (a.r)</td>
<td>12 MPa</td>
<td>~1.0 nmol/g</td>
</tr>
<tr>
<td>Muderong Shale (dried)</td>
<td>12 MPa</td>
<td>0.4 nmol/g</td>
</tr>
<tr>
<td><strong>Heller and Zoback (2010) CO₂ adsorption at constant 40°C – Volumetric Method</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barnett Shale</td>
<td>~4 MPa</td>
<td>~80 SCF/ton</td>
</tr>
<tr>
<td><strong>Fujii et al. (2009) CO₂ adsorption at constant 40°C – Volumetric Method</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kimachi Sandstone</td>
<td>18 MPa</td>
<td>~1.5 mmol/g</td>
</tr>
<tr>
<td>Iidate Granite</td>
<td>~18 MPa</td>
<td>~0.75 mmol/g</td>
</tr>
<tr>
<td><strong>Fujii et al. (2010) CO₂ adsorption at constant 50°C – Gravimetric Method</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berea Sandstone</td>
<td>~20 MPa</td>
<td>~1.75 mmol/g</td>
</tr>
<tr>
<td>Granite</td>
<td>~12 MPa</td>
<td>~0.75 mmol/g</td>
</tr>
<tr>
<td>Shale</td>
<td>~12 MPa</td>
<td>1.0 mmol/g</td>
</tr>
</tbody>
</table>
Chapter 3 Research Methodology

To achieve the aims and objectives of this study, this chapter will address the methodology regarding sampling and the approach relating to each analytical technique. The methodology was conducted in a systematic manner, where each analytical assessment technique applied to the geological samples leads onto the next, creating a comprehensive understanding of the study. The analyses characterised and classified the geological samples according to their mineralogy (petrography and XRD), porosity (BET) and CO₂ adsorption potential (HPVA). Most of the analysis were conducted in South Africa, apart from the HPVA which was conducted at the Illinois State Geological Survey (ISGS) in the United States. Table 3.1 provides an overview of the methodology followed.

Table 3.1: Summary Workflow Diagram

3.1 Sampling

Samples were acquired from borehole KWV-01, drilled in the Willowvale area within the Eastern Cape, South Africa (Fig. 1.1). This borehole is one of two drilled as part of a drilling project conducted by CIMERA under the umbrella of the KARIN project (de Kock et al., 2016). Drilling intercepted the Beaufort, Ecca and Dwyka Groups of the Karoo Supergroup. Samples were taken from the Ecca Group at depths below 800m, specifically between 812 – 2304m, targeting various lithological units (Figs 1.3 and 1.4a and 1.4b). For the purposes of the current study, 10 samples were selected, based on lithology and constrained by the budget; the HPVA analyses were very costly. Samples were selected from different geological horizons of thickly layered sandstones and shales, as well as an intruding dolerite samples. Dolerite was included as this rock type is ubiquitous within the geological basin and it is necessary to understand
the role this lithology may play in terms of CO$_2$ sorption. The units sampled consist of the Trumpeters, Wonderfontein and Pluto’s Vale Members (of the Ripon Formation), where one set of overlying shale and underlying sandstone where taken from each Member (Fig. 3.1). The Whitehill Formation was sampled more extensively, where two sets of shale and sandstone were obtained. Each core sample ranged in length between 14 and 20cm. The core was segmented, with half retained at the CGS, Donkerhoek core shed, as part of the core database. Portions of each segmented core were dedicated to a specific analysis and therefore had to be prepared in accordance for each analytical technique (Table 3.2); each segment appeared homogeneous.

Figure 3.1 - The KWV-Willowvale drill- core consisting of: A) Trumpeters Member B) Wonderfontein Member C) Pluto’s Vale Member D) Whitehill Formation of the Ecca Group
Table 3.2 - Tabulated sample location, lithology, preparation of samples and type analysis

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>FROM</th>
<th>TO</th>
<th>Stratigraphic Unit</th>
<th>Lithology Confirmed by de Kock et al. (2016)</th>
<th>Sample Prep</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-01</td>
<td>812.141</td>
<td>812.34</td>
<td>Trumpeters Member</td>
<td>Massive Silty Shale</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
</tr>
<tr>
<td>KWV-02</td>
<td>813.8</td>
<td>814</td>
<td>Trumpeters Member</td>
<td>Massive Sandstone</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
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<tr>
<td>KWV-05</td>
<td>836.3</td>
<td>836.5</td>
<td>Wonderfontein Formation</td>
<td>Massive Shale</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
</tr>
<tr>
<td>KWV-06</td>
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<td>838.25</td>
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<td>Massive Sandstone</td>
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<td>1502.25</td>
<td>Pluto’s Vale Member</td>
<td>Siltstone</td>
<td>Thin sections Powdered</td>
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</tr>
<tr>
<td>KWV-10</td>
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<td>1504.35</td>
<td>Pluto’s Vale Member</td>
<td>Massive Sandstone</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
</tr>
<tr>
<td>KWV-15</td>
<td>2277.15</td>
<td>2277.35</td>
<td>Whitehill Formation</td>
<td>Dolerite</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
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<td>Dolerite</td>
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<td>2296.62</td>
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<td>Carbonaceous Shale</td>
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<td>KWV-16</td>
<td>2304.74</td>
<td>2304.88</td>
<td>Whitehill Formation</td>
<td>Carbonaceous Shale</td>
<td>Thin sections Powdered</td>
<td>Microscopy XRD BET HPVA</td>
</tr>
</tbody>
</table>

3.2 Sample Preparation

The selected core samples were further split in half, where half was made into blocks and other sections of the sample were crushed with a hammer. The blocks were used for thin sections and the crushed samples were placed in the mill to powder the sample. (Table. 3.2).

3.2.1 Thin Sections
Thin sections were prepared in a manner to observe porosity within the geological samples. This is done by submerging the 20 x 30 x 8 mm rock samples in tinted epoxy resin and placing them under a vacuum for two days so that the coloured epoxy resin could seep into and impregnate the pore spaces of the rock. After this, the sample was ground and mounted on frosted glass (using none tinted epoxy resin), then polished to a 30 µm thickness and covered using a coverslip (Fig. 3.2). The sample preparation was conducted by Baldwin in the Geology Department sample preparation facility at UJ. Thin sections prepared in this manner are typically used in research conducted by the oil and gas industries to identify possible reservoirs which contain hydrocarbons (Bachu, 2000) and therefore can be repurposed for identifying storage reservoirs with similar results.

3.2.2 Powders

Samples in a powdered form where required for certain analyses. The crushed particles of each geological sample were placed in an agate and milled using an excenter rotor for approximately 3 minutes per sample. The homogenized sample consisted of particles 20µm. Particle size was determined using routine sieving techniques. The powdered samples were used for multiple analyses including XRD and volumetric studies conducted in this research. XRD analysis required samples prepared in this way as the PANalytical X’Pert Pro powder diffractometer can only assess powdered geological samples for optimal and accurate results. Similarly, for the volumetric experimental apparatus, powdered samples were required due to instrumental limitations which restrict the analysis of whole rock samples in order to reproduce isotherms with a high accuracy. The BET analytical technique requires powdered samples with particle size of -75 µm, following Okolo et al. (2017).

3.3 Characterisation Techniques

Four main types of sample characterization were conducted during this study, namely: 1) thin section petrography; 2) XRD; 3) BET and; 4) HPVA. These techniques were used to identify the samples mineralogical, physical, and chemical characteristics, respectively.

3.3.1 Thin Section Petrography
Thin sections were used to study the mineralogy and to identify pore spaces and their geometries. A mineral guide was used to identify minerals, the occurrence of which were later confirmed by XRD. The vacant pore spaces were occupied by the luminescent yellow dyed epoxy for ease of identification. All microscopy work was done in the CIMERA offices at UJ, using an Olympus microscope. Rocks were classified using the guide of Nichols (2013) using both grain size and texture as defining factors.

3.3.2 XRD

The XRD was used to confirm the mineralogy identified during thin section examination. Sample powders were used. The type of minerals present in rock samples plays a role in the potential for CO₂ adsorption (Fuji et al., 2010; Heller and Zoback, 2014). These experiments were done at UJ SPECTRAU.

3.3.2.1 Principles of XRD

XRD is considered one of the best techniques available to identify and quantify most mineral content in rocks containing clay (Środoń, 2001). This technique is primarily used on crystalline material to identify its phase and provide information on unit cell dimensions (Dutrow and Clark, 2016). The interference caused by the bombardment of the sample with electrons and the constructive interference (diffraction rays) produced from that is due to compliance with Bragg’s Law (Dutrow and Clark, 2016): (nλ = 2dsinθ, where n = order of diffraction peak; λ = wavelength of x-ray radiation; d = inter-planar (lattice) spacing; θ = diffraction angle). Bragg’s Law is described as the wavelength produced by diffraction of electromagnetic radiation and the angle it diffracts, as well as the lattice spacing in a crystalline material (Fultz and Howe, 2013; Dutrow and Clark, 2016). According to Dutrow and Clark (2016), the diffracted x-rays (which are processed and counted through the instrument by scanning and analysing the sample) can therefore determine the 2θ angles properties. All possible diffraction directions of the lattice should be obtained due to the sample being in a powdered form as to cater for random orientation of the individual particle material (Dutrow and Clark, 2016). The conversion between the diffraction peaks and d-spacing allows for identification of minerals (or other material), as each mineral has a unique combination of d-spacing known as a “fingerprint” (Dutrow and Clark, 2016). Thereafter, possible minerals are determined through matching of referencing standard fingerprints to this effect.

According to Dutrow and Clark (2016) and Fultz and Howe (2013), the following describes the specifics of how powdered XRD works:

- The X-Ray Diffractometer consists of three main components: X-Ray tube; sample holder; and an X-Ray detector. In the x-ray tube, x-rays are created in a cathode ray
by applying voltage to a filament which in turn produces electrons that accelerate towards the sample, bombarding the sample material with electrons.

- At the point where electrons can displace inner shell electrons of the target material, representative x-ray spectra (of variable wavelengths and intensities) are created. The $K_{\alpha 1}$ emission has a slightly shorter wavelength, as well as twice the wave intensity as $K_{\alpha 2}$. The defined wavelengths produced by the target material are usually specific to samples consisting of Cu, Fe, Mo and Cr.
- These X-rays are then accurately aligned and directed at the target material whereby they are fixed on the sample.
- Both the sample and detector are rotated, and the intensity of the reflected X-rays are recorded.
- The detector then converts the processed X-ray signal, and interprets the signal as count rates, which is sent as an output to a computer or printed out. The positioning of the X-ray diffractometer is orientated so that the sample rotates in the path of the collimated X-ray beam at an angle $\theta$ whilst the detector is mounted on an arm to collect the diffracted X-rays as the rotation occurs at 2$\theta$ angle (this angle is maintained through the goniometer). The typical pattern for powdered samples are collected at 2$\theta$ from ~5 to 70° angles which are present in the X-ray scan.

XRD's key functionality is to identify crystalline phases through the diffraction method described above (Fultz and Howe, 2013). Through the use of Bragg’s law and computer software, over 200,000 mostly metal crystalline phases, as well as other inorganic crystalline materials, can be identified. This analytical technique is useful for applications such as: identifying crystalline material, identification of fine-grained minerals such as clays (and other minerals which are optically difficult to identify); determining unit cell dimensions; and sample purity (Dutrow and Clark, 2016). Furthermore, it can quantify major mineral phases using Rietveld refinement (not used in this study).

According to Dutrow and Clark (2016) the following strengths of XRD are:

- XRD is a very powerful tool for classification of inorganic material, especially so for identification of unknown minerals in geological samples.
- It has the ability to rapidly identify unknown minerals, for the most part unambiguously, in 20 minutes or less per mineral phase. This can be done with minimal sample preparation.
- XRD equipment is largely available in most research facilities around the world.
- Data interpretation is relatively easy to understand and straightforward.
Dutrow and Clark (2016) also discusses limitations in terms of its analytical capacity:

- Homogeneous and single-phase samples are favoured for classifying an unknown.
- Access to a standard referencing file (d-spacing) of inorganic compounds is required for identification to take place.

3.3.2.2 Experimental Procedure

The analysis was done using a PANalytical X'Pert Pro powder diffractometer, fitted with an X'Celerator detector with a Cu divergence slit and a Ni filter. The XRD sample spinner stage was loaded via a back-loading technique using powdered samples. Each sample was compacted, being careful to remove excess sample powder, before being securely clipped in and loaded into the sample loader cartridge (which can take a total of 15 samples at a time). Each sample was run for 2 hours, with a total experimental time duration of approximately 20 hours for all the samples to be analysed. The various phases were identified using X'Pert Highscore + software with a digital standard used for inorganic and mineral composition identification. Each peak was defined to provide a result which takes into consideration all possible mineral compositions, and by use of geological knowledge of the rock samples and minerals which are most likely part of the bulk composition of the geological samples were identified and recorded.

3.3.3 BET Analytical Technique

The BET technique is used to quantify porosity in terms of surface area and volume of the pores within rock samples.

3.3.3.1 Background

One of the most critical points when assessing a potential CO\textsubscript{2} storage reservoir is to quantify the available storage space, i.e. vacant pore spaces. The purpose of the BET analysis is to determine the porosity of the geological samples. This is done to quantify the pore size by using the principle of multilayer adsorption proposed by Brunauer (1938) (Park and Seo, 2011). CO\textsubscript{2} was used as the adsorbate, providing a realistic quantification of pore-spaces for CO\textsubscript{2} occupancy. The BET apparatus used here was the Micrometrics ASAP 2020 surface area and porosity analyser. As this is an adsorption analytical technique at STP, the BET results were used to select the samples for the HPVA tests.

3.3.3.2 Theoretical Adsorption Models
Adsorption isotherms graphically display the quantity of gas adsorbed (here CO\textsubscript{2} was used) onto a porous solid. The solids in this study were sandstones, shales, and dolerites (non-porous). The experimental results obtained from the complete adsorption process were used and theoretical adsorption models were applied to interpret the experimental data. The results were evaluated using the: 1) Dubinin-Radushkevich (D-R), 2) Dubinin-Astakhov (D-A), and 3) Brunauer-Emmet-Teller (BET) method/models.

1) Dubinin-Radushkevich (D-R) Model: this model was used in this study to interpret experimental results via the equipment software. The D-R model was developed to analyse subcritical vapours within microporous adsorbents conforming to the pore filling mechanism (Foo and Hameed, 2010). Generally, it is used to describe the adsorption mechanism with a Gaussian energy distribution on a heterogeneous surface (Dąbrowski, 2001; Foo and Hameed, 2010; Günay et al., 2007).

The D-R model is given by:

\[ q_e = (q_s) \exp(-k_{ad} \varepsilon^2) \] \hspace{1cm} \text{(non-linear form)} \hspace{1cm} \text{(Eq. 1)}

\[ \ln(q_e) = \ln(q_s) - k_{ad} \varepsilon^2 \] \hspace{1cm} \text{(Eq. 2)}

\[ \ln(q_s) \text{ vs } \varepsilon^2 \] \hspace{1cm} \text{(Eq. 3)}

Where:

- \( q_e \) – Amount of adsorbate in the adsorbent at equilibrium (mg/g)
- \( q_s \) – Theoretical isotherm saturation capacity
- \( \varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \)
- \( R \) – Universal gas constant (8.314 J/mol K)
- \( C_e \) – Equilibrium concentration (mg/L)

2) Dubinin-Astakhov (D-A) Model: the model was developed to determine adsorption equilibrium of gases and vapours on non-homogeneous carbonaceous solids with a wider range of pore size distribution (Dubinin, 1975; Singh and Kumar, 2016). The D-A equation (Eq. 4) describes the relationship between equilibrium pressure, adsorption temperature and the amount of CO\textsubscript{2} adsorbed through onto an adsorbent solid through the micropore volume filling model (Singh and Kumar, 2016; Srinivasan et al., 2012). There are 3 essential parameters on which the D-A model is based on: (1) the limiting volumetric adsorbate uptake (given by \( q_0 \)); (2) the mean free energy (E); and (3) the adsorbent solid surface-structural heterogeneity limit (n) were assessed for isotherm data by using linear regression analysis for best fit (Singh and Kumar, 2016; Saha et al., 2007; Saha et al., 2011).
The D-A equation follows the same principles as the D-R equation, deferring by a factor of $n = 2$ (equation 1), where D-A (Roque-Malherbe, 2000; Wood, 2001):

$$q = q_o \cdot \exp\left(-\frac{E}{P}\right).$$

(2) Brunauer-Emmet-Teller (BET) method: the model was developed based on what is known as a multilayer adsorption theory (BET Theory). Building on the premise of the Langmuir monolayer theory, the BET theory extends to a multilayer adsorption. The BET equation is used to determine the monolayer volume of adsorbed gas; thereafter it can be implemented to calculate the surface area of the adsorbent. The BET theory is derived from 3 main hypotheses:

1) A surface is homogeneous energetically, i.e. all adsorption sites on solid surfaces have the same adsorption energy ($E_1$);
2) There is no lateral interaction between adsorbed molecules;
3) Adsorption energies from $E_3$ and higher layers are equal to condensation energy of the adsorptive ($E_1$).

* $E_1$ is the heat of adsorption for the first layer.

The BET equation (Eq. 5) was first proposed by Brunauer, Emmett and Teller. This model is the best mode for interpreting multilayer adsorption isotherms, specifically for the type II and type III isotherms (Andrade et al., 2011).

$$\frac{V_mC_p}{(P_o-P)}\left[1+\frac{(C-1)P}{P_o}\right] = \frac{1}{1+\frac{(C-1)P}{P_o}}$$

(Eq. 5) (Brunauer et al., 1938; Henson, 1969)

Where,

- $V_m$ - is the volume of gas adsorbed onto the solid adsorbent
- $P/P_o$ - relative pressure
- $C$ – is the constant characteristic of the gas-solid pair
- $V_m$ – is the monolayer capacity

The D-R and D-A models give the most suitable experimental points, which indicates that the best representation of the ion exchange processes through the micropore volume filling theory (Singh and Kumar, 2016). The BET equation is the basis of interpretation of isotherms given by non-porous solids (Sing, 1985).

### 3.3.3.3 BET Theory - Gas Adsorption Isotherms

There is a direct relationship between gas adsorbed onto a solid, the mass of the sample, the temperature and pressure, and the nature of both the solid and the molecules of gas (Gregg and Sing, 1982). The adsorption capability of a gas on a solid can be represented by an
adsorption isotherm. The isotherm shows the amount of gas adsorbed as a function of relative pressure at constant temperature. Sing (1985) describes these 6 idealized models (adapted into the IUPAC classification) of adsorption isotherms to interpret BET isotherm data according to the geometry of these graphs. This provides insight, which is essential in interpreting the adsorption isotherms in terms of the physical adsorption properties of the adsorbent and porosity thereafter. The adsorption isotherms produced by using the BET data are classified as Type I – V:

- **Type I Isotherms**: are characterized by a virtually horizontal plateau of an isotherm (Fig. 3.3). When approaching the $P/P_0 = 1$ axis, the isotherm may cut the axis or exponentially increases in a “tail” shape when approaching pressure saturation (Greg and Sing, 1982). Type I isotherms usually indicate a dominant micropore filling process. This is an indication of pore-sizes of $< 2$ nm. This type of isotherm is known as the Langmuir type isotherm.

- **Type II Isotherms**: differs vastly from the Langmuir Model. This type of isotherm is typical of an isotherm attained by macroporous or non-porous adsorbents (Sing, 1985). The point where the isotherm begins to gradually increase linearly through adsorption given by the mid-section of the isotherm (point B on Fig. 3.3); usually interpreted as the path where monolayer coverage is complete and the multilayer adsorption processes begin (Sing, 1985).

- **Type III Isotherms**: are convex towards the relative pressure axis and have no point B (Fig. 3.3). This isotherm is uncommon. This isotherm, the adsorbate-adsorbate interactions are the most important functional process in attaining this type of isotherm (Sing, 1985). The type III isotherms are an indication of characteristics pertaining to non-porous or macroporous solids (Greg and Sing, 1982).

- **Type IV Isotherms**: in the low-pressure region, the type IV isotherm follows the same path as the type II isotherm (Greg and Sing, 1982). Thereafter, at a certain point adsorption begins to increase until at higher pressures (Fig. 3.3) where it plateaus (Greg and Sing, 1982). This indicates monolayer-multilayer adsorption similarly to Type II (Sing, 1985). This type of isotherm is described as a hysteresis loop, where condensation occurs within the mesopores of the solid adsorbent, thus limiting uptake in high relative pressure ranges (Sing, 1985). This isotherm generally indicates mesoporous solids (Sing, 1985).

- **Type V Isotherms**: are uncommon. They have a similar convexity away from the $P/P_0$ axis during the initial course of the isotherm as the Type III isotherm. Thereafter, the isotherm encounters a point of inflection at high relative pressures (Fig. 3.3), usually after $\sim 0.5$ or higher (Greg and Sing, 1982). Sometimes there is a final upward step to
the isotherm which is usually an indication of mesoporosity (Greg and Sing, 1982). Type V isotherms are usually given by mesoporous or microporous solids (Greg and Sing, 1982).

- Type VI Isotherms: these isotherms are identified by their sharpness of the steps of the isotherm path, which are temperature and pressure dependent (Sing, 1985). For step height elevation of the isotherm (Fig. 3.3) is indicative of the monolayer adsorption capacity for each adsorbed layer (Sing, 1985).

![Image of isotherms](image.png)

Figure 3.3 - The 6 idealised isotherms showing the types of physisorption (Sing, 1985)

3.3.3.4 BET Strengths and Limitations

Volumetric analyses, such as the BET technique, are powerful tools for determining physical features of a solid (adsorbent) such as: pore size, multiple surface areas, and energies of adsorption (Condon, 2006). Physical features such as porosity of a solid can be determined with a certain degree of confidence, but only when certain theoretical assumptions and pertinent mathematical manipulations are made (Condon, 2006).

The theoretical assumptions used in the technique are described by Brame and Griggs (2016):

- Homogeneous surfaces of the adsorbent material;
- Limited molecular interactions i.e. no intermolecular interactions are considered;
- Local equilibrium: the rate of adsorption is equal to the rate of desorption;
- Kinetically limited process: the rate of reactions is limited by kinetics other than diffusion constrains.
The BET theory is the most widely used theory when calculating surface area in porous solids, but not without serious faults due to it not being rigorously tested (Condon, 2006). The theories which are commonly used produce different values, and currently there is uncertainty as to which theory yields accurate results (Condon, 2006). Some theories claim to be able to quantify these physical properties, but realistically are unable to definitively (Condon, 2006). Almost all theories are accurate to a factor of 10 as a result of the apparent features of the isotherm which allows for theoretical assumptions to be made (Condon, 2006). There are a number of methods to make use of when calculating pore radius, but most are dependent on the BET method (Condon, 2006).

3.3.3.5 Experimental Procedure

The BET method used in this study was conducted at North-West University, Potchefstroom Campus and operated by Gregory Okolo. A Micromeritics ASAP 2020 surface area and porosity analyser was used. The sample was flushed with nitrogen gas and stored in a thick polyethylene container, vacuum sealed and preserved in a desiccator prior to analysis (Okolo et al., 2017). Analysis required ~2.5 mg of dried powdered sample (to evacuate any moisture which can result an error in calculation), placed in a sample tube. Before degassing, samples were loaded into the sample tube via a filler rod for accuracy. During degassing, samples should not be exposed to temperatures above 350°C so as to not cause any structural change within the sample. The mass of the sample was then obtained in the sample tube for accuracy by subtracting the mass of empty sample tube from the mass of sample tube plus sample record this value as the mass of sample (Micromeritics, 2011). The samples were first degassed under vacuum with 10 µmHg pressures at 90°C for approximately 2800 minutes on the degassing port of the apparatus before adsorption analysis begun. The sample was then transferred into the analysis port. Parameters were set via the ASAP 2010 v4.0 software before analysis took place. Thereafter, the adsorption data was automatically calculated by the software with relative pressure ranges (P/P₀) 0 to 0.033 for CO₂, similar to the method done by Okolo et al. (2017).

3.3.4 HPVA

High Pressure Volumetric Analysis was conducted to observe CO₂ adsorption potential at high pressures. The experimental equipment was unavailable in South Africa, and so the analysis was subcontracted to the ISGS, USA, funded by SACCCS.
3.3.4.1 Background

Comparable experiments were conducted to quantify CO$_2$ adsorption of similar rock types in various studies (Busch et al., 2008; Fuji et al., 2009; Heller and Zoback, 2014). Eight samples of the 10 samples were selected based on the BET results, selecting the most adsorptive samples as well as including at least one sample of each rock type. Samples KWV-9 and KWV-15 were excluded from the HPVA study as a result of low adsorption trends. The HPVA experiments were carried out at the ISGS and raw volumetric datasets were obtained.

3.3.4.2 Experimental Procedure

An experimental schematic is shown in Fig 3.4, describing the experimental apparatus used by ISGS.

Firstly, a measurement of density of the sample was taken, calculating its volume by H$_2$ expansion into a chamber of known volume. Thereafter, a known mass of sample was placed in the sample chamber and then vacuumed. After opening the valve between the CO$_2$ and sample chamber (Fig. 3.4), the gas then expanded into the chamber. Knowing the volume of the system on either side of the valve allowed for the calculation to determine how much gas adsorbed onto the sample substrate. The experimental setup as described up to this point is similar to the one used by Fuji et al. (2009) and Busch et al. (2008) but differs significantly hereafter. After the system equilibrated, a program began on the syringe pump which increased the pressure on the system as a step function every 20 minutes (Busch et al. (2008), listed 15 minutes as the equilibrium time). The amount of CO$_2$ adsorbed was calculated based on the amount of mineral oil the pump had to inject to reach the target pressure.

The advantage of this system is that it takes far less operator time as almost everything is automated, and this leads to lower (relative) costs and more data points. In theory, the system can collect 30 data points a day and the samples were analysed to completion within 4 weeks. The operator setup the instrument for ~30 minutes in the morning to allow for analysis to take place throughout the day. The alternative to this is using Busch et al. (2008) method and re-vacuuming the sample after every data point. Busch et al. (2008) method would require ~40 minutes a sample and an operator to be present. These constraints limit it to, at most, 12 data points a day adding to the cost as the operator’s time is taken into consideration.
The system (Fig 3.4) works by:

1. A set amount of CO$_2$ is added to the piston chamber;
2. The syringe pump pushes up the piston which pressurises the CO$_2$ gas to a set pressure;
3. The volume of CO$_2$ is measured before and after V1 is opened;
4. When the desired pressure is reached, V2 is opened and the CO$_2$ is allowed to expand into the sample chamber;
5. System was left until equilibrium was reached and for adsorption to occur onto the rock sample.
Volumetric Calculations
To obtain the amount of CO\textsubscript{2} adsorbed, a series of calculations where done on the raw data from the data logger. Calculations commenced with determining the system volume \(V_s\). This is the volume of the CO\textsubscript{2} in the piston cylinder, tubing, and pressure transducer up until the valve that opens into the sample chamber, \(V_2\) (Fig. 3.4). The determination is made by measuring the pressure at two points and the amount of mineral oil injected to change between those pressures. The amount of CO\textsubscript{2} in the system remained constant during this process. Firstly, a calculated density of CO\textsubscript{2} at the points before and after the change in pressure were made using Span and Wagner (1996) equation of state.

Because the mass is constant, it is known that,
\[
\rho_1 V_s = \rho_2 (V_s - \text{disp}) \tag{Eq. 6}
\]

Therefore, for \(V_s\),
\[
V_s = \frac{-\text{disp} \cdot \rho_2}{\rho_1 - \rho_2} \tag{Eq. 7}
\]

\(V_s\) is then the volume of the system at the beginning of the volume check. It changes as the pump either injects or removes mineral oil to maintain a certain pressure. Much like the \(V_s\), the pump reading at the beginning of the volume check is what values are measured relative to. The pump is capable of holding \(\sim 508\) ml of oil and reads 508 when full, so a decrease in the pump reading means the pump injected mineral oil into the cylinder.

The volume once \(V_2\) is opened,
\[
V_t = V_s + V_c - V_r + D_p \tag{Eq. 8}
\]

Where \(V_t\) is the total volume, \(V_s\) is the system volume, \(V_c\) is the chamber volume, \(V_r\) is the rock volume, and \(D_p\) is the relative pump displacement.

Given \(V_t\), the pressure (taken from the pressure data log), temperature (constant 45 °C), the density and from the density and volume you get the mass of CO\textsubscript{2} in the \(V_t\). Given the initial mass, \(\rho_1 \cdot V_s\) in equation 1, the amount adsorbed will be
\[
m_s = \rho_1 V_s - \rho_c V_t \tag{Eq. 9}
\]

Where \(m_s\) is the mass of CO\textsubscript{2} adsorbed, \(\rho_c\) is the density of CO\textsubscript{2} at the time of the reading, and \(V_t\) is the total volume at the time of the reading.

There was another event known as venting, where analysis started out with a small volume of CO\textsubscript{2} at high pressure and then increased the volume of the system, sometimes vice versa. At
times the piston cylinder did not have enough capacity to expand over the entire range of the experiment, therefore the system would vent out CO$_2$, decrease the system volume, and vacuum out the sample chamber. This leads to a loss of mass and the total amount of CO$_2$ after these events would no longer be $\rho_1 V_S$. In this case the new amount of CO$_2$ in the system would be

$$m = \rho_0 (V_S + D_p)$$

(Eq. 10)

Which would be used in place of $\rho_1 V_S$ in equation 9 after venting.

It typically took two to three venting attempts to go the full range of 1-18 mPa. The samples equilibrate for one hour and take two readings of the pump volume during that time. There were some instances where the system clearly had not equilibrated, and continued more readings at that pressure until it stabilized.

Finally, excess adsorption of the sample is calculated using equation adapted by Ozdemir et al. (2003):

$$m_{ex} = m(1 - \rho_{CO2}/\rho_{sample})$$

(Eq. 11)

$m$ = the mass of CO$_2$ adsorbed. The final excess adsorption is reported as moles CO$_2$ per gram of sample (mol/g). Excess adsorption is calculated assuming temperature is constant and above critical (31.1°C) over entire pressure range as per Dubinin (1965) stipulation. Thereafter, the number of moles of CO$_2$ adsorbed was calculated assuming STP molar mass (44.01 g).
Chapter 4 – Results

4.1 Introduction

There are four main analyses used in this study, namely: petrography, XRD, BET, and HPVA. A systematic approach was used as some observations had to be made before the next stage of analysis could begin (Fig. 4.1). Hand specimens were studied to identify the lithology. Petrography was used for preliminary mineral identification. Minerals identified under the microscope were confirmed by XRD. Data from the BET was used to select samples for HPVA, the final stage of analysis.

4.2 Hand Specimens and Petrography

Hand specimen descriptions were made at the time of sampling in the core shed at the CGS in Pretoria. These samples where described in core form noting all contact types, general structures, fractures, average grain size and basic mineral content. Basic core descriptions for all 10 samples selected are compiled in Table 4.1. The descriptions included in Table 4.1 considers the lithologies found at depths below 800m, as required for CO₂ storage. Thin sections were prepared from these samples and assessed microscopically where grain size, bulk composition (Table 4.2) and porosity properties were described.

4.2.1 Hand Specimen Descriptions

Table 4.1 shows the lithologies found at the specific depths with basic hand specimen descriptions using Cairncross (2013) guide for logging Karoo core. These observations were confirmed with core logs recorded by de Kock et al. (2016). It is important to understand the physical nature of the rock samples, specifically grain size, contact relationships and mineralogy, to classify these samples in terms of their potential suitability for CO₂ storage.
<table>
<thead>
<tr>
<th>Sample I.D</th>
<th>DEPTH (m)</th>
<th>Stratigraphic Unit</th>
<th>Lithology</th>
<th>Core Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-2</td>
<td>813.8</td>
<td>Trumpeters Member</td>
<td>Sandstone</td>
<td>Light grey, fine grained, moderate to well sorted, massive with fractures. Interbedded Breccia, grey, angular massive Shale fragments, in fine grained sand as matrix (not incl. in sample interval)</td>
</tr>
<tr>
<td>KWV-5</td>
<td>836.3</td>
<td>Wonderfontein Member</td>
<td>Silty Shale</td>
<td>Massive dark grey to black mudstone with silt to clay sized particles. Burrowing in places.</td>
</tr>
<tr>
<td>KWV-6</td>
<td>838.06</td>
<td>Wonderfontein Member</td>
<td>Sandstone</td>
<td>Medium grey, fine grained, planar lamination of fine grained dark possible carbonaceous material, ~6m thick. Highly fractured with calcite infill.</td>
</tr>
<tr>
<td>KWV-10</td>
<td>1504.15</td>
<td>Pluto’s Vale Member</td>
<td>Sandstone</td>
<td>Sharp base, minor mudstone clasts, calcite veining present</td>
</tr>
<tr>
<td>KWV-15</td>
<td>2277.15</td>
<td>Whitehill Formation</td>
<td>Dolerite</td>
<td>Fine grained crystalline, calcite veins present.</td>
</tr>
<tr>
<td>KWV-13</td>
<td>2294.8</td>
<td>Whitehill Formation</td>
<td>Dolerite</td>
<td>Grey green very fine crystalline. Upper and lower contacts are irregular but horizontal</td>
</tr>
<tr>
<td>KWV-14</td>
<td>2296.5</td>
<td>Whitehill Formation</td>
<td>Carbonaceous Shale</td>
<td>Black, massive, with clay sized particle matrix. Bedding defined by thin sandstone beds. Disseminated pyrite grains (from &lt;1mm) throughout and on bedding planes.</td>
</tr>
<tr>
<td>KWV-16</td>
<td>2304.74</td>
<td>Whitehill Formation</td>
<td>Carbonaceous Shale</td>
<td>Black, massive, with clay sized particle matrix. Bedding defined by thin sandstone beds. Disseminated pyrite grains (from &lt;1mm to 5mm in size) throughout and confined on certain bedding planes as wavy laminae.</td>
</tr>
</tbody>
</table>
All the shale samples consist of the same facies apart from the carbonaceous shales of the Whitehill Formation. Conventionally, shales are considered for their possible seal potential and sandstones for their storage potential within the CCS context. Shale samples: KWV-1; KWV-5; KWV-9 (due to speculated low permeability) would be more likely to have a seal potential, and sandstone samples: KWV-2; KWV-6; KWV-10 (due to higher porosity) should have better storage potential. Saghafi et al. (2008) found that due to the low diffusivity of dolerites, they can act as traps for gas storage. The dolerites discussed by Saghafi et al. (2008) are similar to dolerites: KWV-15; KWV-13 described in Table 4.1, and therefore have potential to seal a storage basin. Busch et al. (2008) found that shales could have the potential for CO₂ storage granted they have a good adsorption capacity. Nuttal et al. (2005) particularly found a positive relation with high Total Organic Content (TOC) in mudstones and CO₂ storage potential, hence, carbonaceous shales: KWV-14; KWV-16 could have storage potential due to high TOC found in these samples by de Kock et al. (2016).

4.2.2 Petrography

All 10 samples were examined under reflected and transmitted light to assess opaque and non-opaque minerals, prepared as thin sections for observing mineralogy, texture and porosity. Basic descriptions were made with regards to mineral content, structures and porosity (Table 4.2). Both plane polarized light (PPL) and cross polarized light (XPL) was used to assess optical properties for mineral identification. The Wentworth-Udden scale for sediment grain size classification was used in conjunction with Nichols (2013) textural classification of shales specifically. General grain size classification were used for igneous rock equivalents and textural descriptions were made using Winter (2015) as reference.

Each sample is discussed in conjunction with Table 4.2 and Figures 4.2 – 4.11
Table 4.2 Approximate mineral abundance and grain sizes are observed petrographically

<table>
<thead>
<tr>
<th>Sample I.D and Depth</th>
<th>Approx. Bulk Composition</th>
<th>Approx. Grain Size</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KWV-1</strong> 812 m</td>
<td>Quartz – 25%</td>
<td>10 – 20 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 15%</td>
<td>± 20 µm</td>
</tr>
<tr>
<td></td>
<td>Orthoclase - &lt; 5%</td>
<td>15 µm</td>
</tr>
<tr>
<td></td>
<td>Albite – 5%</td>
<td>10 – 15 µm</td>
</tr>
<tr>
<td></td>
<td>Opaques (organic content) – 50%</td>
<td></td>
</tr>
<tr>
<td><strong>KWV-2</strong> 813 m</td>
<td>Microcline – 3%</td>
<td>50 – 100 µm</td>
</tr>
<tr>
<td></td>
<td>Albite – 5%</td>
<td>800 – 200 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 5%</td>
<td>200 µm (max grain size)</td>
</tr>
<tr>
<td></td>
<td>Quartz – 75%</td>
<td>80 – 400 µm</td>
</tr>
<tr>
<td></td>
<td>Chert – 2%</td>
<td>100 µm (as lithic fragments)</td>
</tr>
<tr>
<td></td>
<td>Plagioclase - &lt; 2%</td>
<td>50 – 60 µm</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 10%</td>
<td></td>
</tr>
<tr>
<td><strong>KWV-5</strong> 836 m</td>
<td>Albite – 2%</td>
<td>± 20 µm</td>
</tr>
<tr>
<td></td>
<td>Quartz – 40%</td>
<td>40 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 8%</td>
<td>20 µm</td>
</tr>
<tr>
<td></td>
<td>Biotite – 35%</td>
<td>20 – 30 µm</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 15%</td>
<td></td>
</tr>
<tr>
<td><strong>KWV-6</strong> 838 m</td>
<td>Quartz – 75%</td>
<td>± 80 µm</td>
</tr>
<tr>
<td></td>
<td>Albite – 5%</td>
<td>20 – 30 µm</td>
</tr>
<tr>
<td></td>
<td>Biotite – 2%</td>
<td>20 – 40 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – &lt; 2%</td>
<td>10 µm</td>
</tr>
<tr>
<td></td>
<td>K-Feldspar – 2%</td>
<td>10 – 20 µm</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 15%</td>
<td></td>
</tr>
<tr>
<td><strong>KWV-9</strong> 1502 m</td>
<td>Quartz – 70%</td>
<td>20 – 50 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 15%</td>
<td>10 – 20 µm</td>
</tr>
<tr>
<td></td>
<td>Albite – &lt; 2%</td>
<td>20 – 30 µm</td>
</tr>
<tr>
<td></td>
<td>K-Feldspar – 2%</td>
<td>10 – 20 µm</td>
</tr>
<tr>
<td></td>
<td>Chlorite - &lt; 1%</td>
<td>10 – 30 µm</td>
</tr>
<tr>
<td></td>
<td>Clay containing lithic fragments – 10%</td>
<td>30 µm</td>
</tr>
<tr>
<td><strong>KWV-10</strong> 1504 m</td>
<td>Quartz – 80%</td>
<td>40 – 10 µm</td>
</tr>
<tr>
<td></td>
<td>Albite – 5%</td>
<td>40 – 50 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 5%</td>
<td>180 µm</td>
</tr>
<tr>
<td></td>
<td>Biotite – 5%</td>
<td>5 – 10 µm</td>
</tr>
<tr>
<td></td>
<td>Chert – 5%</td>
<td>± 50 µm (as lithic fragments)</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 5%</td>
<td></td>
</tr>
<tr>
<td><strong>KWV-13</strong> 2294 m</td>
<td>Plagioclase – 70%</td>
<td>100 µm</td>
</tr>
<tr>
<td></td>
<td>Clinopyroxene – 15%</td>
<td>200 µm</td>
</tr>
<tr>
<td></td>
<td>Biotite – 5%</td>
<td>± 50 µm</td>
</tr>
<tr>
<td></td>
<td>Opaques – 5%</td>
<td>20 – 50 µm</td>
</tr>
<tr>
<td></td>
<td>Orthopyroxene – 5%</td>
<td>100 – 200 µm</td>
</tr>
<tr>
<td><strong>KWV-14</strong> 2296 m</td>
<td>Quartz – 42%</td>
<td>40 µm</td>
</tr>
<tr>
<td></td>
<td>Pyrite – 4%</td>
<td>10 – 50 µm</td>
</tr>
<tr>
<td></td>
<td>Muscovite – 4%</td>
<td>10 – 20 µm</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 50%</td>
<td>&lt; 5 µm</td>
</tr>
<tr>
<td><strong>KWV-15</strong> 2277 m</td>
<td>Plagioclase – 75%</td>
<td>100 – 300 µm</td>
</tr>
<tr>
<td></td>
<td>Orthopyroxene – 20%</td>
<td>100 – 1000 µm</td>
</tr>
<tr>
<td></td>
<td>Biotite – 5%</td>
<td>± 50 µm</td>
</tr>
<tr>
<td><strong>KWV-16</strong> 2304 m</td>
<td>Quartz – 10%</td>
<td>&gt;15 µm</td>
</tr>
<tr>
<td></td>
<td>Pyrite – 15%</td>
<td>± 100 µm</td>
</tr>
<tr>
<td></td>
<td>Clay minerals – 15%</td>
<td>&lt; 0.1 µm</td>
</tr>
<tr>
<td></td>
<td>Opaque (organic content) – 60%</td>
<td></td>
</tr>
</tbody>
</table>
Sample KWV-1: This rock consists of a silty shale, with an average grain-size of approximately <10 µm, classified as fine to clay sized particles forming the matrix (Fig. 4.2). The mineralogical composition this sample consists mostly of quartz (Table 4.2). The sample is moderately sorted with a few larger grains (>20 µm), which are matrix supported. Clusters of finer grained minerals have a cloudy appearance. Organic components appear opaque and occur within concretion spaces contouring between mineral grains with a total abundance of 25%, with the remaining 75% accounting for terrigenous input. Quartz grains occur with organic material forming the matrix of the rock. This sample has no visible porosity.

Sample KWV-2: This rock is a sandstone consisting of very fine to medium sand-sized particles. The particles are moderately sorted in thin section (Fig. 4.3). The sample consists of mostly quartz (Table 4.2). 10% of the bulk composition is regarded as organic, consisting of dark almost opaque particles peppered throughout the thin section (Fig. 4.3). Both albite and microcline feldspars occur as euhedral to subhedral crystal grains. Muscovite occurs as lathes in certain areas of the thin section. Quartz found in this sample occurs as subrounded to angular particles with both straight and sutured contacts. There is evidence of secondary porosity in alteration zones. Primary porosity between large quartz grains, as highlighted by the fluorescent dye are ± 200 µm in size. Pore spaces are enclosed by grain boundries and show no evidence of permeability in this regard.

Sample KWV-5: This rock is a silty shale with an average grain size of ± 20 µm, which classified the sample as medium silt (Fig. 4.4). The bulk composition consists mostly of quartz (Table 4.2). Quartz occurs as a microcrystalline variety closely associated with carbonate grains which have been partially replaced by chert. Biotite forms interstitially between larger quartz grains together with the matrix as linear orientated platy lathes. Some biotite grains are replaced by chlorite. 15% of the thin section consists of organics. There is no visible porosity found in this sample.

Sample KWV-6: This rock is a very-fine sandstone consisting of an average grain size of 80 – 100 µm in diameter, hence classified as very fine sand (Fig. 4.5). The mineral composition consists mostly of quartz (Table 4.2). The remaining 10% is regarded as a clay matrix, consisting of silt to clay sized particles. Carbonate cement occurs with cloudy clay matrix interstitially between larger minerals. Lithic fragments of chert occur less frequently in the thin section as slightly rounded components. Quartz grains have both straight and sutured contacts as subrounded to anhedral grains. Albite and K-feldspar occurs as subhedral to anhedral formed crystals. Muscovite occurs as lathes in certain areas of the thin section. Biotite occurs as lathes in alteration zones within the thin section, where it alters to chlorite. The clay sized matrix occurs between larger quartz minerals and associated with muscovite grains. The
organic content in this sample makes up 15%, with the remaining 75% as terrigenous input. The organic material forms interstitially together with the matrix in vein-like structures and concretion zones. There is no observed porosity in this thin section.

Sample KWV-9: This rock is a siltstone consisting of an average grain size of 15 µm, which is classified as fine silt. The particles are overall moderately sorted (Fig. 4.6) without fissility. Mineral composition consists mostly of quartz (Table 4.2). Chert fragments are found within the thin section with an abundance of < 1%. Quartz show grain contacts which are mostly long with fewer grains which are isolated in the surrounding matrix as well as forming minor quartz veining within the sample. Albite appears as poorly formed crystals with altered grain boundaries. Most of the larger grains of albite and quartz are fractured. Grains of albite usually form subangular to angular grains. Evidence of soft sediment clay concretions is present within the thin section in certain segments. No porosity was determined in thin section using the fluorescent dye method.

Sample KWV-10: This rock is a sandstone consisting of an average grain size of ± 100 µm, with particles moderately sorted throughout. The sample is thus classified as fine sand (Fig. 4.7). The mineralogy is similar to other sandstone samples, predominantly quartz (Table 4.2). Quartz grains occur as subangular particles. There is very little matrix (10%). Muscovite and biotite occur as lathes (ranging between 100 – 200 µm in length) throughout the thin section. Biotite is replaced by chlorite in a few altered zones. Albite forms subhedral detrital grains. The sample has a low organic content (5%), with 95% of the thin section classified as terrigenous. The high amount of stable minerals (quartz) defines this sample as being compositionally mature. Due to the roundness of the grains, the textural maturity of this sediment is said to be texturally submature. Most of the larger grains are moderately fractured. Porosity was not identified in this sample.

Sample KWV-13: This rock is a dolerite, and it consists of fine crystalline grains ranging from 100 – 200 µm (Fig. 4.8). The mineral composition consists predominately of mafic minerals, with plagioclase being the most predominant (Table 4.2). Plagioclase and clinopyroxene form well-developed euhedral crystals, whereas the remaining minerals form subhedral to anhedral grains. A brown, moderate to high relief mineral, termed biotite, has a tendency to occur within alteration zones associated with opaque minerals and pyroxenes. Plagioclase occurs as needle-like interstitial lathes scattered throughout the thin section or as radial clusters, forming the majority of the groundmass. Oikocryst masses of pyroxene enclose plagioclase. The sample is generally porphyritic dominated by phenocrysts of pyroxene (diopside). Some opaques occur as blotches throughout the thin section. Some plagioclase crystals form larger 2 mm phenocrysts with fractures, and within these fractures smaller enclosed grains of
pyroxene can be found enclosed within these larger crystals of plagioclase. No porosity found as grains are interlocking in texture.

Sample KWV-14: This rock is a carbonaceous shale consisting of an average grain size of between averages of 1 – 2 µm, thus classified as clay-sized grains (Fig. 4.9). In terms of mineral content, this sample consists mostly of quartz (Table 4.2). The quartz grains are rounded consisting mostly of a microcrystalline variation. The remaining composition of the rock sample is composed of opaques with assumed organic origin. The thin section displays well-developed layers where lamellae of microcrystalline quartz grains mark the bedding planes. In some places cherty veinlets crosscut the bedding. The matrix consists of clay to fine silt sized particles with pyrite disseminated throughout the thin section. Small amounts of muscovite occur as small grains within the matrix. No porosity was found in this thin section.

Sample KWV-15: This rock is a dolerite, with an average grain size ranging between 100 µm and 1 mm in size, which classifies the particles as a fine to medium grained crystalline (Fig 4.10). The predominant groundmass is plagioclase (Table 4.2), which commonly forms radial clusters of euhedral to subhedral grains. Some of the larger plagioclase grains show normal zoning under crossed-polarized light. Pyroxenes predominately occur as porphyroblasts with a poikilitic texture. The brown mineral, considered to be biotite, occurs in alteration zones commonly found at the boundaries of plagioclase grains. No porosity was found due to textural constraints regarding interlocking nature of the grains.

Sample KWV-16: This rock is a carbonaceous silty shale, with an average visible grain size < 10 µm, classified as clay to very fine silt sized particles (Fig. 4.11). The mineral content consists of mostly pyrite and clay minerals (Table 4.2). The bulk composition (60%) appears as opaque and barely translucent particles, possibly of organic content origin – take into consideration the black nature of the hand specimen. This could also be due to the fact that the high temperature regime of which this rock has been exposed to introduced by the intruding dolerites as indicated by de Kock et al. (2016), which has possibly destroyed most textural features and discernable composition making it difficult to describe under the microscope. There is extensive quartz veining throughout the thin section. Pyrite is predominantly confined between layers, as well as disseminated throughout the sample as euhedral grains or occurring in veinlets. Sample is generally moderately sorted. No visible porosity was observed.
Figure 4.2 – Sample KWV-1 silty shale: A) (PPL) carbonate vein (left) occurring with albite and clinochlore (brown); B) (XPL) muscovite in a fine quartz matrix with opaque organic matter and finer clays forming concretions.

Figure 4.3 – Sample KWV-2 sandstone: A) (PPL) fine to medium quartz grains with primary porosity in yellow fluorescent dye; B) (XPL) very fine quartz matrix occurring with larger albite and quartz mineral grains with carbonate cementation. Secondary micropores of dissolute carbonate cement highlighted in yellow fluorescent dye.

Figure 4.4 – Sample KWV-5 silty shale: A) (PPL) biotite occurring between quartz grains with opaque organic matter occupying porespaces B) (XPL) calcite forming interstitially between quartz grains amongst lathes of biotite.
Chapter 4: Results

Figure 4.5 – Sample KWV-6 very-fine sandstone: A) (PPL) angular quartz grains amongst a matrix of clay sized particles with a cloudy appearance. Isolated pore-space highlighted with epoxy dye (yellow); B) (XPL) straight and sutured contacts between quartz grains with clay sized particles occurring with minor carbonate cement

Figure 4.6 – Sample KWV-9 siltstone: A) (PPL) Clay minerals occur interstitially between larger grains with soft sediment concretions clay clast between quartz grains; B) (XPL) quartz vein through a predominately quartz matrix (minor clays) quartz occurs anhedral angular grains

Figure 4.7 – Sample KWV-10 sandstone: A) (PPL) muscovite lath occurring with quartz grains and minor clays and organic matter; B) (XPL) replacement of calcite, being chertified which form between quartz and minor muscovite grains
Figure 4.8 – Sample KWV-13 dolerite: A) (PPL) orthopyroxene with plagioclase forming oikilitically within larger pyroxene and brown mineral (biotite) occurring between larger grains; B) (XPL) clinopyroxene showing straight contact relationship with plagioclase

Figure 4.9 – Sample KWV-14 carbonaceous shale: A) (PPL) crosscutting quartz veins through a matrix of very fine grain and quartz opaque particles consist of organic material and pyrite; B) (Reflected light) Pyrite vein crosscutting through thin section

Figure 4.10 – Sample KWV-15 dolerite: A) (PPL) Plagioclase forming radial clusters occurring with porphyroblastic pyroxenes; B) (XPL) large plagioclase grain showing zoning amongst a finer groundmass of plagioclase occurring with pyroxene and biotite (brown)
4.2.2.1 Petrography: Discussion

The sandstone samples (K WV-2; K WV-6; K WV-10) consist of moderately sorted grains. Poorly-sorted sandstones are usually a sign of low porosity. The shales samples (K WV-9; K WV-16) are the only samples found to contain clay minerals. The dolerite samples (K WV-13; K WV-15), have low permeability and porosity given by their intergranular texture. K WV-16 showed little to no translucency which could be given by its exposure to high temperatures supplied by dolerite intrusions into this part of the stratigraphy. de Kock et al. (2016) used this argument to suggest reasoning as to why little shale gas was found in these lithologies.

The dyed epoxy proved largely ineffective as these rocks did not have large enough pore space to be occupied by the dyed epoxy. Only in some rare cases in sandstones K WV-2 and K WV-6 porosity was found (Figs. 4.3 and 4.5). As all the lithologies appear to have low porosity, and low permeability, a poor potential for CO₂ storage is predicted. The shale and dolerite samples could potentially be a very good seal. This is given by the visually low permeability due to dolerite’s interlocking grain texture and the fine grain nature of the shales which show platy overlap of clay minerals indicating low diffusivity, all of which are ideal for a seal layer.

4.3 XRD Results

XRD was conducted to identify major mineral phases occurring in the selected rock samples, to complement the petrographic observations. Each sample was analyzed for 20 minutes using an automatic loader. Results were given as a diffractogram and major mineral peaks were identified using specialized software, as explained in Section 3.3. The results are tabulated in Table 4.3. The diffractograms and peak lists can be found in APPENDIX A.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Matrix</th>
<th>Carbonate Shale</th>
<th>Clay Minerals</th>
<th>Quartz</th>
<th>Albite</th>
<th>Albite (Plag.)</th>
<th>Albitic Quartz</th>
<th>Chlorite (Chlorite)</th>
<th>Carbonates</th>
<th>Accessory Minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-16</td>
<td>Dolerite</td>
<td>Calcite</td>
<td>Illite</td>
<td>Cristobalite</td>
<td>Nimite</td>
<td>Willemseite</td>
<td>Pyrite</td>
<td>Iliite</td>
<td>Willemseite</td>
<td>Pyrrhotite</td>
</tr>
<tr>
<td>KWV-15</td>
<td>Dolerite</td>
<td>Albite</td>
<td>Quartz</td>
<td>Pyrrhotite</td>
<td>Muscovite</td>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-14</td>
<td>Shale</td>
<td>Albite</td>
<td>Quartz</td>
<td>Albite</td>
<td>Muscovite</td>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-13</td>
<td>Dolerite</td>
<td>Anorthite</td>
<td>Quartz</td>
<td>Albite</td>
<td>Muscovite</td>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-10</td>
<td>Sandstone</td>
<td>Orthoclase</td>
<td>Quartz</td>
<td>Albite</td>
<td>Muscovite</td>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-9</td>
<td>Siltstone</td>
<td>Quartz</td>
<td>Albite</td>
<td>Albite</td>
<td>Muscovite</td>
<td>Biotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-6</td>
<td>Sandstone</td>
<td>Quartz</td>
<td>Albite</td>
<td>Chlorite</td>
<td>Muscovite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-5</td>
<td>Shale</td>
<td>Quartz</td>
<td>Albite</td>
<td>Chlorite</td>
<td>Muscovite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-2</td>
<td>Sandstone</td>
<td>Quartz</td>
<td>Albite</td>
<td>Chlorite</td>
<td>Muscovite</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>KWV-1</td>
<td>Shale</td>
<td>Quartz</td>
<td>Albite</td>
<td>Chlorite</td>
<td>Muscovite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.1 Discussion

Most of the XRD results support the thin section petrographic observations. Typical sandstone samples consist of quartz, feldspars, and mica, with no clays. The feldspar commonly found in all the sandstone samples is albite, occurring in the Trumpeters Member, Wonderfontein Formation and the Pluto’s Vale Member (KWV-2; KWV-6; KWV-10 respectively). Both the Trumpeters and Pluto’s Vale members sandstones (KWV-2; KWV-10) contain orthoclase. The Wonderfontein Formation sandstone is the only sandstone of the three that contains sanidine. All three sandstone samples contain comparable micas, chlorite, and muscovite.

The shale samples (KWV-1, KWV-5 and, KWV-9) have a comparable mineralogy. However, the carbonaceous shales from the Whitehill Formation (KWV-14; KWV-16) contain sulphides (pyrite and pyrrhotite). All the shale samples are dominated by quartz in their composition. Shales of the Trumpeters Member, Wonderfontein Formation and the Pluto’s Vale all contain feldspar (orthoclase and albite) and micas (muscovite and chlorite). Important to note is that the shale samples from the Pluto’s Vale (KWV-9) and Whitehill Formation (KWV-16) contain carbonate minerals and, more noteworthy, illite in their composition. Carbonates were observed as extremely small particles in veins or cement in thin section but are partially replaced by chert (as seen in thin section). This could be due to chertification which may have occurred. The two Whitehill shales both contain pyrite, formed diagenetically as noted by the textural relationship to the other particles.

The two dolerite samples (KWV-13; KWV-15), differ mildly in terms of mineralogy. Both samples contain quartz (possibly secondary due to the occurrence of anorthite), diopside and biotite, but with different plagioclase end-members. Sample KWV-13 contains anorthite and sample KWV-15 contains albite. Taking into account fractional crystallisation and the Bowen’s reaction series, KWV-13 (found at a greater depth to KWV-15) this is expected.

Mineralogy is important when considering CO₂ adsorption in geological materials. Heller and Zoback (2014) found that shales with a high clay content (and TOC) tend to have higher adsorption capacities. As a preliminary observation, shales KWV-9 and KWV-16 (with 3.04 % TOC reported by de Kock et al., 2016) should show a higher CO₂ adsorption capacity compared to the other samples in this regard.

4.4 BET Results

All BET results obtained are summarised in Table. 4.4 with their corresponding method of calculation as indicated. Raw BET data can be found in APPENDIX B.
The CO$_2$ adsorption isotherms (Fig. 4.12) are given for low pressure conditions, with absolute pressures from 0 – 0.04 MPa. Adsorption isotherms show the relationship between the amount of adsorbed CO$_2$ (Y-axis) and pressure of the adsorptive material (X-axis) at a constant temperature (Fig. 4.12). The amount of adsorbed CO$_2$ is shown in cm$^3$/g, where the volume (cm$^3$) of CO$_2$ per gram of adsorptive material. Using the amount of CO$_2$ adsorbed onto the absorptive material, an accurate estimation of porosity can be determined. The micropore surface areas (measured in m$^2$/g) and monolayer capacity (cm$^3$/g) of the solid samples were determined using low pressure CO$_2$ adsorption data collected by use of the D-R method. The CO$_2$ adsorption data was used to construct a differential pore volume distribution plot (Fig. 4.13), where pore volume is linked to the pore width. The H-K method was used to determine maximum pore volumes (Fig 4.13).

All the samples report a mean micropore width falling in the range of 3.25 Å < d$_p$ < 5.25 Å (Fig. 4.13). Sample KWV-15 shows high differential pore size distribution (PSD) (cm$^3$/gÅ) with large pore widths when approaching 5 Å (Fig. 4.13). Sample KWV-16 shows an overall high PSD throughout a range of pore widths. Sample KWV-10 displays the lowest overall PSD, and therefore the lowest volume of micropores, of all ten samples across all pore width ranges. Dolerite sample KWV-15 displays low PSD except when approaching 5 Å pore widths, where PSD is higher than all the other samples. The carbonaceous shale sample (KWV-14) shows the highest capacity in terms of pore volume distribution as the consistency in pore width and PSD remains constant as pore width increases.

Using the BET adsorption isotherms, sample KWV-16 (organic shale) shows the highest adsorption capacity of CO$_2$ (maximum adsorption of 2.53 cm$^3$/g at 0.033 P/P$_o$), as anticipated. The potential reservoir rocks (sandstones) have shown lower adsorption, with the highest adsorption observed in the KWV-2 Trumpeters Member Sandstone (maximum adsorption of 2.17 cm$^3$/g at 0.033 P/P$_o$). As expected, the highest adsorption observed in each sample was found at the highest pressure (± 0.033 P$_o$/P or absolute pressures of 0.19 MPa). It was found that sample KWV-16 (carbonaceous shale) had the highest maximum pore volume of 0.473 x10$^2$ cm$^3$/g (Fig.4.14) and with a porosity (vol. %) of 1.424%.
Table 4.4 – Physical Characterisation of Samples using BET CO$_2$ Adsorption Data for Porosity

<table>
<thead>
<tr>
<th>Sample I.D</th>
<th>Bulk Density</th>
<th>Limiting Micropore Vol. x 10$^{-2}$ (cm$^3$/g)</th>
<th>Maximum Pore Vol. x 10$^{-2}$ (cm$^3$/g)</th>
<th>Maximum Porosity (Vol. %)</th>
<th>Limiting Micropore Capacity (cm$^3$/g)</th>
<th>Micropore Surface Area (m$^2$/g)</th>
<th>Mean Pore Width (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-1</td>
<td>2.703</td>
<td>9.075</td>
<td>0.383</td>
<td>1.036</td>
<td>4.500</td>
<td>20.555</td>
<td>4.107</td>
</tr>
<tr>
<td>KWV-2</td>
<td>2.658</td>
<td>7.712</td>
<td>0.397</td>
<td>1.056</td>
<td>4.401</td>
<td>20.106</td>
<td>4.077</td>
</tr>
<tr>
<td>KWV-5</td>
<td>2.622</td>
<td>7.560</td>
<td>0.442</td>
<td>1.161</td>
<td>4.779</td>
<td>21.833</td>
<td>4.065</td>
</tr>
<tr>
<td>KWV-6</td>
<td>2.829</td>
<td>7.445</td>
<td>0.358</td>
<td>1.021</td>
<td>4.013</td>
<td>18.334</td>
<td>4.104</td>
</tr>
<tr>
<td>KWV-9</td>
<td>2.688</td>
<td>5.110</td>
<td>0.394</td>
<td>1.060</td>
<td>3.782</td>
<td>17.279</td>
<td>4.068</td>
</tr>
<tr>
<td>KWV-10</td>
<td>2.787</td>
<td>6.241</td>
<td>0.330</td>
<td>0.997</td>
<td>3.569</td>
<td>16.303</td>
<td>4.113</td>
</tr>
<tr>
<td>KWV-13</td>
<td>3.142</td>
<td>11.373</td>
<td>0.328</td>
<td>1.029</td>
<td>4.232</td>
<td>19.334</td>
<td>4.176</td>
</tr>
<tr>
<td>KWV-15</td>
<td>3.096</td>
<td>11.073</td>
<td>0.359</td>
<td>1.114</td>
<td>4.579</td>
<td>20.919</td>
<td>4.154</td>
</tr>
<tr>
<td>KWV-14</td>
<td>2.949</td>
<td>6.672</td>
<td>0.367</td>
<td>1.082</td>
<td>4.161</td>
<td>19.009</td>
<td>4.031</td>
</tr>
<tr>
<td>KWV-16</td>
<td>3.013</td>
<td>6.653</td>
<td>0.473</td>
<td>1.424</td>
<td>4.863</td>
<td>22.216</td>
<td>4.051</td>
</tr>
</tbody>
</table>

Nomenclature:
* D-R: Dubinin-Radushkevich
* D-A: Dubinin-Astakhov
* H-K: Horvath-Kawazoe
* CO$_2$ Ads Data: CO$_2$ Adsorption Data
* P/P$_0$: Relative pressure
CO₂ adsorption isotherm (low pressure)

Figure 4.12 – CO₂ adsorption isotherms found using STP experimental conditions for BET analysis

H-K Micropore Diameter Distribution

Figure 4.13 - Micropore distribution using the H-K method showing differential pore volume distributions of the rock samples found
4.4.1 Discussion

Although the sandstone sample KWV-10 was expected to show high pore, the contrary was found. Sample KWV-10 has the lowest porosity values of the 10 samples analysed (0.997 vol. %); Okolo et al. (2017) found higher maximum pore volumes in bituminous coals of South Africa. The reason for this low porosity could be caused by high density of clay sized particles that occur in-between the larger grains, as seen in thin section (Fig. 4.7). This indicates that this sample has poor CO\textsubscript{2} storage potential.

The dolerite sample (KWV-15) shows high differential pore volume only at large pore widths (Fig. 4.13). Hence, this could indicate to a high density of large widths of pores (as fractures); but this has no correlation to maximum pore volume (Fig 4.14). The other dolerite sample (KWV-13) shows high adsorption potential (Fig. 4.12), but very low maximum pore volumes (Fig. 4.14). This indicates poor potential capacity to store large volumes of CO\textsubscript{2} in terms of pore-space availability.

Typically, the shale samples (KWV-1; KWV-5; KWV-13; KWV-16) show the highest adsorption as observed on the isotherm curves (Fig. 4.12). Sample KWV-16 (organic-rich shale) showed the highest CO\textsubscript{2} adsorption at STP as anticipated. This is related to the fact that this sample has the highest TOC (3.04 % TOC found by de Kock et al., 2016) of all the other samples, and therefore has the highest capacity for CO\textsubscript{2} adsorption even at these low pressures. This agrees with Grobe et al. (2009) and Heller and Zoback (2014), where it was found that the higher the TOC, the greater amount of CO\textsubscript{2} adsorbed.
The higher the pressure, the greater the adsorption of CO\textsubscript{2} onto the adsorptive material, as shown by the positive relationship shown in Fig. 4.12. The isotherms produced (Fig. 4.12) are similar to a Type VI isotherm (Fig 3.3) and are indicative of the monolayer adsorption capacity given by the step height elevation (although steps are not as steep and pronounce compared to the idealised Type VI isotherm) of the isotherm (Sing, 1985). Generally, all the samples show low adsorption (at STP) and therefore low porosity volumes, indicating a poor estimated volume for CO\textsubscript{2} storage.

Using the adsorption isotherm in Fig. 4.12, the 8 most adsorptive samples (KWV-1, KWV-5, KWV-6, KWV-10, KWV-14 and KWV-16) were selected and sent to ISGS to undergo HPVA; this is a costly and timeous analysis. These 8 samples should, in theory, show the highest potential for adsorption at high pressure according to their adsorption performance at STP.

4.5 HPVA Results

The HPVA were conducted under specific conditions to simulate deep geological conditions. The experimental setup (explained in Section 3.5) was designed to observe CO\textsubscript{2} adsorption capacities of the various rock samples at simulated pressure ranges and temperatures typically found at depths of > 800 m. The parameters set for this analysis were systematic: samples were exposed to a constant temperature of 45 °C, and pressure increased from 1 – 18 MPa in a stepwise manner for the duration of the analysis. For each pressure step, the system was allowed to equilibrate for ~30 minutes in order for an accurate CO\textsubscript{2} adsorption reading to be obtained.

The results are reported as a change in volume and the mass of CO\textsubscript{2} adsorbed was calculated (as explained in Section 3.5). The amount of CO\textsubscript{2} adsorbed is represented in this chapter as isotherms, with the ratio of excess moles of CO\textsubscript{2} per gram of the sample (mol/g), representing the Y-axis, and X-axis representing the pressure (MPa).

Concerns were raised regarding the raw data received from ISGS (APPENDIX C.1).

- The data provided were difficult to decipher and were not clear in the way it was presented. Multiple venting procedures were initiated because of a lack of CO\textsubscript{2} gas in the system. This was a cause for concern in that this may have affected the accuracy of the data due to the “stop-start” events during the analyses.
- The ISGS produced raw data with recommended calculations to obtain CO\textsubscript{2} adsorption quantities for the various samples provided. These calculations were cross-checked multiple times by the author, supervisor, and the ISGS lab technician. All discrepancies found were rectified and had little effect on the bloated adsorption values. The ISGS lab technician suggested the Equation of State for calculating CO\textsubscript{2} density may have
caused inflated adsorption values. This was cross-checked with Ouyang (2011) proposed prediction for CO$_2$ density. But the result was further inflation of the data and, hence, it was not utilised in this study.

Steps in cross-checking the results included the following:
1. Results received from the laboratory were done to determine adsorption of CO$_2$.
2. Calculations were cross-checked by lab and results were still inflated
3. Lab technician ran the samples again.
4. Values were still inflated and were very different to the original calculated adsorption quantities. For example, in sample KVV-16, with the first run showed a maximum adsorption of 1.025 mol/g and in the 2nd run 0.136 mol/g.
5. Lab technician facilitated equipment diagnostics and found no leakages or software errors with the equipment. Some seals were replaced.
6. Samples were analysed for the 3rd time and still values were inflated and did not correspond to the previous values obtained from the first two tests.

- The actual adsorption values provided by ISGS are considered to be unrealistic values, most likely due to experimental error. The laboratory at ISGS failed to provide suitable data and therefore the actual amounts of CO$_2$ adsorbed appear grossly exaggerated.
- There was missing data due to problems with the data-logger and some points for certain samples were missing.
- After all the concerns were raised with the technician, the ISGS technician then explained that the experimental setup of this kind had not been previously undertaken. A similar setup had been used for another project, but the paper had not been published due to similar errors. This information only came to light once all funding and time had been exhausted.
- A few samples were commissioned for re-testing to see whether results showed positive changes. The excess adsorption was calculated using molar mass of CO$_2$ at STP (Eq. 11) which does not cater for high pressure molecular density changes in CO$_2$. Whilst the actual values are inflated, the isotherm trends are comparable to those found in literature for the specific rock types under consideration.

The results are discussed in conjunction with Figures 4.15 – 4.27 and Table 4.6. All calculated spreadsheets are included in APPENDIX C.1.
4.5.1 KWV-1

Sample KWV-1 represents the silty shale of the Trumpeters Member, Ecca Group. This sample shows good CO2 adsorption under pressure. The peak CO2 adsorption is represented by the inflection point found at 9 MPa (Fig. 4.15), showing an excess adsorption of 1.16 mol/g. After peak adsorption is reached, the isotherm decreases and remains constant throughout the remaining pressure ranges.

Figure 4.15 - Adsorption isotherm of sample KWV-1 (silty shale) at constant temperature of 45 °C

4.5.2 KWV-2

Sample KWV-2 is a massive sandstone of the Trumpeters Member, Ecca Group. This sample shows good adsorption with a maximum excess adsorption of ~1.18 mol/g found at inflection point at 6 MPa (Fig. 4.16). The adsorption rate increases rapidly after 4 MPa, as demonstrated by the steep incline before inflection point.
Chapter 4: Results

4.5.3 KWV-5

Sample KWV-5 represents the silty shale of the Wonderfontein Formation, Ecca Group. This sample shows good adsorption, with a maximum excess adsorption of ~0.41 mol/g represented by the inflection point found at 9 MPa (Fig. 4.17). At pressures > 9 MPa the amount of CO₂ adsorbed steadily decreases and reaches a plateau at ~ -0.1 mol/g.

Figure 4.16 - Adsorption isotherm of sample KWV-2 (sandstone) at constant temperature of 45 °C

Figure 4.17 - Adsorption isotherm of sample KWV-5 (silty shale) at constant temperature of 45 °C
4.5.4 KWV-6

Sample KWV-6 represents the very fine sandstone of the Wonderfontein Formation, Ecca Group. The sample shows good adsorption capacity, with a maximum excess adsorption of ~0.31 mol/g at 9 MPa (Fig 4.18). After the inflection point, adsorption is found to gradually decline with increasing pressure to > 9 MPa and remain stable at ~0.3 mol/g.

4.5.5 KWV-10

KWV-10 represents the massive sandstone of the Pluto's Vale Member, Ecca Group. The adsorption rate takes a steep incline at > 6 MPa pressures. The inflection point is found at pressure 9 MPa, similar to KWV-5 and KWV-6 (Figs. 4.17 and 4.18), with maximum adsorption of 1.11 mol/g (Fig. 4.19). At pressures > 9 MPa the adsorption rate steadily declines and remains stable at ~0.18 mol/g.
4.5.6 KWV-13

Sample KWV-13 is a sample from the Karoo Dolerite, which intrudes into the Whitehill Formation. The isotherm indicates poor adsorption capacity. The highest amount of excess adsorption adsorbed is ~0.04 mol/g (Fig. 4.20). A negative trend is found, with an adsorption value of approximately -0.89 mol/g at 6 MPa.

![Figure 4.20 - Adsorption isotherm of sample KWV-13 (dolerite) at constant temperature of 45 °C](image)

4.5.7 KWV-14

This sample is from the carbonaceous shale of the Whitehill Formation and shows evidence of CO₂ adsorption. At > 7 MPa, the isotherm shows steady increase in adsorption with increasing pressure. At 18 MPa the highest excess adsorption of ~1.7 mol/g (Fig 4.21) occurred.

![Figure 4.21 - Adsorption isotherm of sample KWV-14 (carbonaceous shale) at constant temperature of 45 °C](image)
4.5.8 KWV-16

This sample represents the carbonaceous shale of the Whitehill Formation of the Karoo Ecca Group. The sample shows good adsorption, with a peak excess adsorption of \( \sim 1.025 \text{ mol/g} \) at 8 MPa (Fig. 4.22). Adsorption takes a steep incline at above 7 MPa and steadily declines at pressures above 8 MPa.

![Figure 4.22 - Adsorption isotherm for sample KWV-16 (carbonaceous shale) at constant temperature of 45 °C](image)

4.5.9 HPVA Re-tested Samples

Due to the results being irregular in terms of over estimation of adsorbed CO\(_2\) mass, it was a few samples were re-assessed. Samples: KWV-1, KWV-2, KWV-13, and KWV-16 were analysed. The raw data was treated in the same manner as the first set of HPVA results. The main difference in the second run on these particular samples is that during the venting stages, system volume was recalculated due to volume checks initialised at each venting stage. This was not done in the initial analysis. A slightly different approach was taken in terms of the pressure step increments, where increase, 2 MPa pressure increments were implemented (instead of a 1 MPa pressure) to identify any change in adsorption values. This change in experimental protocol was done to help eliminate inflated values with fewer data points and less venting procedures which could have influenced inflated values in the first run.
4.5.9.1 KWV-1 Run 2

After low, constant adsorption rates in the pressure range 2 – 4 MPa, the inflection point of this isotherm occurred at 8 MPa; the inflection adsorption value is ~2.46 mol/g. Above 8 MPa, the curve follows a sharp decrease and to 18 MPa.

![Figure 4.23 – Adsorption isotherm of sample KWV-1 (silty shale) at constant 45 °C from re-analysis data](image)

4.5.9.2 KWV-2 Run 2

Inflection point was found at 8 MPa consisting of a maximum excess adsorption of 1.013 mol/g (Fig. 4.24). A sharp increase above 6 MPa was observed. The isotherm curve is defined with a steady decline above 8 MPa whereas in isotherm KWV-2 (Fig. 4.24) showing a similar trend has a steady decline. The lowest excess adsorption in this isotherm is -0.001 mol/g found at pressure 4 MPa. Over the range of pressure 6 – 9 MPa, adsorption remained constant in the previous isotherm (Fig 4.16), but it is not consistent here as. A steady decline in adsorption after 10 MPa is common in both isotherms.
4.5.9.3 KWV-13 Run 2

Isotherm curve obtained from sample KWV-13 is defined with a point of deflection at 8 MPa, with an excess adsorption of -2.75 mol/g (Fig. 4.25). At 6 MPa, the highest adsorption is found with 0.088 mol/g. After the deflection point at 8 MPa, a sharp increase in adsorption is observed beginning at 10 MPa. This remains constant throughout the remaining pressure range. Similar trends in shape are found in the previous isotherm (Fig. 4.20).
4.5.9.4 KWV-16 Run 2

Sample KWV-16 shows a regular isotherm pattern. The inflection point found at pressure step 8 MPa has obtained an excess adsorption of 0.136 mol/g (Fig. 4.26). At low pressures (2 – 6 MPa), negative excess adsorption was observed, with the lowest found at pressure step 6 MPa (-0.037 mol/g). A steady decline in excess adsorption was observed in pressures over 8 MPa, remaining stable at pressures above 12 MPa. Similar trends in shape are seen in the previous isotherm (Fig. 4.22).

![KWV-16 Run 2](image)

Figure 4.26 – Adsorption isotherm of sample KWV-16 (carbonaceous shale) at constant 45 °C from re-analysis data

4.6 Discussion of HPVA results

For most of the isotherms, the pattern of the curves were generally congruent to those found in literature for comparable rock types (Busch et al. 2008; Fujii et al. 2010; Fujii et al. 2009). The 1st run results for all 8 samples are discussed in Section 4.6.1. A further discussion of the results pertaining to the 4 selected samples of which were re-tested are compared to their corresponding 1st run results in Section 4.6.2.

4.6.1 1st Run HPVA Results Discussion

In general, with the exception of KWV-13 (dolerite), the adsorption isotherms (Fig. 4.15 – 4.22) show increasing CO₂ excess adsorption with increasing pressure, specifically when approaching near critical pressure conditions (> 6 MPa). When the isotherm reaches its inflection point, adsorption decreases gradually with increasing pressure and eventually remains stable at a constant excess adsorption. The shale samples generally reach their inflection point (maximum adsorption) at greater pressure regimes than the sandstone
samples. This should be expected as shales have a larger surface to volume ratio. This can be further confirmed from the low adsorption equivalent (BET adsorption) shown in Table 4.4 where shale samples generally have higher adsorption.

Samples KWV-1 (silty shale), KWV-2 (massive sandstone) KWV-5 (silty shale), KWV-6 (very fine sandstone), and KWV-10 (massive sandstone) all typically follow the trends (Figs. 2.6a and 2.9) presented by Busch et al. (2008) and Fujii et al. (2010). The current samples generally show good adsorption capacity and find their peak excess adsorption between 8 and 11 MPa, similar to Busch et al. (2008), where the inflection point was found at 11 MPa.

Sample KWV-13, a dolerite sample, shows similarity in isotherm trend to the granite sample isotherm (Fig 2.8) found in Fujii et al (2009). Sample KWV-14 (carbonaceous shale) shows an abnormal isotherm trend, similar to Fujii et al. (2010), where the Berea Sandstone showed a constant increase in CO₂ adsorption even far beyond the critical point (Fig. 2.9).

Heller and Zoback (2014) found that the higher the TOC within the geological sample, the higher the adsorption capacity. Table 4.5 shows similar TOC values for the gas shales studied by Heller and Zoback (2014) in comparison to the Whitehill shales assessed here. The TOC values in the borehole KWV-01 of the Whitehill Formation reported by de Kock et al. (2016) are between 2.12 – 6.27 %; Samples KWV-14 and KWV-16 occur within the Whitehill Formation, and thus it is reasonable to assume comparable TOC values, and explains why these two samples show some of the highest excess adsorption in comparison to the other 8 samples.

Also, observations drawn from the Heller and Zoback (2014) study found that illite exhibited a relatively high adsorption capacity. This proves true in that carbonaceous shale sample KWV-16, containing both organic content and illite (picked up by XRD), shows some of the highest adsorption potential of all 8 samples analysed.
Table 4.5 - from: (a) Heller and Zoback (2014) and (b) de Kock et al. (2016) showing depth and TOC of similar shales

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m) by (a)</th>
<th>TOC (%) by (a)</th>
<th>Depth (m) by (b)</th>
<th>TOC (%) by (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barnett 31</td>
<td>2633.7</td>
<td>5.3</td>
<td>2295.05</td>
<td>2.12</td>
</tr>
<tr>
<td>Eagle Ford 127</td>
<td>3893.7</td>
<td>1.8</td>
<td>2299.39</td>
<td>6.27</td>
</tr>
<tr>
<td>Marcellus</td>
<td>1920.73</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Montney</td>
<td>2321.5</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KWV-14</td>
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<td>2.12</td>
<td>2299.05</td>
<td>6.27</td>
</tr>
<tr>
<td>KWV-16</td>
<td>2304.74</td>
<td>6.27</td>
<td>2299.39</td>
<td>6.27</td>
</tr>
</tbody>
</table>

The negative adsorption trends found in some samples can be explained as mineral swelling. Studies, such as that by Ozdemir et al. (2003), showed CO₂ adsorption in coal to alter the structure of the adsorbent, known as swelling, similar to its effect on minerals. A study by Krooss et al. (2002) termed this phenomenon as the volumetric effect, given by anomalies of decreasing and negative adsorption values found usually between pressures 8 MPa and 12 MPa.

In Table 4.6, summarised BET and HPVA data are provided. The maximum pore volume, found by use of BET, has no real correlation with HPVA CO₂ adsorption data generated by ISGS. Samples KWV-2 (massive sandstone with 1.056 vol.% porosity), KWV-14 (carbonaceous shale with 1.082 vol.% porosity), and KWV-16 (carbonaceous shale with 1.424 vol.% porosity) could be considered to have good storage potential, as they have the best porosity and CO₂ adsorption potential of all the other samples tested. These rocks can therefore be considered the most suitable rocks, of the targeted sample set, for CO₂ storage in this particular location.

Samples KWV-5 (silty shale with 1.161 vol.% porosity) and KWV-13 (dolerite with 0.997 vol.% porosity) have very low CO₂ storage potential and can be disregarded as a storage horizon, on the grounds of low porosity and low CO₂ adsorption potential.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum Porosity (Vol. %)</th>
<th>Inflection Pressure (MPa)</th>
<th>Highest Excess Adsorption (mol/g)</th>
<th>Lowest Excess Adsorption Pressure (MPa)</th>
<th>Lowest Excess Adsorption (mol/g)</th>
<th>Rock Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-1</td>
<td>1.036</td>
<td>9</td>
<td>1.164</td>
<td>3</td>
<td>-0.010</td>
<td>Silty shale</td>
</tr>
<tr>
<td>KWV-2</td>
<td>1.056</td>
<td>6</td>
<td>1.18</td>
<td>3</td>
<td>0.006</td>
<td>Sandstone</td>
</tr>
<tr>
<td>KWV-5</td>
<td>1.161</td>
<td>9</td>
<td>0.415</td>
<td>18</td>
<td>-1.120</td>
<td>Silty shale</td>
</tr>
<tr>
<td>KWV-6</td>
<td>1.021</td>
<td>9</td>
<td>0.314</td>
<td>2</td>
<td>0.001</td>
<td>Very fine Sandstone</td>
</tr>
<tr>
<td>KWV-10</td>
<td>1.060</td>
<td>6</td>
<td>1.112</td>
<td>4</td>
<td>0.002</td>
<td>Sandstone</td>
</tr>
<tr>
<td>KWV-13</td>
<td>0.997</td>
<td>9</td>
<td>0.042</td>
<td>6</td>
<td>-0.890</td>
<td>Dolerite</td>
</tr>
<tr>
<td>KWV-14</td>
<td>1.082</td>
<td>10</td>
<td>1.696</td>
<td>3</td>
<td>-0.310</td>
<td>Carbonaceous shale</td>
</tr>
<tr>
<td>KWV-16</td>
<td>1.424</td>
<td>8</td>
<td>1.025</td>
<td>7</td>
<td>0.001</td>
<td>Carbonaceous shale</td>
</tr>
</tbody>
</table>

**Re-tested Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum Porosity (Vol. %)</th>
<th>Inflection Pressure (MPa)</th>
<th>Highest Excess Adsorption (mol/g)</th>
<th>Lowest Excess Adsorption Pressure (MPa)</th>
<th>Lowest Excess Adsorption (mol/g)</th>
<th>Rock Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>KWV-1</td>
<td>1.036</td>
<td>5</td>
<td>3.274</td>
<td>2</td>
<td>-0.012</td>
<td>Silty shale</td>
</tr>
<tr>
<td>KWV-2</td>
<td>1.056</td>
<td>8</td>
<td>1.013</td>
<td>4</td>
<td>-0.001</td>
<td>Sandstone</td>
</tr>
<tr>
<td>KWV-13</td>
<td>0.997</td>
<td>6</td>
<td>0.088</td>
<td>8</td>
<td>-2.75</td>
<td>Dolerite</td>
</tr>
<tr>
<td>KWV-16</td>
<td>1.424</td>
<td>8</td>
<td>0.136</td>
<td>6</td>
<td>-0.037</td>
<td>Carbonaceous shale</td>
</tr>
</tbody>
</table>
4.6.2 Comparison of 1st and 2nd Run HPVA Results

When studying the adsorption isotherms for the re-analysed samples, there are a few key differences in quantity of adsorption, shape of the isotherm itself and inflection pressure at which maximum excess adsorption is achieved (Fig 4.27).

KWV-1, the silty shale sample from the Trumpeters Member, shows similarity in terms of shape but not in quantity of CO2 adsorbed between the two runs. The increase in adsorption within between 8 – 9 MPa is given by maximum adsorption shown on both isotherms including the stable, constant adsorption seen in pressures above 12 MPa. Although the inflection adsorption of the two runs are found at similar pressures, the 1st run has a significantly lower inflection adsorption (52% less) compared to the 2nd run (Fig. 4.27), therefore the two isotherms are congruent in trend, but inconsistent in excess adsorption.
The massive sandstone of the Trumpeters Member, KWV-2, has some similarity between the two runs. Firstly, adsorption quantities are comparable, with maximum adsorption showing only a 14% difference between both inflection points on both isotherms (Fig. 4.27). The rapid increase in adsorption found at pressures 6 MPa and 8 MPa shown on the 1st and 2nd run isotherms respectively are not consistent in which they have reached their respective inflection points. The general trend and pattern of these isotherms are alike, where the steep decline of adsorption is found after 8 MPa and tails out for the remaining pressure range.

KWV-13, the dolerite sample, has some similarity in shape and trend when comparing the two isotherms (Fig. 4.27). The low adsorption or negative adsorption found in 1 – 6 MPa and 9 – 18 MPa pressure ranges are relatively similar in trend and quantity of both isotherms. The 1st run isotherm results shows a more highly negative adsorption value compared to the 2nd run. Although in the same range of pressure where this phenomenon occurs, there is a significant difference of about 72% between both deflection points of each analyses run.

Sample KWV-16, a carbonaceous shale of the Whitehill Formation generally shows some similarity in trend and shape of the two isotherms, but differs greatly in quantity of adsorption. Both inflection points on each of the isotherms occur at 8 MPa and gradually declines and tails out at higher pressures. Even at lower pressures of between 2 and 6 MPa, there is a similar pattern of low adsorption which occurs. The main difference is in the inflection values of maximum adsorption where there is an exaggerated difference of about 87% when comparing both runs of analyses.

In summary, there are generally a few differences in terms of both adsorption and in some cases inflection pressures at which adsorption is at its highest. Broadly, the isotherms produced by both sets of data retrieved from each run have similar trends and shape.
Chapter 5 – Conclusions and Recommendations

A potential CO\textsubscript{2} geological storage basin essentially requires a reservoir rock and a cap/seal rock. Ten samples were selected from a borehole core drilled at the Willowvale site in the Eastern Cape of South Africa, which intercepted the Ecca Group of the Karoo Supergroup. The samples associated with seal / reservoir rock types were studied here in terms of three main aspects, namely: 1) composition of rock type; 2) porosity; and 3) CO\textsubscript{2} adsorption capacity. These aspects are of importance when exploring for a potential geological storage basin. The composition of the rock sample was studied to see whether mineralogy may influence adsorption potential, as some studies have shown a link. Porosity gives a good indication as to how much CO\textsubscript{2} could potentially be stored in the lithology. A high adsorption capacity would indicate good CO\textsubscript{2}. The conclusions drawn from these results were discussed, observing the effect that each of the 3 aspects has on the potential seal/reservoir lithologies.

5.1 Composition

The samples were characterised by determining their mineralogical composition. Many studies have shown that mineralogy and TOC have an influencing effect on adsorption capacity. In studies by Heller and Zoback (2014) and Busch et al. (2008), shales containing clay minerals, specifically illite and kaolinite, were reported to have a relatively high capacity for CO\textsubscript{2} adsorption. Furthermore, Heller and Zoback (2014) found that the sample with the high TOC adsorbed the most CO\textsubscript{2}. Similarly, sample KWV-16, a carbonaceous shale from the Whitehill Formation which contains clay (illite) and has a relatively high organic content (2.12 – 6.27 % TOC), had a higher capacity for CO\textsubscript{2} adsorption compared to the other samples. KWV-14, a carbonaceous shale showed the highest adsorption potential with a similar composition to that of KWV-16 in terms of TOC and clays.

In a study by Fujii et al. (2010), it was found that silica and silicate minerals also have the ability to adsorb significant amounts of CO\textsubscript{2}. Fujii et al. (2010) found that arkosic sandstones, specifically the Berea Sandstone (from Ohio, USA) which consists mostly of albite and quartz, was the highest performing sample in terms of adsorption capacity. Similarly, in the current study, it was found that sandstone samples KWV-2 and KWV-10, which contain albite and quartz aggregates, exhibit high adsorption capacities.

The dolerite sample (KWV-13), with a high plagioclase content, reported the lowest CO\textsubscript{2} adsorption. Fujii et al. (2009) found a similar trend where a granite (containing a significant amount of plagioclase) reported the least amount of CO\textsubscript{2} adsorption of all the samples assessed.
Hence, the South African rock samples selected for this study exhibited similar adsorption patterns to comparable samples found in the literature. Mineralogy plays a significant role in the adsorption potential of rocks. The dolerite could be considered as a potential seal rock in this regard. This study does not take into consideration fracturing and long-term mineral alteration through diffusion experiments, thus its sealing integrity cannot yet be conclusively proven.

5.2 Porosity

The porosity and permeability of these samples were predicted, via petrography, to be low. The BET data indicated that the samples used in this study had low porosity, with maximum pore volumes between 0.32 – 0.48 x10^-2 cm³/g and porosity (vol. %) within a range between 0.9 – 1.5 %. When compared to literature, Fujii et al. (2010) and Okolo et al. (2017) found higher porosity in both rock (sandstones, shales, and granites) and coal samples in terms of their porosity volume percentages (ranges of 1 – 20 % and 2.9 - 5.4 %, respectively). Even the sandstone samples (KWV-2; KWV-6; KWV-10), predicted to be porous, reported low BET values. This could be a result of the geological environment in which these rocks formed where there could have been an influx of clay filling pore spaces resulting in low porosity. This finding impacted negatively towards the overall capacity to store CO₂ in these formations as they are situated in this part of the Karoo Basin.

5.3 Adsorption Potential

A HPVA apparatus, housed at the ISGS in Illinois, was used to simulate underground CO₂ adsorption conditions in terms of the pressure and temperature conditions. BET adsorption isotherms, whilst useful, cannot indicate adsorption under high pressure. Typically, at high temperature and pressure (45 °C and 5 – 10 MPa), the sandstone samples (KWV-2; KWV-6; KWV-10) indicated a higher CO₂ adsorption capacity compared to the shale KWV-5, the outlier being silty shale KWV-1. The opposite was found from using the BET adsorption isotherms, where at STP conditions, shales showed higher adsorption capacity.

There is an inherent difference when comparing isotherms produced by BET and HPVA techniques, whereby at high temperature and pressures (especially at near critical pressure regions – supercritical), CO₂ behaves differently due to change within the chemical properties of CO₂ causing it to differ in adsorption trends. Therefore, it can be concluded that BET adsorption isotherms cannot be used to accurately predict adsorption capacity of rocks at elevated temperature and high pressures. By assessing HPVA adsorption of CO₂ on rock samples in this study (Table. 5.1), it was found that CO₂ adsorption does, to a greater or lesser extent, occur in all the rock types assessed. Typically, it was found that with increasing pressure, CO₂ adsorption increases.
### Table 5.1 – Comparison of CO₂ adsorption isotherms found in literature to current data, showing isothermal congruency to similar rock types

<table>
<thead>
<tr>
<th>Trumpeters Member Sandstone</th>
<th>Berea and Kimachi Sandstone Fujii (2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KWV-2</strong></td>
<td><img src="image1.png" alt="Graph" /></td>
</tr>
<tr>
<td>Excess Adsorption (mol/g)</td>
<td></td>
</tr>
<tr>
<td>assuming STP molar volume</td>
<td></td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Whitehill Formation Carbonaceous Shale</th>
<th>Muderong Shale Busch et al., (2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KWV-16</strong></td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>Excess Adsorption (mol/g)</td>
<td></td>
</tr>
<tr>
<td>assuming STP molar volume</td>
<td></td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Karoo Dolerite</th>
<th>Iidate Granite (Fujii et al.,(2009))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KWV-13</strong></td>
<td><img src="image5.png" alt="Graph" /></td>
</tr>
<tr>
<td>Excess Adsorption (mol/g)</td>
<td></td>
</tr>
<tr>
<td>assuming STP molar volume</td>
<td></td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td></td>
</tr>
<tr>
<td></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By assessing literature pertaining to high pressure CO₂ adsorption potential (Fujii et al. 2009; Fujii et al. 2010; Heller and Zoback, 2014) on similar rock types evaluated in this study, it was found that the CO₂ adsorption isotherms were comparable and showed some congruency in terms of shape (Table 5.1). In most cases, inflection CO₂ adsorption (maximum adsorption) was achieved at similar pressures to those in literature. The similarities in trends were found to be lithologically specific in that rocks such as shale, sandstone and intrusive igneous rocks (dolerite and granite) showed similar isothermal patterns (Table 5.1). It must be noted that the HPVA used in this study was not the same equipment and/or experimental setup used by Fujii et al. (2009); Fujii (2010); Heller and Zoback (2014), hence differences in absolute CO₂ adsorption values are expected.

The results were ranked and summarized in Table 5.2 according to each rock samples maximum capacity to adsorb CO₂ and the other aspects (porosity and mineralogy) which may have influenced adsorption capacity. Geological samples KWV-14 and KWV-16, carbonaceous shales (potential cap/reservoir rocks), were found to have some of the highest adsorption potential (Table 5.2). This has positive implications when exploring for a suitable caprock of a potential storage basin, as a high adsorption capacity of a caprock could add additional retention which could mitigate upward migration of CO₂ (Busch et al., 2008).

Potential storage reservoirs like sandstones KWV-10 and KWV-2, and even silty shale KWV-1 (Table 5.2), are some of the highest performing adsorptive samples. This indicates good storage potential on the grounds of adsorption potential, but not necessarily with regards to porosity (Table 5.2).

Dolerite KWV-13 had the least capacity to adsorb CO₂ (Table 5.4), as predicted. These dolerites could therefore be viewed as suitable caprocks. However, due to the nature of the dolerite intrusions through the basin, additional complications arise.

The negative adsorption trends, specifically in the shale and dolerite samples (KWV-1; KWV-5; KWV-13 and KWV-14), could be attributed to the swelling of the adsorbent (rocks). Krooss et al. (2002) found that in coal samples, a negative isotherm trend was observed due to swelling of the adsorbent (coal) during CO₂-induced into the coal samples. This was also observed in rock samples (sandstone and granite) used in a study by Fujii et al. (2009), where similar negative trends in CO₂ adsorption isotherms were found in which they attributed to adsorbent swelling. Some of the rock samples used in this study possess this same negative adsorption trend pattern, and therefore the possibility of swelling could be considered.

As discussed in Section 4.5, technicalities regarding inflated adsorption values were raised as a concern with ISGS. The isotherms constructed from the 2nd HPVA run for selected samples showed discrepancies when compared to the initial data. Although adsorption values were not
identical, the isotherms themselves showed similar trends. Hence, there is value in the fact that trends have not changed and can therefore possess scientific merit when comparing these isotherms to ones found in literature.

Thus, the aims and objectives of the project had been met in that the composition, quantification of porosity and CO₂ adsorption potential of these rocks were assessed. Although CO₂ adsorption potential was found in these rocks, it was not possible to accurately quantify CO₂ adsorption.

5.4 Key Research Questions Answered

The key research questions posed in Section 1.4 have been answered:

a) Composition of the sampled rocks was identified in terms of mineralogy and TOC (for the carbonaceous shale, from de Kock et al (2016), as summarized in Table 5.2.

b) All rock samples showed the capacity to adsorb CO₂ with increasing pressure. Each sample is ranked according to its adsorption potential (Table 5.2).

c) It was found that samples containing clay minerals and TOC adsorbed more CO₂ than other samples. Dolerite samples, which consisted of mostly plagioclase (Table. 4.2), adsorbed the least CO₂.

d) The composition of the sandstones and shales indicate potential for CO₂ storage, in terms of their ability to adsorb CO₂. The high adsorption trends in potential shale caprocks is good to impede upward migration of the CO₂ plume.

e) Porosity is significantly low (~1 vol. %) and therefore the lithology’s assessed do not appear suitable to store large volumes of CO₂ on a scale for CCS.

f) Isotherms produced are comparable to literature according to their respective lithotype (Table. 5.1).

g) Although the rocks have potential to adsorb CO₂, on the grounds of low porosity, this area of the South-Eastern Karoo Basin is unlikely to be suitable for unconventional CO₂ storage.
<table>
<thead>
<tr>
<th>Rank</th>
<th>Sample I.D</th>
<th>Stratigraphy</th>
<th>Rock Type</th>
<th>TOC (%)</th>
<th>Mineralogy</th>
<th>Maximum Pore Volume (cm$^3$/g)</th>
<th>Porosity (Vol. %)</th>
<th>Maximum Adsorption (mol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>KWV-14</td>
<td>Whitehill Fm.</td>
<td>Carbonaceous Shale</td>
<td>~2.12</td>
<td>Albite Quartz Pyrrhotite Muscovite</td>
<td>0.0037</td>
<td>1.082</td>
<td>1.70</td>
</tr>
<tr>
<td>2</td>
<td>KWV-2</td>
<td>Trumpeters Member</td>
<td>Sandstone</td>
<td>N/A</td>
<td>Quartz Albite Chlorite Orthoclase</td>
<td>0.0040</td>
<td>1.056</td>
<td>1.18</td>
</tr>
<tr>
<td>3</td>
<td>KWV-1</td>
<td>Trumpeters Member</td>
<td>Silty Shale</td>
<td>N/A</td>
<td>Quartz Albite Chlorite Orthoclase Muscovite</td>
<td>0.0038</td>
<td>1.036</td>
<td>1.16</td>
</tr>
<tr>
<td>4</td>
<td>KWV-10</td>
<td>Plutos Vale Member</td>
<td>Sandstone</td>
<td>N/A</td>
<td>Quartz Albite Chlorite Orthoclase Muscovite</td>
<td>0.0033</td>
<td>0.997</td>
<td>1.11</td>
</tr>
<tr>
<td>5</td>
<td>KWV-16</td>
<td>Whitehill Fm.</td>
<td>Carbonaceous Shale</td>
<td>~6.27</td>
<td>Calcite Pyrite Iiite</td>
<td>Cristobalite Ninite Willemsite Pyrrhotite</td>
<td>0.0047</td>
<td>1.424</td>
</tr>
<tr>
<td>6</td>
<td>KWV-5</td>
<td>Wonderfontein Fm.</td>
<td>Silty Shale</td>
<td>N/A</td>
<td>Quartz Albite Chlorite Orthoclase Muscovite</td>
<td>0.0040</td>
<td>1.161</td>
<td>0.41</td>
</tr>
<tr>
<td>7</td>
<td>KWV-6</td>
<td>Wonderfontein Fm.</td>
<td>Very Fine Sandstone</td>
<td>N/A</td>
<td>Quartz Albite Chlorite Calcite Sanidine Muscovite</td>
<td>0.0036</td>
<td>1.021</td>
<td>0.31</td>
</tr>
<tr>
<td>8</td>
<td>KWV-13</td>
<td>Karoo Dolerite</td>
<td>Dolerite</td>
<td>N/A</td>
<td>Anorthite (plg.) Quartz Diopside Biotite</td>
<td>0.0033</td>
<td>1.029</td>
<td>0.04</td>
</tr>
</tbody>
</table>
5.5 Recommendations

Porosity and CO\textsubscript{2} adsorption capacity are essential aspects when assessing for potential geological CO\textsubscript{2} storage basins. Although porosity volumes were significantly low in this part of the Karoo Basin, there might be potential for larger pore space in other parts of the Karoo Basin where sediments might be more loosely packed or better sorted, or less matrix.... Hence, the Karoo Basin could be explored further in terms of CCS.

BET analysis, by use of CO\textsubscript{2} gas as the adsorbent, is a good tool to use for exploration of suitable storage lithologies as this gives a more accurate indication to the pore volume for occupation of CO\textsubscript{2} in comparison to N\textsubscript{2} BET. Although BET is good for porosity measurements, it cannot be used at a tool to predict CO\textsubscript{2} adsorption at high temperature and pressure. APPENDIX B which comprises information such as surface area plots, H-K isotherms, D-A isotherms which could be used for further studies regarding BET interpretations not included in this dissertation.

The HPVA system used in this study produced inflated CO\textsubscript{2} adsorption values due to experimental error. The system encountered various problems regarding general accuracy attributed by the multiple venting procedures in every set of analysis done on each sample. Efforts towards general calibration of the experimental equipment, specifically aimed at streamlining the event at which the CO\textsubscript{2} gas/liquid was administered into the sample cell, as well as pressure and volume sensors, all need to be assessed for more accurate future volumetric work. APPENDIX C.1 consists of tables showing volumetric data acquired from the ISGS lab which could be used for further investigation into why inflated values were found regarding CO\textsubscript{2} adsorption, or, if a new way of assessing the data is proposed in the future, it could potentially help with understanding this data better.

Although the approach of studying the adsorption potential and porosity of rocks are good tools for assessing a potential storage basin, there are more factors to consider for long-term storage of CO\textsubscript{2}. More detailed future studies would be beneficial to fully understanding the overall potential to store CO\textsubscript{2}. Aspects discussed below could help guide future studies for CCS potential in the South-Eastern Main Karoo Basin:

- Investigations by use of diffusion experiments which assess long-term alteration of minerals are suggested to further understand mineral CO\textsubscript{2} trapping as well as possible implications towards porosity and permeability, i.e. swelling of minerals.

- Comparison of various other hypothetical storage models based on: monolayer adsorption model; solubility model and pore-filling model are considered beneficial to understand the mechanism for CO\textsubscript{2}-rock interaction for potential CO\textsubscript{2} injection and may be considered for future work.


Lohmann, R. (2017). Microplastics are not important for the cycling and bioaccumulation of organic pollutants in the oceans—but should microplastics be considered POPs themselves?. Integrated Environmental Assessment and Management, 13(3), pp.460-465.


Nandi, J. (2013). China represents 68% of increase in global CO₂ emissions, India represents 8%: Study. [online] Available at:
[ Accessed 7 Oct. 2016 ]


APPENDIX A:

XRD DIFFRACTOGRAMS
KWV-9

Peak List

91-076-0823; Orthoclase
91-079-1910; Quartz
91-080-1094; Albite low
90-029-0737; Chlorite, 1111, MIRG#1, 1111, UMBURG, ferroan
90-029-0911; Illite, MIRG#1 [NR]
91-076-0566; Muscovite 2111, MIRG#1
91-079-2406; Dolomite

Counts

UNIVERSITY OF JOHANNESBURG
KWV-15

Peak List

01-075-1149: sodium calcium tecto-alumosilicate. Albite, calcian

01-085-0865: α-Si O2; Quartz, syn

01-081-1302; Diopside

01-081-3406; Biotite

Counts

Position [%] (Copper (Cu))

KWV-15

Position [%] (Copper (Cu))
### Peak List

<table>
<thead>
<tr>
<th>Code</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-085-2334</td>
<td>Calcite</td>
</tr>
<tr>
<td>01-071-2219</td>
<td>Pyrite, syn</td>
</tr>
<tr>
<td>00-026-0911</td>
<td>Illite-2lTMNG#1 [NR]</td>
</tr>
<tr>
<td>01-092-1232</td>
<td>Cristobalite BOA</td>
</tr>
<tr>
<td>00-005-0490</td>
<td>Quartz, low</td>
</tr>
<tr>
<td>00-022-0711</td>
<td>Nimite-1lTMNG#1 [NR]</td>
</tr>
<tr>
<td>00-022-0711</td>
<td>Willemsite</td>
</tr>
<tr>
<td>01-075-0600</td>
<td>Pyrrhotite 1lTTIRG</td>
</tr>
</tbody>
</table>

### Counts

```
Position [°2θ] (Copper (Cu))
```

```
15000
10000
5000
0
```

```
15
10
5
0
```

### Position [°2θ] (Copper (Cu))
APPENDIX B:

BET RESULTS
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Summary Report

Surface Area
Single point surface area at P/P₀ = 0.033562878: 9.2387 m²/g
BET Surface Area: 169.9091 m²/g
Langmuir Surface Area: 434.5895 m²/g

Horvath-Kawazoe
Maximum pore volume at P/P₀ = 0.033562878: 0.003831 cm³/g
Median pore width: 4.107 Å

Dubinin-Astakhov
Micropore surface area: 134.564523 m²/g
Limiting micropore volume: 0.090755 cm³/g
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000712515</td>
<td>18.626570</td>
<td>0.0590</td>
<td>02:30</td>
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Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

Isotherm Linear Plot

745- Rowen UJ KWV-1 - Adsorption
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

 Isotherm Log Plot

![Isotherm Log Plot](image-url)
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.5288 cm³ Measured
Thermal Correction: No
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

BET Surface Area Report
BET Surface Area: 169.9091 ± 204.1952 m²/g
Slope: 0.00989 ± 0.032306 g/cm³ STP
Y-Intercept: 0.016997 ± 0.000594 g/cm³ STP
C: 1.581766
Qm: 37.1941 cm³/g STP
Correlation Coefficient: 0.0700496
Molecular Cross-Sectional Area: 0.1700 nm²

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<tr>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
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Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM  Analysis Adsorptive: CO2
Completed: 6/1/2016 6:28:03AM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2550 g  Warm Free Space: 27.5288 cm³ Measured
Cold Free Space: 29.3691 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Notes:

BET Surface Area Plot

1/[Q(Po/P - 1)]
0.000  0.002  0.004  0.006  0.008  0.010  0.012  0.014  0.016  0.018
0.000  0.005  0.010  0.015  0.020  0.025  0.030
Relative Pressure (P/Po)
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:04AM
File: C:\2020\DATA\745.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

Langmuir Surface Area Report
Langmuir Surface Area: 434.5895 ± 1616.5114 m²/g
Slope: 0.010511 ± 0.039099 g/cm³ STP
Y-Intercept: 432.585853 ± 19.031595 mmHg·g/cm³ STP
b: 0.000024 1/mmHg
Qm: 95.1342 cm³/g STP
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

Langmuir Surface Area Plot
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Analysis Adsorptive: CO2
Completed: 6/1/2016 6:28:03AM
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Sample Mass: 0.2550 g
Warm Free Space: 27.5288 cm³ Measured
Cold Free Space: 29.3691 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Notes:

Freundlich Reports

Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Full Report Set

Sample: 745- Rowen UJ KWV-1  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM  
Completed: 6/1/2016 6:28:03AM  
Analysis Adsorptive: CO2

Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.5288 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g  
Cold Free Space: 29.3691 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Notes:

Temkin Reports

Primary Data
4058- At least two data points are needed for Temkin calculations.

Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 745- Rowen UJ KWV-1  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM  
Completed: 6/1/2016 6:28:03AM  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.5288 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g  
Cold Free Space: 29.3691 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Notes:

t-Plot Reports

Primary Data  
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Alpha-S Method
Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 745- Rowen UJ KWV-1  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM  
Completed: 6/1/2016 6:28:03AM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No

Warm Free Space: 27.5288 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g  
Cold Free Space: 29.3691 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Notes:

f-Ratio Method
A reference file has not been chosen.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

BJH Adsorption Reports
Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

D-H Adsorption Reports
Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

- Started: 5/31/2016 10:47:38PM
- Completed: 6/1/2016 6:28:03AM
- Sample Mass: 0.2550 g
- Cold Free Space: 29.3691 cm³
- Ambient Temperature: 22.00 °C
- Automatic Degas: Yes
- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Thermal Correction: No
- Warm Free Space: 27.5288 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP

Notes:

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 745- Rowen UJ KWV-1  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM  
Completed: 6/1/2016 6:28:03AM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.5288 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Options Report

Sample Tube
- Warm free space: 1.0000 cm³  
- Cold free space: 1.0000 cm³  
- Non-ideality factor: 0.0000620  
- Use Isothermal Jacket: Yes  
- Use Filler Rod: Yes  
- Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
- Fast evacuation: No  
- Unrestricted evacuation from: 30.0 mmHg  
- Vacuum setpoint: 10 µmHg  
- Evacuation time: 0.50 h  
- Leak test: No  
- Use TranSeal: No

Free Space
- Free-space type: Measured  
- Lower dewar for evacuation: Yes  
- Evacuation time: 1.00 h  
- Outgas test: No

Po and Temperature
- Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.  
  Po: 26142.000 mmHg  
  Temperature: 0.000 °C  
  Ambient temperature: 22.00 °C

Dosing
- Use first pressure fixed dose: No  
- Use maximum volume increment: No  
- Target tolerance: 5.0% or 5.000 mmHg  
- Low pressure dosing: Yes  
- Dose amount: 3.0000 cm³/g STP  
- Minimum equilibration delay: 0.00 h  
- Maximum equilibration delay: 999.00 h

Equilibration
- Equilibration time (P/Po = 1.000000000): 60 s  
- Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
- Backfill at start of analysis: Yes  
- Backfill at end of analysis: Yes
Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Sample Backfill
Backfill gas: CO₂

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 745- Rowen UJ KWV-1  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\745.SMP

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/29/2016</td>
<td>3:21:57AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>5/29/2016</td>
<td>3:24:49AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
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<tr>
<td>5/30/2016</td>
<td>3:38:10AM</td>
<td>Started cool-down wait.</td>
</tr>
<tr>
<td>5/30/2016</td>
<td>3:38:10AM</td>
<td>Started cool-down wait.</td>
</tr>
<tr>
<td>5/30/2016</td>
<td>4:05:56PM</td>
<td>Degas operation done.</td>
</tr>
<tr>
<td>5/30/2016</td>
<td>4:19:45PM</td>
<td>Degas operation started on Unit 1 - S/N: 715, port 1.</td>
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<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
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Sample: 745- Rowen UJ KWV-1
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\745.SMP

Started: 5/31/2016 10:47:38PM
Completed: 6/1/2016 6:28:03AM
Sample Mass: 0.2550 g
Cold Free Space: 29.3691 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.5288 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed

Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.
Surface area: Passed

Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM  
Completed: 6/2/2016 5:45:37AM  
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6711 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Summary Report

Surface Area
Single point surface area at P/Po = 0.033561234: 9.5782 m²/g
BET Surface Area: 41.4064 m²/g
Langmuir Surface Area: 52.3910 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.033561234: 0.003972 cm³/g
Median pore width: 4.077 Å

Dubinin-Astakhov
Micropore surface area: 116.724627 m²/g
Limiting micropore volume: 0.077121 cm³/g
Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP

Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM  
Completed: 6/2/2016 5:45:37AM  
Report Time: 6/2/2016 5:45:37AM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6711 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Linear Plot
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
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Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Log Plot

Relative Pressure (P/Po)

Quantity Adsorbed (cm³/g STP)
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
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Sample Mass: 0.2554 g
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Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BET Surface Area Report
BET Surface Area: 41.4064 ± 12.2311 m²/g
Slope: 0.096288 ± 0.032584 g/cm³ STP
Y-Intercept: 0.014038 ± 0.000585 g/cm³ STP
C: 7.859279
Qm: 9.0641 cm³/g STP
Correlation Coefficient: 0.5512913
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
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<tr>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
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</table>
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BET Surface Area Plot

+ 748- Rowen UJ- KWV-2

0.000  0.005  0.010  0.015  0.020  0.025  0.030
Relative Pressure (P/Po)

0.002  0.004  0.006  0.008  0.010  0.012  0.014  0.016
1/[Q(PoP - 1)]

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**Langmuir Surface Area Report**

Langmuir Surface Area: 52.3910 ± 24.5646 m²/g  
Slope: 0.087194 ± 0.040883 g/cm³ STP  
Y-Intercept: 360.927335 ± 19.899333 mmHg·g/cm³ STP  
\( b \): 0.000242 1/mmHg  
\( Q_m \): 11.4687 cm³/g STP  
Correlation Coefficient: 0.495211  
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP

- Started: 6/1/2016 9:52:50PM  
- Completed: 6/2/2016 5:45:37AM  
- Report Time: 6/2/2016 5:45:37AM  
- Sample Mass: 0.2554 g  
- Cold Free Space: 29.5651 cm³  
- Ambient Temperature: 22.00 °C  
- Automatic Degas: Yes  
- Analysis Adsorptive: CO2  
- Analysis Bath Temp.: 0.000 °C  
- Thermal Correction: No  
- Warm Free Space: 27.6711 cm³ Measured  
- Equilibration Interval: 60 s  
- Low Pressure Dose: 3.000 cm³/g STP

Freundlich Reports

Primary Data  
4057- At least two data points are needed for Freundlich calculations.
Primary Data  
4057- At least two data points are needed for Freundlich calculations.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports

Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

**t-Plot Reports**

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports

Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

- Started: 6/1/2016 9:52:50PM
- Completed: 6/2/2016 5:45:37AM
- Report Time: 6/2/2016 5:45:37AM
- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Thermal Correction: No
- Warm Free Space: 27.6711 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP
- Ambient Temperature: 22.00 °C
- Cold Free Space: 29.5651 cm³
- Automatic Degas: Yes

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP

Sample Mass: 0.2554 g  
Cold Free Space: 29.5651 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6711 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).  
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP  

Sample Mass: 0.2554 g  
Cold Free Space: 29.5651 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Warm Free Space: 27.6711 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Options Report

Sample Tube
Warm free space: 1.0000 cm³  
Cold free space: 1.0000 cm³  
Non-ideality factor: 0.0000620  
Use Isothermal Jacket: Yes  
Use Filler Rod: Yes  
Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
Fast evacuation: No  
Unrestricted evacuation from: 30.0 mmHg  
Vacuum setpoint: 10 µmHg  
Evacuation time: 0.50 h  
Leak test: No  
Use TranSeal: No

Free Space
Free-space type: Measured  
Lower dewar for evacuation: Yes  
Evacuation time: 1.00 h  
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.  
Po: 26142.000 mmHg  
Temperature: 0.000 °C  
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No  
Use maximum volume increment: No  
Target tolerance: 5.0% or 5.000 mmHg  
Low pressure dosing: Yes  
Dose amount: 3.0000 cm³/g STP  
Minimum equilibration delay: 0.00 h  
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s  
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes  
Backfill at end of analysis: Yes  
Backfill gas: CO2
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:37AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 748- Rowen UJ- KWV-2
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM
Completed: 6/2/2016 5:45:37AM
Report Time: 6/2/2016 5:45:38AM
Sample Mass: 0.2554 g
Cold Free Space: 29.5651 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6711 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Log Report

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/31/2016</td>
<td>10:54:41PM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>5/31/2016</td>
<td>10:57:45PM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>5/31/2016</td>
<td>11:06:54PM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>9:50:06PM</td>
<td>Started cool-down wait.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>5:45:37AM</td>
<td>Analysis done.</td>
</tr>
</tbody>
</table>
Sample: 748- Rowen UJ- KWV-2  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\748.SMP

Started: 6/1/2016 9:52:50PM  
Completed: 6/2/2016 5:45:37AM  
Report Time: 6/2/2016 5:45:38AM  
Sample Mass: 0.2554 g  
Cold Free Space: 29.5651 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6711 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.  
Po: Passed  
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed  
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.  
Surface area: Passed  
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

- Completed: 6/2/2016 11:05:36PM
- Report Time: 6/2/2016 11:05:36PM
- Sample Mass: 0.2551 g
- Cold Free Space: 29.7033 cm³
- Ambient Temperature: 22.00 °C
- Automatic Degas: Yes

- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Thermal Correction: No
- Warm Free Space: 27.7294 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP

Summary Report

**Surface Area**

- Single point surface area at P/Po = 0.032985951: 10.6717 m²/g
- BET Surface Area: 31.1214 m²/g
- Langmuir Surface Area: 37.0079 m²/g

**Horvath-Kawazoe**

- Maximum pore volume at P/Po = 0.032985951: 0.004422 cm³/g
- Median pore width: 4.065 Å

**Dubinin-Astakhov**

- Micropore surface area: 116.176525 m²/g
- Limiting micropore volume: 0.075599 cm³/g
**Isotherm Tabular Report**

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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<tr>
<td>0.008683330</td>
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</table>
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Log Plot

Relative Pressure (P/Po)

Quantity Adsorbed (cm³/g STP)
Sample: 749-Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

**BET Surface Area Report**

BET Surface Area: $31.1214 \pm 6.1872$ m²/g
Slope: $0.135630 \pm 0.029178$ g/cm³ STP
Y-Intercept: $0.011155 \pm 0.000522$ g/cm³ STP
C: $13.158194$
Qm: $6.8127$ cm³/g STP
Correlation Coefficient: 0.7206391
Molecular Cross-Sectional Area: $0.1700$ nm²

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
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<tbody>
<tr>
<td>0.000697359</td>
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</table>
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Report Time: 6/2/2016 11:05:37PM
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Sample Mass: 0.2551 g
Equilibration Interval: 60 s
Cold Free Space: 29.7033 cm³
Low Pressure Dose: 3.000 cm³/g STP
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

BET Surface Area Plot

UNIVERSITY OF JOHANNESBURG
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM Analysis Bath Temp.: 0.000 °C
Report Time: 6/2/2016 11:05:37PM Thermal Correction: No
Sample Mass: 0.2551 g Warm Free Space: 27.7294 cm³ Measured
Cold Free Space: 29.7033 cm³ Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Langmuir Surface Area Report
Langmuir Surface Area: 37.0079 ± 11.0172 m²/g
Slope: 0.123438 ± 0.036747 g/cm³ STP
Y-Intercept: 288.677977 ± 17.822890 mmHg·g/cm³ STP
b: 0.000428 1/mmHg
Qm: 8.1013 cm³/g STP
Correlation Coefficient: 0.668042
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.230371</td>
<td>0.0867</td>
<td>210.370</td>
</tr>
<tr>
<td>24.012470</td>
<td>0.1071</td>
<td>224.141</td>
</tr>
<tr>
<td>45.805962</td>
<td>0.1694</td>
<td>270.350</td>
</tr>
<tr>
<td>136.466583</td>
<td>0.4090</td>
<td>333.672</td>
</tr>
<tr>
<td>181.933105</td>
<td>0.5220</td>
<td>348.517</td>
</tr>
<tr>
<td>226.999603</td>
<td>0.6417</td>
<td>353.741</td>
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<tr>
<td>272.779572</td>
<td>0.7483</td>
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<tr>
<td>318.274658</td>
<td>0.8777</td>
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<tr>
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<td>1.0888</td>
<td>375.561</td>
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<tr>
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<td>370.077</td>
</tr>
<tr>
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<td>1.4313</td>
<td>374.903</td>
</tr>
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<td>1.5945</td>
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Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Langmuir Surface Area Plot

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<td>200</td>
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</tr>
<tr>
<td>700</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0</td>
</tr>
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</table>

+ 749- Rowen UJ- KWV-5
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Freundlich Reports
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports
Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

---

t-Plot Reports

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
Sample: 749- Rowen UJ- KWV-5  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\749.SMP

- Completed: 6/2/2016 11:05:36PM  
- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C  
- Thermal Correction: No
- Warm Free Space: 27.7294 cm³ Measured  
- Equilibration Interval: 60 s  
- Low Pressure Dose: 3.000 cm³/g STP  
- Sample Mass: 0.2551 g
- Cold Free Space: 29.7033 cm³  
- Ambient Temperature: 22.00 °C  
- Automatic Degas: Yes

---

**Alpha-S Method**

Primary Data

4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports
Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 749- Rowen UJ- KWV-5  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\749.SMP

| Analysis Bath Temp.: 0.000 °C  
| Thermal Correction: No  
| Warm Free Space: 27.7294 cm³ Measured  
| Equilibration Interval: 60 s  
| Low Pressure Dose: 3.000 cm³/g STP  
| Sample Mass: 0.2551 g  
| Cold Free Space: 29.7033 cm³  
| Ambient Temperature: 22.00 °C  
| Automatic Degas: Yes  

**BJH Desorption Reports**

Primary Data  
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Desorption Reports
Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Options Report

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions
Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 749- Rowen UJ- KWV-5  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\749.SMP  

- Completed: 6/2/2016 11:05:36PM  
- Analysis Adsorptive: CO2  
- Analysis Bath Temp.: 0.000 °C  
- Thermal Correction: No  
- Warm Free Space: 27.7294 cm³ Measured  
- Equilibration Interval: 60 s  
- Low Pressure Dose: 3.000 cm³/g STP

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/1/2016</td>
<td>6:39:22AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>6:42:44AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>6:52:00AM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>7:09:56AM</td>
<td>Degas operation done.</td>
</tr>
</tbody>
</table>
Sample: 749- Rowen UJ- KWV-5
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\749.SMP

Completed: 6/2/2016 11:05:36PM
Report Time: 6/2/2016 11:05:37PM
Sample Mass: 0.2551 g
Cold Free Space: 29.7033 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7294 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.

Surface area: Passed

Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Summary Report
Surface Area
Single point surface area at P/Po = 0.033006058: 8.6409 m²/g
BET Surface Area: 66.8864 m²/g
Langmuir Surface Area: 91.7630 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.033006058: 0.003581 cm³/g
Median pore width: 4.104 Å

Dubinin-Astakhov
Micropore surface area: 111.792549 m²/g
Limiting micropore volume: 0.074454 cm³/g
### Sample Information
- Sample: 750- Rowen UJ KWV-6
- Operator: Gregory
- Submitter: Rowen UJ
- File: C:\2020\DATA\750.SMP

### Analysis Details
- Started: 6/2/2016 11:09:44PM
- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Thermal Correction: No
- Warm Free Space: 27.8094 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP

### Isotherm Tabular Report

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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</thead>
<tbody>
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</tr>
</tbody>
</table>
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
 Ambient Temperature: 22.00 °C
 Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

Isotherm Linear Plot
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Warm Free Space: 27.8094 cm³ Measured
Ambient Temperature: 22.00 °C
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Automated Degas: Yes
Thermal Correction: No

Relative Pressure (P/Po)
0.001
0.005
0.01

Quantity Adsorbed (cm³/g STP)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0

Isotherm Log Plot

750- Rowen UJ KWV-6 - Adsorption

UNIVERSITY
OF
JOHANNESBURG
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Completed: 6/3/2016 6:38:25AM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2526 g  Warm Free Space: 27.8094 cm³ Measured
Cold Free Space: 29.5794 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

BET Surface Area Report
BET Surface Area: 66.8864 ± 41.3000 m²/g
Slope: 0.051226 ± 0.042164 g/cm³ STP
Y-Intercept: 0.017071 ± 0.000775 g/cm³ STP
C: 4.000792
Qm: 14.6418 cm³/g STP
Correlation Coefficient: 0.2684901
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000697865</td>
<td>0.0610</td>
<td>0.011451</td>
</tr>
<tr>
<td>0.000912938</td>
<td>0.0691</td>
<td>0.013229</td>
</tr>
<tr>
<td>0.001816150</td>
<td>0.1119</td>
<td>0.016265</td>
</tr>
<tr>
<td>0.003485906</td>
<td>0.1943</td>
<td>0.018001</td>
</tr>
<tr>
<td>0.005226638</td>
<td>0.2739</td>
<td>0.019181</td>
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<td>0.019441</td>
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<td>0.4128</td>
<td>0.019305</td>
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<td>0.4598</td>
<td>0.019087</td>
</tr>
<tr>
<td>0.010429862</td>
<td>0.5430</td>
<td>0.019410</td>
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<td>0.011044689</td>
<td>0.5918</td>
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<td>0.013893106</td>
<td>0.7314</td>
<td>0.019263</td>
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<tr>
<td>0.015639206</td>
<td>0.8245</td>
<td>0.019270</td>
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<tr>
<td>0.017380037</td>
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<td>0.018635</td>
</tr>
<tr>
<td>0.020533098</td>
<td>1.1264</td>
<td>0.018612</td>
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<tr>
<td>0.020853685</td>
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<td>0.018160</td>
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<td>0.025832842</td>
<td>1.4702</td>
<td>0.018037</td>
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<td>1.7505</td>
<td>0.017721</td>
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<tr>
<td>0.031264104</td>
<td>1.8515</td>
<td>0.017430</td>
</tr>
<tr>
<td>0.033006058</td>
<td>1.9561</td>
<td>0.017449</td>
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</table>
Sample: 750- Rowen UJ KWV-6  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8094 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2526 g  
Cold Free Space: 29.5794 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

BET Surface Area Plot
Langmuir Surface Area Report

Langmuir Surface Area: 91.7630 ± 95.3374 m²/g
Slope: 0.049782 ± 0.051721 g/cm³ STP
Y-Intercept: 433.711826 ± 25.164692 mmHg·g/cm³ STP
b: 0.000115 1/mmHg
Qm: 20.0875 cm³/g STP
Correlation Coefficient: 0.249130
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.243591</td>
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<td>299.133</td>
</tr>
<tr>
<td>23.866030</td>
<td>0.0691</td>
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<tr>
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<td>862.844360</td>
<td>1.9561</td>
<td>441.103</td>
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</tbody>
</table>
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Freundlich Reports
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports
Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.

T-Plot Reports
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 750- Rowen UJ KWV-6  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM  

Sample Mass: 0.2526 g  
Cold Free Space: 29.5794 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Analysis Adsorptive: CO₂  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8094 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method

Primary Data  
A reference file has not been chosen.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports

Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Desorption Reports

Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 750- Rowen UJ KWV-6  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8094 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2526 g  
Cold Free Space: 29.5794 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions
Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 750- Rowen UJ KWV-6  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\750.SMP  

Started: 6/2/2016 11:09:44PM  
Sample Mass: 0.2526 g  
Cold Free Space: 29.5794 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8094 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP  

Adsorptive Properties  
Adsorptive: Carbon Dioxide @ 273.15 K  
Maximum manifold pressure: 925.00 mmHg  
Non-ideality factor: 0.0000000  
Density conversion factor: 0.0018306  
Therm. tran. hard-sphere diameter: 3.604 Å  
Molecular cross-sectional area: 0.170 nm²  
Inside diameter of sample tube: 9.53 mm
Full Report Set

Sample: 750- Rowen UJ KWV-6
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM
Sample Mass: 0.2526 g
Cold Free Space: 29.5794 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8094 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Log Report

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/2/2016</td>
<td>12:20:06AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>12:22:45AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>12:31:57AM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>10:22:31PM</td>
<td>Started checking degas at 5 µmHg.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>10:22:39PM</td>
<td>Completed checking degas after 7 sec: outgas rate = 0.0 µmHg/min.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>11:02:35PM</td>
<td>Operation skipped.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>11:02:35PM</td>
<td>Started cool-down wait.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>11:09:45PM</td>
<td>Analysis started.</td>
</tr>
</tbody>
</table>
Sample: 750- Rowen UJ KWV-6  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\750.SMP

Started: 6/2/2016 11:09:44PM  
Sample Mass: 0.2526 g  
Cold Free Space: 29.5794 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8094 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose:  3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed  
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed  
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.  
Surface area: Passed
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Summary Report

Surface Area

Single point surface area at P/Po = 0.033557429: 9.5029 m²/g
BET Surface Area: 23.4105 m²/g
Langmuir Surface Area: 24.7045 m²/g

Horvath-Kawazoe

Maximum pore volume at P/Po = 0.033557429: 0.003940 cm³/g
Median pore width: 4.068 Å

Dubinin-Astakhov

Micropore surface area: 80.632214 m²/g
Limiting micropore volume: 0.051097 cm³/g
Sample: 751-Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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<td>0.1181</td>
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<tr>
<td>0.001814387</td>
<td>47.431717</td>
<td>0.1713</td>
<td>02:52</td>
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<tr>
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<td>0.005224213</td>
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<td>03:15</td>
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<td>0.006956405</td>
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<td>03:27</td>
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<td>0.5162</td>
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</table>
Sample: 751- Rowen UJ KWV-9  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\751.SMP

Analysis Adsorptive: CO2

Analysis Bath Temp.: 0.000 °C

Sample Mass: 0.2568 g  
Warm Free Space: 27.7818 cm³ Measured

Cold Free Space: 29.5163 cm³  
Equilibration Interval: 60 s

Ambient Temperature: 22.00 °C  
Low Pressure Dose: 3.000 cm³/g STP

Automatic Degas: Yes

Relative Pressure (P/Po)
0.000 0.005 0.010 0.015 0.020 0.025 0.030
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2

Quantity Adsorbed (cm³/g STP)

Isotherm Linear Plot

751- Rowen UJ KWV-9 - Adsorption
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Log Plot

751- Rowen UJ KWV-9 - Adsorption
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BET Surface Area Report
BET Surface Area: 23.4105 ± 5.5409 m²/g
Slope: 0.183211 ± 0.046177 g/cm³ STP
Y-Intercept: 0.011922 ± 0.000849 g/cm³ STP
C: 16.366971
Qm: 5.1247 cm³/g STP
Correlation Coefficient: 0.6731327
Molecular Cross-Sectional Area: 0.1700 nm²

| Relative | Quantity | 1/(Q(Po/P - 1)) |
| Pressure | Adsorbed | (cm³/g STP)     |
| (P/Po)   | (cm³/g)  |              |
| 0.000701147 | 0.1089   | 0.006445     |
| 0.000922937 | 0.1181   | 0.007823     |
| 0.001814387 | 0.1713   | 0.010610     |
| 0.003479352 | 0.2730   | 0.012790     |
| 0.005224213 | 0.3654   | 0.014371     |
| 0.006956405 | 0.4643   | 0.015086     |
| 0.007909144 | 0.5162   | 0.015445     |
| 0.008695193 | 0.5712   | 0.015356     |
| 0.010427767 | 0.6602   | 0.015962     |
| 0.011628678 | 0.7326   | 0.016060     |
| 0.013900833 | 0.8733   | 0.016143     |
| 0.015631891 | 0.9640   | 0.016473     |
| 0.017375646 | 1.0884   | 0.016246     |
| 0.020530800 | 1.2684   | 0.016526     |
| 0.020851855 | 1.3182   | 0.016155     |
| 0.024880019 | 1.5283   | 0.016695     |
| 0.025267644 | 1.5900   | 0.016303     |
| 0.027783847 | 1.7612   | 0.016227     |
| 0.029999807 | 1.9335   | 0.015996     |
| 0.031271489 | 2.0254   | 0.015938     |
| 0.033557429 | 2.1525   | 0.016131     |
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Completed: 6/4/2016 7:20:39AM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2568 g  Warm Free Space: 27.7818 cm³ Measured
Cold Free Space: 29.5163 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose:  3.000 cm³/g STP
Automatic Degas: Yes

BET Surface Area Plot
Full Report Set

Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Langmuir Surface Area Report

Langmuir Surface Area: 24.7045 ± 7.4453 m²/g
Slope: 0.184913 ± 0.055728 g/cm³ STP
Y-Intercept: 298.496401 ± 27.123052 mmHg·g/cm³ STP
b: 0.000619 1/mmHg
Qm: 5.4080 cm³/g STP
Correlation Coefficient: 0.663493
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
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<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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</table>
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Langmuir Surface Area Plot
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMPL


Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Freundlich Reports

Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports
Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

-Plot Reports

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
Full Report Set

Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports
Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Automatic Degas: Yes

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Adsorption Reports
Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Sample Mass: 0.2568 g
Warm Free Space: 27.7818 cm³ Measured
Cold Free Space: 29.5163 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports
Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions
Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2568 g
Warm Free Space: 27.7818 cm³ Measured
Cold Free Space: 29.5163 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose:  3.000 cm³/g STP
Automatic Degas: Yes
Thermal Correction: No

Sample Log Report

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<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
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<tbody>
<tr>
<td>6/2/2016</td>
<td>11:12:16PM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>11:15:05PM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>6/2/2016</td>
<td>11:20:38PM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
</tbody>
</table>
Sample: 751- Rowen UJ KWV-9
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\751.SMP

Sample Mass: 0.2568 g
Cold Free Space: 29.5163 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7818 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.
Surface area: Passed
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Full Report Set

Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Completed: 6/5/2016 7:08:47AM Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2559 g Warm Free Space: 27.7570 cm³ Measured
Cold Free Space: 29.4579 cm³ Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Summary Report

Surface Area
Single point surface area at P/Po = 0.032986796: 7.9555 m²/g
BET Surface Area: 40.1884 m²/g
Langmuir Surface Area: 48.7355 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.032986796: 0.003297 cm³/g
Median pore width: 4.113 Å

Dubinin-Astakhov
Micropore surface area: 94.507954 m²/g
Limiting micropore volume: 0.062412 cm³/g
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

 Started: 6/4/2016 11:08:14PM
 Completed: 6/5/2016 7:08:47AM
 Analysis Adsorptive: CO2
 Analysis Bath Temp.: 0.000 °C
 Thermal Correction: No
 Warm Free Space: 27.7570 cm³ Measured
 Equilibration Interval: 60 s
 Low Pressure Dose: 3.000 cm³/g STP

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 ºC
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 ºC
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Linear Plot

---

Quantity Adsorbed (cm³/g STP)

Relative Pressure (P/Po)
Sample: 752- Rowen UJ- KWV-10  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM  
Completed: 6/5/2016 7:08:47AM  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No

Sample Mass: 0.2559 g  
Cold Free Space: 29.4579 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Warm Free Space: 27.7570 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

** Isotherm Log Plot **

---

** 752- Rowen UJ- KWV-10 - Adsorption **

---

![Graph](image-url)
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BET Surface Area Report
BET Surface Area: 40.1884 ± 16.6497 m²/g
Slope: 0.095952 ± 0.047084 g/cm³ STP
Y-Intercept: 0.017717 ± 0.000863 g/cm³ STP
C: 6.415764
Qm: 8.7975 cm³/g STP
Correlation Coefficient: 0.4235218
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>1/(Q(Po/P - 1))</th>
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Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

BET Surface Area Plot

+ 752- Rowen UJ- KWV-10

UNIVERSITY OF JOHANNESBURG
Sample: 752- Rowen UJ- KWV-10  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\752.SMP  

Started: 6/4/2016 11:08:14PM  
Completed: 6/5/2016 7:08:47AM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.7570 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP  

Langmuir Surface Area Report  
Langmuir Surface Area: 48.7355 ± 29.9084 m²/g  
Slope: 0.093734 ± 0.057523 g/cm³ STP  
Y-Intercept: 450.134335 ± 27.902151 mmHg·g/cm³ STP  
b: 0.000208 1/mmHg  
Qm: 10.6685 cm³/g STP  
Correlation Coefficient: 0.399279  
Molecular Cross-Sectional Area: 0.1700 nm²  

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<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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<tbody>
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<td>306.342</td>
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<td>23.875486</td>
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Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Langmuir Surface Area Plot

P/Q (mmHg·g/cm³ STP)

Pressure (mmHg)
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

<table>
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<tr>
<th>Started</th>
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<th>Analysis Bath Temp.</th>
<th>Thermal Correction</th>
<th>Warm Free Space</th>
<th>Equilibration Interval</th>
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<td>CO2</td>
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<td>No</td>
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<td>3.000 cm³/g STP</td>
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**Freundlich Reports**

Primary Data
4057- At least two data points are needed for Freundlich calculations.

Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 752- Rowen UJ- KVV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Completed: 6/5/2016 7:08:47AM Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2559 g Warm Free Space: 27.7570 cm³ Measured
Cold Free Space: 29.4579 cm³ Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Temkin Reports

Primary Data
4058- At least two data points are needed for Temkin calculations.

Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2559 g
Warm Free Space: 27.7570 cm³ Measured
Cold Free Space: 29.4579 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.

---

**t-Plot Reports**

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports

Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Desorption Reports
Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports
Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Options Report

Analysis Conditions

Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 μmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Sample Mass: 0.2559 g
Cold Free Space: 29.4579 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.7570 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Sample Log Report

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<th>Time</th>
<th>Message</th>
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<tr>
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<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
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<td>4:07:18PM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
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<td>Started temperature hold at 75 °C for 1440 minutes.</td>
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Sample: 752- Rowen UJ- KWV-10
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\752.SMP

Started: 6/4/2016 11:08:14PM
Completed: 6/5/2016 7:08:47AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2559 g
Thermal Correction: No
Cold Free Space: 29.4579 cm³
Warm Free Space: 27.7570 cm³ Measured
Ambient Temperature: 22.00 °C
Equilibration Interval: 60 s
Automatic Degas: Yes
Low Pressure Dose: 3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.
Surface area: Passed
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 754- Rowen UJ KWV-13 Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\754.SMP  

Started: 6/6/2016 1:33:59AM  
Completed: 6/6/2016 9:15:03AM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8303 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP  

Sample Mass: 0.2535 g  
Cold Free Space: 29.5506 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Summary Report

Surface Area
Single point surface area at P/Po = 0.032993602: 6.9932 m²/g
BET Surface Area: -4.1714 m²/g
Langmuir Surface Area: -3.5975 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.032993602: 0.002898 cm³/g
Median pore width: 4.193 Å

Dubinin-Astakhov
Micropore surface area: 328.894658 m²/g
Limiting micropore volume: 0.246211 cm³/g
### Isotherm Tabular Report

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<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Equilibration Interval: 60 s

Relative Pressure (P/P₀) | Absolute Pressure (mmHg) | Quantity Adsorbed (cm³/g STP) | Elapsed Time (h:min) | Saturation Pressure (mmHg) |
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26142.000000
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Linear Plot

---

Relative Pressure (P/Po)
---

Quantity Adsorbed (cm³/g STP)
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Isotherm Log Plot

754- Rowen UJ KWV-13 Repeat - Adsorption
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C

Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

BET Surface Area Report
BET Surface Area: -4.1714 ± 0.9831 m²/g
Slope: -1.146899 ± 0.258045 g/cm³ STP
Y-Intercept: 0.051776 ± 0.004730 g/cm³ STP
C: -21.150979
Qm: -0.9131 cm³/g STP
Correlation Coefficient: -0.7139534
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>1/[Q(Po/P - 1)]</th>
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### BET Surface Area Plot

**Sample:** 754- Rowen UJ KWV-13 Repeat  
**Operator:** Gregory  
**Submitter:** Rowen UJ  
**File:** C:\2020\DATA\754.SMP

- **Started:** 6/6/2016 1:33:59AM  
- **Completed:** 6/6/2016 9:15:03AM  
- **Report Time:** 6/6/2016 9:15:03AM  
- **Analysis Adsorptive:** CO2  
- **Analysis Bath Temp.:** 0.000 °C  
- **Thermal Correction:** No  
- **Warm Free Space:** 27.8303 cm³ Measured  
- **Equilibration Interval:** 60 s  
- **Low Pressure Dose:** 3.000 cm³/g STP  
- **Sample Mass:** 0.2535 g  
- **Cold Free Space:** 29.5506 cm³  
- **Ambient Temperature:** 22.00 °C  
- **Automatic Degas:** Yes

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259
Langmuir Surface Area Report

Langmuir Surface Area: -3.5975 ± 0.9098 m²/g
Slope: -1.269823 ± 0.321119 g/cm³ STP
Y-Intercept: 1421.964926 ± 155.767210 mmHg·g/cm³ STP
b: -0.000893 1/mmHg
Qm: -0.7875 cm³/g STP
Correlation Coefficient: -0.726373
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.594299</td>
<td>0.0157</td>
<td>1183.581</td>
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<tr>
<td>24.181854</td>
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<tr>
<td>136.599197</td>
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<tr>
<td>181.526138</td>
<td>0.1951</td>
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<td>227.414398</td>
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<tr>
<td>862.518738</td>
<td>1.5831</td>
<td>544.834</td>
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</table>
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Langmuir Surface Area Plot
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Completed: 6/6/2016 9:15:03AM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2535 g  Warm Free Space: 27.8303 cm³ Measured
Cold Free Space: 29.5506 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose:  3.000 cm³/g STP
Automatic Degas: Yes

Freundlich Reports
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:/2020/DATA/754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports
Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

t-Plot Reports
4055- A positive BET surface area was not calculated.
4055- A positive BET surface area was not calculated.
4055- A positive BET surface area was not calculated.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

**Alpha-S Method**

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports

Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

 BJH Desorption Reports

Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Adsorption Reports
Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Options Report

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Completed: 6/6/2016 9:15:03AM
Sample Mass: 0.2535 g
Cold Free Space: 29.5506 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8303 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 754- Rowen UJ KWV-13 Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\754.SMP  

started: 6/6/2016 1:33:59AM  
Completed: 6/6/2016 9:15:03AM  
Sample Mass: 0.2535 g  
Cold Free Space: 29.5506 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8303 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/3/2016</td>
<td>11:43:58PM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/3/2016</td>
<td>11:46:04PM</td>
<td>Started temperature ramp at 5.0 °C/min to 30 °C.</td>
</tr>
<tr>
<td>6/3/2016</td>
<td>11:51:00PM</td>
<td>Started temperature hold at 30 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>01:03:32AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>01:08:31AM</td>
<td>Started temperature ramp at 5.0 °C/min to 30 °C.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>01:08:32AM</td>
<td>Started temperature hold at 30 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>07:38:02AM</td>
<td>Analysis done.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>08:10:03AM</td>
<td>Analysis done.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>08:38:04AM</td>
<td>6538- Power failure detected. The sample is in an unknown condition. A run termination will be performed for safety. Analysis canceled.</td>
</tr>
</tbody>
</table>
Sample: 754- Rowen UJ KWV-13 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\754.SMP

Started: 6/6/2016 1:33:59AM
Analysis Adsorptive: CO₂
Completed: 6/6/2016 9:15:03AM
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Sample Mass: 0.2535 g
Warm Free Space: 27.8303 cm³ Measured
Cold Free Space: 29.5506 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Sample Log Report

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/6/2016</td>
<td>9:15:03AM</td>
<td>Analysis done.</td>
</tr>
</tbody>
</table>
Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.

Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: C value is low. Select a new range, removing some of the higher pressure points.

Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.

Surface area: Review the isotherm. Negative surface area is the result of an inaccurate isotherm.

Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Summary Report

Surface Area
Single point surface area at P/Po = 0.032995563: 8.8535 m²/g
BET Surface Area: 25.7045 m²/g
Langmuir Surface Area: 30.3162 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.032995563: 0.003669 cm³/g
Median pore width: 4.031 Å

Dubinin-Astakhov
Micropore surface area: 102.250614 m²/g
Limiting micropore volume: 0.066723 cm³/g
### Sample: 747- Rowen UJ- KWV-14 Repeat 4
- Operator: Gregory
- Submitter: Rowen UJ
- File: C:\2020\DATA\747.SMP

- Started: 6/1/2016 6:37:18AM
- Completed: 6/1/2016 2:28:35PM
- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Thermal Correction: No
- Warm Free Space: 27.8481 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP

#### Isotherm Tabular Report

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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<td>0.016375938</td>
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<td>1.0036</td>
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<tr>
<td>0.017387121</td>
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<tr>
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</tbody>
</table>
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Linear Plot

--- 747- Rowen UJ- KWV-14 Repeat 4 - Adsorption ---
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Log Plot

747- Rowen UJ- KWV-14 Repeat 4 - Adsorption
BET Surface Area Report

BET Surface Area: 25.7045 ± 3.9145 m²/g
Slope: 0.164767 ± 0.027060 g/cm³ STP
Y-Intercept: 0.012952 ± 0.000485 g/cm³ STP
C: 13.721807
Qm: 5.6269 cm³/g STP
Correlation Coefficient: 0.8059646
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00698618</td>
<td>0.0737</td>
<td>0.009487</td>
</tr>
<tr>
<td>0.00912578</td>
<td>0.0850</td>
<td>0.010740</td>
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<td>0.01591460</td>
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<td>0.01755275</td>
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<td>0.012854</td>
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<tr>
<td>0.003473633</td>
<td>0.2482</td>
<td>0.014042</td>
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<td>0.3574</td>
<td>0.014674</td>
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<tr>
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<td>0.4545</td>
<td>0.015394</td>
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<tr>
<td>0.008698698</td>
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<td>0.016083</td>
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<td>0.017118</td>
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</tr>
<tr>
<td>0.032995563</td>
<td>2.0042</td>
<td>0.017025</td>
</tr>
</tbody>
</table>
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes
Langmuir Surface Area Report

Langmuir Surface Area: 30.3162 ± 7.0429 m²/g
Slope: 0.150684 ± 0.035006 g/cm³ STP
Y-Intercept: 335.194291 ± 16.983183 mmHg·g/cm³ STP
b: 0.000450 1/mmHg
Qm: 6.6364 cm³/g STP
Correlation Coefficient: 0.754728
Molecular Cross-Sectional Area: 0.1700 nm²

<table>
<thead>
<tr>
<th>Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.263283</td>
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<tr>
<td>23.856617</td>
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<td>0.4545</td>
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</tbody>
</table>
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes
Sample: 747- Rowen UJ- KWV-14 Repeat 4  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM  
Completed: 6/1/2016 2:28:35PM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8481 cm³  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2533 g  
Cold Free Space: 29.5250 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Freundlich Reports

Primary Data  
4057- At least two data points are needed for Freundlich calculations.  
Primary Data  
4057- At least two data points are needed for Freundlich calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Temkin Reports

Primary Data
4058- At least two data points are needed for Temkin calculations.
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Primary Data
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.
4054- Fewer than two data points are inside the fitted thickness range.

**t-Plot Reports**

- Fewer than two data points are inside the fitted thickness range.
- Fewer than two data points are inside the fitted thickness range.
- Fewer than two data points are inside the fitted thickness range.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 747- Rowen UJ- KWV-14 Repeat 4  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM  
Completed: 6/1/2016 2:28:35PM  
Analysis Adsorptive: CO₂  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8481 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2533 g  
Cold Free Space: 29.5250 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

BJH Adsorption Reports

Primary Data  
1093- The adsorbate property factor must be positive nonzero.  
1026- Calculations failed for BJH primary data.  
1093- The adsorbate property factor must be positive nonzero.  
1026- Calculations failed for BJH primary data.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

**BJH Desorption Reports**

1045- Fewer than 2 points available for BJH Desorption calculations.

UNIVERSITY OF JOHANNESBURG
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Analysis Adsorptive: CO2
Completed: 6/1/2016 2:28:35PM
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Sample Mass: 0.2533 g
Warm Free Space: 27.8481 cm³ Measured
Cold Free Space: 29.5250 cm³
Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C
Low Pressure Dose:  3.000 cm³/g STP
Automatic Degas: Yes

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM
Completed: 6/1/2016 2:28:35PM
Sample Mass: 0.2533 g
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.8481 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM  
Completed: 6/1/2016 2:28:35PM  
Sample Mass: 0.2533 g  
Cold Free Space: 29.5250 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8481 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports

Primary Data  
4073- The analysis gas (CO2) does not match the model gas (AR).  
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 747- Rowen UJ- KWV-14 Repeat 4  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\747.SMP

Started: 6/1/2016 6:37:18AM  
Completed: 6/1/2016 2:28:35PM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.8481 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose:  3.000 cm³/g STP

Sample Mass: 0.2533 g  
Cold Free Space: 29.5250 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

MP-Method Reports

Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Completed: 6/1/2016 2:28:35PM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2533 g  Warm Free Space: 27.8481 cm³ Measured
Cold Free Space: 29.5250 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Options Report

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
| **Sample:** 747- Rowen UJ- KWV-14 Repeat 4  | **Analysis Adsorptive:** CO2 |
| **Operator:** Gregory | **Analysis Bath Temp.:** 0.000 °C |
| **Submitter:** Rowen UJ | **Thermal Correction:** No |
| **File:** C:\2020\DATA\747.SMP | **Warm Free Space:** 27.8481 cm³ Measured |
| **Started:** 6/1/2016 6:37:18AM | **Equilibration Interval:** 60 s |
| **Completed:** 6/1/2016 2:28:35PM | **Low Pressure Dose:** 3.000 cm³/g STP |
| **Report Time:** 6/1/2016 2:28:35PM | |
| **Sample Mass:** 0.2533 g | |
| **Cold Free Space:** 29.5250 cm³ | |
| **Ambient Temperature:** 22.00 °C | |
| **Automatic Degas:** Yes | |

**Adsorptive Properties**

- **Adsorptive:** Carbon Dioxide @ 273.15 K
- **Maximum manifold pressure:** 925.00 mmHg
- **Non-ideality factor:** 0.0000000
- **Density conversion factor:** 0.0018306
- **Therm. tran. hard-sphere diameter:** 3.604 Å
- **Molecular cross-sectional area:** 0.170 nm²
- **Inside diameter of sample tube:** 9.53 mm
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Sample Mass: 0.2533 g
Warm Free Space: 27.8481 cm³ Measured
Cold Free Space: 29.5250 cm³
Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP

Sample Log Report

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/31/2016</td>
<td>2:14:36AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>5/31/2016</td>
<td>2:17:49AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>5/31/2016</td>
<td>2:26:57AM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>1:30:45AM</td>
<td>Started checking degas at 5 µmHg.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>1:30:58AM</td>
<td>Completed checking degas after 13 sec: outgas rate = 0.0 µmHg/min.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>1:32:34AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>1:34:47AM</td>
<td>Started temperature ramp at 5.0 °C/min to 30 °C.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>2:05:29AM</td>
<td>Started temperature hold at 30 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>6:34:34AM</td>
<td>Started backfilling.</td>
</tr>
<tr>
<td>6/1/2016</td>
<td>2:28:35PM</td>
<td>Analysis done.</td>
</tr>
</tbody>
</table>
Sample: 747- Rowen UJ- KWV-14 Repeat 4
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\747.SMP

Completed: 6/1/2016 2:28:35PM  Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2533 g  Warm Free Space: 27.8481 cm³ Measured
Cold Free Space: 29.5250 cm³  Equilibration Interval: 60 s
Ambient Temperature: 22.00 °C  Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.
Surface area: Passed
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Summary Report

Surface Area
Single point surface area at P/Po = 0.033554949: 8.6648 m²/g
BET Surface Area: -35.4514 m²/g
Langmuir Surface Area: -29.5777 m²/g

Horvath-Kawazoe
Maximum pore volume at P/Po = 0.033554949: 0.003593 cm³/g
Median pore width: 4.159 Å

Dubinin-Astakhov
Micropore surface area: 159.721880 m²/g
Limiting micropore volume: 0.110736 cm³/g
### Isotherm Tabular Report

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>02:31</td>
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<tr>
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Total: 26142.000000
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

Isotherm Linear Plot

Relative Pressure (P/Po)

Quantity Adsorbed (cm³/g STP)
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

Isotherm Log Plot

756- Rowen UJ KWV-15 Repeat - Adsorption
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

**BET Surface Area Report**

BET Surface Area: -35.4514 ± 8.4659 m²/g
Slope: -0.151773 ± 0.030766 g/cm³ STP
Y-Intercept: 0.022916 ± 0.000565 g/cm³ STP
C: -5.622992
Qm: -7.7605 cm³/g STP
Correlation Coefficient: -0.7493728
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>Relative Pressure (P/Po)</th>
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</table>
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Notes:

BET Surface Area Plot
Sample: 756- Rowen UJ KWV-15 Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM  

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6465 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2534 g  
Cold Free Space: 29.5536 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Notes:

**Langmuir Surface Area Report**

Langmuir Surface Area: -29.5777 ± 7.2611 m²/g

Slope: -0.154447 ± 0.037916 g/cm³ STP

Y-Intercept: 589.577514 ± 18.452742 mmHg·g/cm³ STP

b: -0.00262 1/mmHg

Qm: -6.4747 cm³/g STP

Correlation Coefficient: -0.736461

Molecular Cross-Sectional Area: 0.1700 nm²

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<th>P/Q (mmHg·g/cm³ STP)</th>
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Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Langmuir Surface Area Plot
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Freundlich Reports
Primary Data
4057- At least two data points are needed for Freundlich calculations.
Primary Data
4057- At least two data points are needed for Freundlich calculations.
**Sample:** 756- Rowen UJ KWV-15 Repeat  
**Operator:** Gregory  
**Submitter:** Rowen UJ  
**File:** C:\2020\DATA\756.SMP  

<table>
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<th>Analysis Adsorptive: CO2</th>
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<tbody>
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<td>Completed: 6/8/2016 3:39:45AM</td>
<td>Analysis Bath Temp.: 0.000 °C</td>
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**Sample Mass:** 0.2534 g  
**Warm Free Space:** 27.6465 cm³ Measured  
**Analysis Adsorptive:** CO2  
**Analysis Bath Temp.:** 0.000 °C  
**Completed:** 6/8/2016 3:39:45AM  
**Report Time:** 6/8/2016 3:39:46AM  
**Thermal Correction:** No  
**Sample Mass:** 0.2534 g  
**Warm Free Space:** 27.6465 cm³ Measured  
**Equilibration Interval:** 60 s  
**COLD FREE SPACE:** 29.5536 cm³  
**Ambient Temperature:** 22.00 °C  
**Low Pressure Dose:** 3.000 cm³/g STP  

**Notes:**

**Temkin Reports**

4058- At least two data points are needed for Temkin calculations.
**Primary Data**
4058- At least two data points are needed for Temkin calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

**t-Plot Reports**
4055- A positive BET surface area was not calculated.
4055- A positive BET surface area was not calculated.
4055- A positive BET surface area was not calculated.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Primary Data
A reference file has not been chosen.

f-Ratio Method
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

BJH Adsorption Reports
Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2534 g
Thermal Correction: No
Cold Free Space: 29.5536 cm³
Warm Free Space: 27.6465 cm³ Measured
Ambient Temperature: 22.00 °C
Equilibration Interval: 60 s
Automatic Degas: Yes
Low Pressure Dose: 3.000 cm³/g STP

Notes:

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

<table>
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<tr>
<th>Started:</th>
<th>6/7/2016 7:58:18PM</th>
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<tbody>
<tr>
<td>Sample Mass:</td>
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<tr>
<td>Cold Free Space:</td>
<td>29.5536 cm³</td>
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<td>Ambient Temperature:</td>
<td>22.00 °C</td>
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<td>Automatic Degas:</td>
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Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

D-H Desorption Reports

Primary Data
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Sample Mass: 0.2534 g
Thermal Correction: No
Cold Free Space: 29.5536 cm³
Warm Free Space: 27.6465 cm³ Measured
Ambient Temperature: 22.00 °C
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Notes:

DFT Surface Energy Reports

Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Cold Free Space: 29.5536 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.6465 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Notes:

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM
Sample Mass: 0.2534 g
Ambient Temperature: 22.00 °C

table:

- Sample: 756- Rowen UJ KWV-15 Repeat
- Operator: Gregory
- Submitter: Rowen UJ
- File: C:\2020\DATA\756.SMP
- Started: 6/7/2016 7:58:18PM
- Sample Mass: 0.2534 g
- Ambient Temperature: 22.00 °C

Notes:

- Analysis Adsorptive: CO2
- Analysis Bath Temp.: 0.000 °C
- Warm Free Space: 27.6465 cm³ Measured
- Equilibration Interval: 60 s
- Low Pressure Dose: 3.000 cm³/g STP

Options Report

Sample Tube
- Warm free space: 1.0000 cm³
- Cold free space: 1.0000 cm³
- Non-ideality factor: 0.0000620
- Use Isothermal Jacket: Yes
- Use Filler Rod: Yes
- Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
- Fast evacuation: No
- Unrestricted evacuation from: 30.0 mmHg
- Vacuum setpoint: 10 µmHg
- Evacuation time: 0.50 h
- Leak test: No
- Use TranSeal: No

Free Space
- Free-space type: Measured
- Lower dewar for evacuation: Yes
- Evacuation time: 1.00 h
- Outgas test: No

Po and Temperature
- Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
  - Po: 26142.000 mmHg
  - Temperature: 0.000 °C
  - Ambient temperature: 22.00 °C

Dosing
- Use first pressure fixed dose: No
- Use maximum volume increment: No
- Target tolerance: 5.0% or 5.000 mmHg
- Low pressure dosing: Yes
- Dose amount: 3.0000 cm³/g STP
- Minimum equilibration delay: 0.00 h
- Maximum equilibration delay: 999.00 h

Equilibration
- Equilibration time (P/Po = 1.000000000): 60 s
- Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
- Backfill at start of analysis: Yes
- Backfill at end of analysis: Yes
Sample: 756- Rowen UJ KWV-15 Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM  

Sample Mass: 0.2534 g  
Cold Free Space: 29.5536 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6465 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Notes:

Sample Backfill  
Backfill gas: CO2  

Adsorptive Properties  
Adsorptive: Carbon Dioxide @ 273.15 K  
Maximum manifold pressure: 925.00 mmHg  
Non-ideality factor: 0.0000000  
Density conversion factor: 0.0018306  
Therm. tran. hard-sphere diameter: 3.604 Å  
Molecular cross-sectional area: 0.170 nm²  
Inside diameter of sample tube: 9.53 mm
Sample: 756- Rowen UJ KWV-15 Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\756.SMP

Sample Log Report

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
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<tbody>
<tr>
<td>6/5/2016</td>
<td>7:19:43AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>7:22:14AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>7:31:33AM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>7:34:03AM</td>
<td>Degas operation done.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>7:54:54AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>8:29:19AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>8:31:20AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
</tr>
<tr>
<td>6/5/2016</td>
<td>8:39:42AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
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<td>6/5/2016</td>
<td>8:41:50AM</td>
<td>Started temperature ramp at 5.0 °C/min to 75 °C.</td>
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<tr>
<td>6/5/2016</td>
<td>8:49:26AM</td>
<td>Started temperature hold at 75 °C for 1440 minutes.</td>
</tr>
<tr>
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<td>1:40:26AM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
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<td>Started temperature ramp at 5.0 °C/min to 30 °C.</td>
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<td>6/7/2016</td>
<td>2:14:26AM</td>
<td>Started cool-down wait.</td>
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<tr>
<td>6/7/2016</td>
<td>7:58:19PM</td>
<td>Analysis started.</td>
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</table>
Sample: 756- Rowen UJ KWV-15 Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\756.SMP

Started: 6/7/2016 7:58:18PM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.6465 cm³ Measured 
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2534 g  
Cold Free Space: 29.5536 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Notes:

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.

Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: C value is low. Select a new range, removing some of the higher pressure points.

Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.

Surface area: Review the isotherm. Negative surface area is the result of an inaccurate isotherm.

Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Summary Report

Dubinin-Radushkevich
Micropore surface area: 23.447679 m²/g
Monolayer capacity: 5.132837 cm³/g
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Report Time: 5/31/2016 10:52:58PM
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Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Tabular Report

<table>
<thead>
<tr>
<th>Relative Pressure (P/Po)</th>
<th>Absolute Pressure (mmHg)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Elapsed Time (h:min)</th>
<th>Saturation Pressure (mmHg)</th>
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<tbody>
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<tr>
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26142.000000
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

 Started: 5/30/2016 11:51:25PM
 Completed: 5/31/2016 7:31:30AM
 Report Time: 5/31/2016 10:52:58PM
 Sample Mass: 0.2562 g
 Cold Free Space: 29.7419 cm³
 Ambient Temperature: 22.00 °C
 Automatic Degas: Yes

 Analysis Adsorptive: CO2
 Analysis Bath Temp.: 0.000 °C
 Thermal Correction: No
 Warm Free Space: 27.9493 cm³ Measured
 Equilibration Interval: 60 s
 Low Pressure Dose: 3.000 cm³/g STP

 Isotherm Linear Plot

 --- 744- Rowen UJ KWV-16 CO2 ads Repeat - Adsorption
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
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Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Isotherm Log Plot

744- Rowen UJ KWV-16 CO2 ads Repeat - Adsorption
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
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Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BET Surface Area Report
BET Surface Area: 37.5325 ± 8.3885 m²/g
Slope: 0.110771 ± 0.027198 g/cm³ STP
Y-Intercept: 0.010942 ± 0.000499 g/cm³ STP
C: 11.123621
Qm: 8.2161 cm³/g STP
Correlation Coefficient: 0.6827147
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>Quantity Adsorbed (cm³/g STP)</th>
<th>1/[Q(Po/P - 1)]</th>
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Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

BET Surface Area Plot
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes
Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

**Langmuir Surface Area Report**

Langmuir Surface Area: 42.3891 ± 12.9052 m²/g
Slope: 0.107768 ± 0.032809 g/cm³ STP
Y-Intercept: 278.175837 ± 15.913601 mmHg·g/cm³ STP
b: 0.000387 1/mmHg
Qm: 9.2792 cm³/g STP
Correlation Coefficient: 0.659721
Molecular Cross-Sectional Area: 0.1700 nm²

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<th>Quantity Adsorbed (cm³/g STP)</th>
<th>P/Q (mmHg·g/cm³ STP)</th>
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Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

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Report Time: 5/31/2016 10:52:58PM

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

- 744- Rowen UJ KWV-16 CO2 ads Repeat

Langmuir Surface Area Plot

P/Q (mmHg·g/cm³ STP)

Pressure (mmHg)
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

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Low Pressure Dose: 3.000 cm³/g STP

Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Freundlich Reports

Primary Data
4057- At least two data points are needed for Freundlich calculations.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
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Ambient Temperature: 22.00 °C
Low Pressure Dose: 3.000 cm³/g STP
Automatic Degas: Yes

Temkin Reports
Primary Data
4058- At least two data points are needed for Temkin calculations.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

---

4054- Fewer than two data points are inside the fitted thickness range.
4055- Fewer than two data points are inside the fitted thickness range.

---

334
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose:  3.000 cm³/g STP

Alpha-S Method

Primary Data
4029- At least two fitted data points are needed for Alpha-S calculations.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

f-Ratio Method
Primary Data
A reference file has not been chosen.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Adsorption Reports
Primary Data
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
1093- The adsorbate property factor must be positive nonzero.
1026- Calculations failed for BJH primary data.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

BJH Desorption Reports
Primary Data
1045- Fewer than 2 points available for BJH Desorption calculations.
1045- Fewer than 2 points available for BJH Desorption calculations.
Sample: 744- Rowen UJ KJV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
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<tr>
<td>Started:</td>
<td>5/30/2016 11:51:25PM</td>
</tr>
<tr>
<td>Completed:</td>
<td>5/31/2016 7:31:30AM</td>
</tr>
<tr>
<td>Report Time:</td>
<td>5/31/2016 10:52:58PM</td>
</tr>
<tr>
<td>Sample Mass:</td>
<td>0.2562 g</td>
</tr>
<tr>
<td>Cold Free Space:</td>
<td>29.7419 cm³</td>
</tr>
<tr>
<td>Ambient Temperature:</td>
<td>22.00 °C</td>
</tr>
<tr>
<td>Automatic Degas:</td>
<td>Yes</td>
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<tr>
<td>Analysis Adsorptive:</td>
<td>CO2</td>
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<tr>
<td>Analysis Bath Temp.:</td>
<td>0.000 °C</td>
</tr>
<tr>
<td>Thermal Correction:</td>
<td>No</td>
</tr>
<tr>
<td>Warm Free Space:</td>
<td>27.9493 cm³ Measured</td>
</tr>
<tr>
<td>Equilibration Interval:</td>
<td>60 s</td>
</tr>
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<td>Low Pressure Dose:</td>
<td>3.000 cm³/g STP</td>
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</tbody>
</table>

D-H Adsorption Reports

Primary Data
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
1043- Fewer than 2 points available for Dollimore-Heal Adsorption calculations.
**Sample:** 744- Rowen UJ KWV-16 CO2 ads Repeat  
**Operator:** Gregory  
**Submitter:** Rowen UJ  
**File:** C:\2020\DATA\744.SMP

<table>
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<tr>
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<th></th>
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<tbody>
<tr>
<td>Completed: 5/31/2016 7:31:30AM</td>
<td>Analysis Bath Temp.: 0.000 °C</td>
</tr>
<tr>
<td>Report Time: 5/31/2016 10:52:58PM</td>
<td>Thermal Correction: No</td>
</tr>
<tr>
<td>Sample Mass: 0.2562 g</td>
<td>Warm Free Space: 27.9493 cm³ Measured</td>
</tr>
<tr>
<td>Cold Free Space: 29.7419 cm³</td>
<td>Equilibration Interval: 60 s</td>
</tr>
<tr>
<td>Ambient Temperature: 22.00 °C</td>
<td>Low Pressure Dose: 3.000 cm³/g STP</td>
</tr>
<tr>
<td>Automatic Degas: Yes</td>
<td></td>
</tr>
</tbody>
</table>

---

**D-H Desorption Reports**

Primary Data  
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.  
1045- Fewer than 2 points available for Dollimore-Heal Desorption calculations.
Sample: 744- Rowen UJ KKW-16 CO2 ads Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM  
Completed: 5/31/2016 7:31:30AM  
Report Time: 5/31/2016 10:52:58PM  
Sample Mass: 0.2562 g  
Cold Free Space: 29.7419 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.9493 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

### Horvath-Kawazoe Report

Slit Pore Geometry (Original H-K)  
Maximum Pore Volume: 0.004632 cm³/g  
at Relative Pressure: 0.032986429  
Median Pore Width: 4.470 Å  
Relative Pressure Range: 6.935e-04 to 3.299e-02  
Diameter of Adsorptive Molecule: 3.230 Å  
Diameter of Adsorptive at Zero Interaction Energy: 2.770 Å  
Diameter of Sample Atom: 3.040 Å  
Diameter of Sample Atom at Zero Interaction Energy: 2.609 Å  
Interaction Parameter: 3.49e-43 erg·cm⁴  
Density Conversion Factor: 0.0018306

<table>
<thead>
<tr>
<th>Absolute Pressure (mmHg)</th>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Pore Width (Å)</th>
<th>Cumulative Pore Volume (cm³/g)</th>
<th>Differential Pore Volume (cm³/g·Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.12841</td>
<td>0.000693459</td>
<td>0.09294</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
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<td>0.000</td>
<td>0.000</td>
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<tr>
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<td>0.30560</td>
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<td>0.0006</td>
<td>0.0002</td>
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<tr>
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<td>1.17083</td>
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</table>
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Horvath-Kawazoe Cumulative Pore Volume Plot
Slit Pore Geometry (Original H-K)
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:58PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Horvath-Kawazoe Differential Pore Volume Plot
Slit Pore Geometry (Original H-K)
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

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Sample Mass: 0.2562 g
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Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

DFT Surface Energy Reports
Primary Data
4073- The analysis gas (CO2) does not match the model gas (AR).
4074- The analysis temperature (0.000 °C) does not match the model temperature (-185.850 °C).
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM  
Completed: 5/31/2016 7:31:30AM  
Report Time: 5/31/2016 10:52:58PM  
Sample Mass: 0.2562 g  
Cold Free Space: 29.7419 cm³  
Ambient Temperature: 22.00 °C  
Automatic Degas: Yes

Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.9493 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

### Dubinin-Radushkevich Tabular Report

<table>
<thead>
<tr>
<th>Absolute Pressure (mmHg)</th>
<th>Relative Pressure (P/Po)</th>
<th>Quantity Adsorbed (cm³/g STP)</th>
<th>Log Quantity Adsorbed</th>
<th>Log (Po/P)^2.0000</th>
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<tbody>
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</table>
Sample: 744- Rowen UJ KWV-16 CO₂ ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO₂
Analysis Bath Temp.: 0.000 °C
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Dubinin-Radushkevich Transformed Isotherm Plot

**Fitted Points**
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 10:52:59PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
 Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
 Thermal Correction: No
 Warm Free Space: 27.9493 cm³ Measured
 Equilibration Interval: 60 s
 Low Pressure Dose: 3.000 cm³/g STP

MP-Method Reports
Primary Data
4059- Fewer than 2 points available for MP-Method calculations.
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:59PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Options Report

Sample Tube
Warm free space: 1.0000 cm³
Cold free space: 1.0000 cm³
Non-ideality factor: 0.0000620
Use Isothermal Jacket: Yes
Use Filler Rod: Yes
Vacuum seal type: Seal Frit

Analysis Conditions

Preparation
Fast evacuation: No
Unrestricted evacuation from: 30.0 mmHg
Vacuum setpoint: 10 µmHg
Evacuation time: 0.50 h
Leak test: No
Use TranSeal: No

Free Space
Free-space type: Measured
Lower dewar for evacuation: Yes
Evacuation time: 1.00 h
Outgas test: No

Po and Temperature
Po and T type: Enter Po below. Enter the Analysis Bath Temperature below.
Po: 26142.000 mmHg
Temperature: 0.000 °C
Ambient temperature: 22.00 °C

Dosing
Use first pressure fixed dose: No
Use maximum volume increment: No
Target tolerance: 5.0% or 5.000 mmHg
Low pressure dosing: Yes
Dose amount: 3.0000 cm³/g STP
Minimum equilibration delay: 0.00 h
Maximum equilibration delay: 999.00 h

Equilibration
Equilibration time (P/Po = 1.000000000): 60 s
Minimum equilibration delay at P/Po >= 0.995: 600 s

Sample Backfill
Backfill at start of analysis: Yes
Backfill at end of analysis: Yes
Backfill gas: CO2
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:59PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Adsorptive Properties
Adsorptive: Carbon Dioxide @ 273.15 K
Maximum manifold pressure: 925.00 mmHg
Non-ideality factor: 0.0000000
Density conversion factor: 0.0018306
Therm. tran. hard-sphere diameter: 3.604 Å
Molecular cross-sectional area: 0.170 nm²
Inside diameter of sample tube: 9.53 mm
Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat  
Operator: Gregory  
Submitter: Rowen UJ  
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM  
Completed: 5/31/2016 7:31:30AM  
Report Time: 5/31/2016 10:52:59PM  
Analysis Adsorptive: CO2  
Analysis Bath Temp.: 0.000 °C  
Thermal Correction: No  
Warm Free Space: 27.9493 cm³ Measured  
Equilibration Interval: 60 s  
Low Pressure Dose: 3.000 cm³/g STP

<table>
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<tr>
<th>Date</th>
<th>Time</th>
<th>Message</th>
</tr>
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<tbody>
<tr>
<td>5/30/2016</td>
<td>4:18:04PM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
</tr>
<tr>
<td>5/30/2016</td>
<td>4:18:13PM</td>
<td>Operation skipped.</td>
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<tr>
<td>5/30/2016</td>
<td>4:19:00PM</td>
<td>Degas operation started on Unit 1 - S/N: 715, port 2.</td>
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<tr>
<td>5/30/2016</td>
<td>4:19:00PM</td>
<td>Started evacuation at 10.0 mmHg/s to 300 µmHg, hold for 0 minutes.</td>
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<tr>
<td>5/30/2016</td>
<td>4:23:25PM</td>
<td>Started temperature ramp at 5.0 °C/min to 30 °C.</td>
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<tr>
<td>5/30/2016</td>
<td>4:23:26PM</td>
<td>Started temperature hold at 30 °C for 1440 minutes.</td>
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<tr>
<td>5/31/2016</td>
<td>7:31:30AM</td>
<td>Analysis done.</td>
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Sample: 744- Rowen UJ KWV-16 CO2 ads Repeat
Operator: Gregory
Submitter: Rowen UJ
File: C:\2020\DATA\744.SMP

Started: 5/30/2016 11:51:25PM
Completed: 5/31/2016 7:31:30AM
Report Time: 5/31/2016 10:52:59PM
Sample Mass: 0.2562 g
Cold Free Space: 29.7419 cm³
Ambient Temperature: 22.00 °C
Automatic Degas: Yes

Analysis Adsorptive: CO2
Analysis Bath Temp.: 0.000 °C
Thermal Correction: No
Warm Free Space: 27.9493 cm³ Measured
Equilibration Interval: 60 s
Low Pressure Dose: 3.000 cm³/g STP

Validation Report

Isotherm Reports
Free Space: Low free space values may be observed when using liquid argon or ice baths.
Po: Passed
Pressure/Volume Adsorbed: Passed

BET Reports
C Value: Passed
Correlation Coefficient: Review the BET plot and see if the correct range has been selected for calculating surface area.
Surface area: Passed
Pressure Range: The selected BET relative pressure range is outside the recommended values of 0.05 to 0.30.
APPENDIX C:

HPVA RESULTS
APPENDIX C.1:

HPVA Results as Received from ISGS Laboratory
As Received data from ISGS

The initial data points were collected every hour as this was done on a weekend. There is a four hour gap in the pressure data on the last day in the data logging stopped overnight. The change in pressure at 16000 kPa was due to a mistake in filling the piston. There is a ~4 hour gap in the pressure data on the last day in the data logging stopped overnight. The change in pressure at 18000 kPa was due to a mistake in filling the piston. There is a ~4 hour gap in the pressure data on the last day in the data logging stopped overnight. The change in pressure at 18000 kPa was due to a mistake in filling the piston.

Volume check. This ends the volume check for the 15000-5000 kPa data points. After this we refilled the cylinder to reach the 18000-16000 data points and let it equilibrate overnight.

Volume check. This ends the volume check for the 15000-5000 kPa data points. After this we refilled the cylinder to reach the 18000-16000 data points and let it equilibrate overnight.

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Volume check. This ends the volume check for the 15000-5000 kPa data points. After this we refilled the cylinder to reach the 18000-16000 data points and let it equilibrate overnight.
APPENDIX C.2:

HPVA ADSORPTION
CALCULATIONS 1ST RUN
Excess Adsorption Calculations for First Run Samples

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<tr>
<th>Pressure (MPa):</th>
<th>CO2 Density:</th>
<th>Adsorbed Mass (g):</th>
<th>Adsorption (mol/g) assuming STP molar volume</th>
<th>Mass Adsorbed/Mass of Sample</th>
<th>Excess adsorption (g)</th>
<th>Excess Adsorption (mol)</th>
<th>Excess adsorption in mol/g Sample Mass (g)</th>
<th>Sample Mass (g)</th>
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<td>Adsorbed Mass (g):</td>
<td>Adsorption (mol/g) assuming STP molar volume</td>
<td>Mass Adsorbed/Mass of Sample</td>
<td>Excess adsorption (g)</td>
<td>Excess Adsorption (mol)</td>
<td>Excess adsorption in mol/g Sample Mass (g)</td>
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<td>CO2 Density:</td>
<td>Adsorbed Mass (g): assuming STP molar volume</td>
<td>Mass Adsorbed/Mass of Sample</td>
<td>Excess adsorption (g)</td>
<td>Excess Adsorption (mol)</td>
<td>Excess adsorption in mol/g Sample Mass (g)</td>
<td>Sample Mass (g)</td>
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<td>0.001 Sample Density</td>
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APPENDIX C.3:

HPVA ADSORPTION CALCULATIONS 2ND RUN
Excess Adsorption Calculations for Retested Samples
KWV-1

Pressure
(MPa):
2
4
6
8
10
12
14
16
18

Adsorbed
CO2 Density: Mass (g):
0.040374443
-0.368
0.078671808
0.251
0.137999938
0.223
0.272713133
84.872
0.550209676
48.606
0.677214107
32.008
0.731747889
24.881
0.768023022
20.140
0.789247615
17.367

Adsorption
(mol/g)
assuming STP
molar volume
-0.008
0.006
0.005
1.928
1.104
0.727
0.565
0.458
0.395

Mass
Adsorbed/M
Excess
Excess
ass of
Excess
Adsorption
adsorption in
Sample
adsorption (g) (mol)
mol/g
Sample Mass (g)
-0.523
-0.363
-0.008
-0.012
0.7046
0.356
0.244
0.006
0.008 Sample Density
0.316
0.211
0.005
0.007
2.703190389
120.454
76.310
1.734
2.461
68.984
38.713
0.880
1.248
45.427
23.989
0.545
0.774
35.313
18.146
0.412
0.585
28.584
14.418
0.328
0.465
24.647
12.296
0.279
0.397
KWV-2

Pressure
(MPa):
2
4
6
8
10
12
14
16
18

Adsorbed
CO2 Density: Mass (g):
0.032394655
0.233
0.088996915
-0.036
0.134470677
0.771
0.28182498
33.282
0.570565084
18.905
0.680712445
8.997
0.73387002
5.050
0.7603355
4.602
0.7892476
1.937

Adsorption
(mol/g)
assuming STP
molar volume
0.005
-0.001
0.018
0.756
0.430
0.204
0.115
0.105
0.044

Mass
Adsorbed/M
Excess
Excess
ass of
Excess
Adsorption
adsorption in
Sample
adsorption (g) (mol)
mol/g
Sample Mass (g)
0.349
0.230
0.005
0.008
0.6671
-0.055
-0.035
-0.001
-0.001 Sample Density
1.156
0.732
0.017
0.025
2.658295863
49.891
29.754
0.676
1.013
28.339
14.847
0.337
0.506
13.486
6.693
0.152
0.228
7.569
3.656
0.083
0.125
6.898
3.285
0.075
0.112
2.904
1.362
0.031
0.046
KWV-13

Pressure
(MPa):
2
4
6
8
10
12
14
16
18

Adsorbed
CO2 Density: Mass (g):
0.041559474
-0.618
0.080233115
-0.604
0.140010897
3.555
0.272801537
-11.656
0.559053903
0.390
0.674073676
0.071
0.732516571
0.529
0.769242888
1.321
0.791643933
2.141

Adsorption
(mol/g)
assuming STP
molar volume
-0.014
-0.014
0.081
-0.265
0.009
0.002
0.012
0.030
0.049

Mass
Adsorbed/M
Excess
Excess
ass of
Excess
Adsorption
adsorption in
Sample
adsorption (g) (mol)
mol/g
Sample Mass (g)
-0.702
-0.610
-0.014
-0.016
0.8806
-0.685
-0.588
-0.013
-0.015 Sample Density
4.037
3.396
0.077
0.088
3.141557553
-13.236
-10.644
-0.242
-0.275
0.443
0.320
0.007
0.008
0.080
0.056
0.001
0.001
0.600
0.405
0.009
0.010
1.500
0.997
0.023
0.026
2.431
1.601
0.036
0.041
KWV-16

Pressure
(MPa):
2
4
6
8
10
12
14
16
18

Adsorbed
CO2 Density: Mass (g):
0.040089498
-0.281
0.09303167
0.904
0.16002082
-1.471
0.289140236
5.693
0.574448026
5.758
0.683094378
3.420
0.735600946
2.814
0.763090901
2.785
0.790573487
1.969

Adsorption
(mol/g)
assuming STP
molar volume
-0.006
0.021
-0.033
0.129
0.131
0.078
0.064
0.063
0.045

Mass
Adsorbed/M
Excess
Excess
ass of
Excess
Adsorption
adsorption in
Sample
adsorption (g) (mol)
mol/g
Sample Mass (g)
-0.326
-0.278
-0.006
-0.007
0.8622
1.049
0.876
0.020
0.023 Sample Density
-1.706
-1.392
-0.032
-0.037
3.012676131
6.603
5.147
0.117
0.136
6.678
4.660
0.106
0.123
3.967
2.645
0.060
0.070
3.263
2.127
0.048
0.056
3.230
2.079
0.047
0.055
2.283
1.452
0.033
0.038

365

