Development of high temperature CO$_2$ sorbents using solid wastes from power generation

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ABSTRACT

One of various ways to curb anthropogenic carbon dioxide (CO₂) emissions is by using Li₄SiO₄ sorbents to capture CO₂, which have shown high CO₂ uptake capacities (up to 367 mg CO₂/g sorbent) at high temperatures (400 to 600 °C). In this study, solid wastes from coal- and biomass-fired boilers that contain high amounts (>47 wt%) of silica were used as precursors in the development of Li₄SiO₄-based high temperature CO₂ sorbents via solid state (SS) and suspended impregnation (SI) methods. Thermogravimetric analyses (TGA) carried out in pure CO₂ environment at sorption temperatures of 500 to 700 °C showed the waste-derived Li₄SiO₄ sorbents have high CO₂ sorption capacities (up to 263 mg CO₂/g sorbent at 700 °C). This study also experimented for the first time the potential of palm oil mill boiler ash (POMBA) as a waste-derived Li₄SiO₄ sorbent precursor. It was found that POMBA-derived sorbents showed high CO₂ sorption capacities (up to 257 mg CO₂/g sorbent at 700 °C in pure CO₂ environment). These waste-derived Li₄SiO₄ sorbents exhibited CO₂ sorption capacities exceeding some of those in published work (27 mg CO₂/g sorbent). Furthermore, this study analysed the effect of excess lithium on waste-derived sorbents. It was found that depending on the materials used, the amount of excess lithium added during the preparation step affected CO₂ sorption performance of the waste-derived sorbents.
Dedication

In the Name of Allah, the Most Merciful, the Most Compassionate. All praise be to Allah, the Lord of the worlds. Prayers and peace be upon Muhammad, His servant and messenger.

There is none worthy of my highest gratitude other than The Creator. The All Knowing, The Wise, The Guide, Infallible Teacher and Knower. All praises due to Him and only Him, The Self-Existing One upon Whom all others depend. For without Him, there would be no knowledge. For without His guidance, all hope was lost.

The most honourable leader ever existed, Muhammad (may peace be upon him), whom has lead and will continue to lead this Ummah by the best of examples until The End of Time.

A deep debt of gratitude to my supervisor and an inspiring role model, Professor Mercedes Maroto-Valer, for her priceless support in research. To everybody in CICCS, I say thank you for fruitful discussions and collaborations, and also all the good laughs. Not to forget the technicians and staff at Heriot-Watt University for the assistance in times of need.

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Lastly but not by any means the least, to friends. You know who you are.
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LIST OF PUBLICATIONS


3. Ramli I., Maroto-Valer M. M., Palm oil mill boiler ash as high temperature CO₂ sorbent. (Draft to be submitted)
Chapter 1 Introduction

1.1. Background literature

Carbon dioxide capture and storage (CCS) is a technological option to reduce anthropogenic carbon dioxide (CO$_2$) emissions and thus, stabilising atmospheric CO$_2$ concentration (IPCC, 2005). Under the concept of CCS, CO$_2$ is captured from large point sources like coal-fired power plants and subsequently transported and sequestered in geologic formations such as depleted oil and gas fields, saline formations and unmineable coal seams (Figueroa et al., 2008; Klara et al., 2003).

The capture of CO$_2$ can be accomplished by three different routes, namely post-combustion, pre-combustion and oxy-combustion (Figueroa et al., 2008). Post-combustion separates CO$_2$ from flue gases and can occur anywhere along the flue gas processing stream from combustor to effluent exhaust, where the CO$_2$ concentration is normally between 3 to 15 vol%. The pre-combustion route involves CO$_2$ capture after the gasification process and prior to the combustion step (IPCC, 2001). In oxy-combustion, pure oxygen substitutes air as combustion gas producing a stream concentrated with CO$_2$ and H$_2$O (GCEP, 2005).

Although CCS provides promising technologies to curb anthropogenic CO$_2$ emissions, it is not without challenges. The CO$_2$ capture step contributes to a large portion of the total cost of the CCS chain. The large capture costs are due to the capture materials as well as capital and operational costs of the capture process.
itself (IEA, 2004). Consequently, high energy efficiency penalty related to CO₂ capture is one of the biggest challenges for implementing CCS. For example, average net energy efficiency penalty related to CO₂ capture for pulverised coal-fired power plants when a post-combustion amine-based system is applied was reported to be approximately 10 percentage points, which translates to 74% increase in costs without capture. The high energy penalty is mostly caused by the solvent regeneration and CO₂ compression process (IEA, 2011).

Solid sorbents have become an increasingly popular area of research, although liquid sorbents are considered as the most mature CO₂ capture technology, going back to the capture of CO₂ for enhanced oil recovery (EOR) operations in the 1970s (Rao and Rubin, 2002). However, liquid solvents like monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) have been found to have problems of scaling and performance stability (Munoz et al., 2009). Furthermore, liquid solvents are prone to degradation and oxidation resulting in products that are corrosive and may require hazardous material handling procedures (Islam et al., 2011). These problems can be resolved using solid sorbents. Additionally, the energy required for regeneration and moving liquid solvents could be reduced with solid sorbents, if high (more than 132 mg CO₂/g sorbent) CO₂ uptake capacity of the sorbent is achieved (Gray et al., 2008). Furthermore, solid sorbents produce no liquid wastes and offer much wider temperature range applications between 25 and 700 °C (Choi et al., 2009; Olivares-Marín & Maroto-Valer, 2012).
Among the solid sorbents studied thus far, alkaline earth metal oxides such as Li$_4$SiO$_4$ have been known to have high CO$_2$ sorption capacity (up to 367 mg CO$_2$/g sorbent). Due to the high CO$_2$ uptake capacity of these sorbents, solid wastes have been proposed as silica sources for lithium-based sorbents in an effort to lower the production cost of the solid sorbents. Additionally, the use of solid wastes as precursors for CO$_2$ capture sorbents provides a good strategy to solid waste management, as these types of waste materials are known to have environmental and health concerns as most of them ended up in landfills in huge ash lagoons or dumped into the sea (Wang et al., 2008; Blisette and Rowson, 2012).

1.2. Knowledge gaps for high temperature CO$_2$ sorbents

Despite the increasing number of on-going research on solid sorbents, there are very limited studies on solid waste materials as precursors for high temperature sorbents. Most of the solid sorbents studied thus far are that of pure sorbents including lithium-based Li$_4$SiO$_4$ (Kato et al., 2005; Ida and Lin, 2005; Yamaguchi et al., 2007). The preparation of these pure solid sorbents is costly due to the use of high purity starting materials such as Li$_2$CO$_3$. Subsequently, this increases the overall cost of capture materials which then contributes significantly to the bulk of the total cost of the CCS chain. By utilising waste materials as precursors for high temperature sorbents, the capture cost could potentially be reduced and at the same time providing an alternative to landfilling.
Improving the CO₂ uptake capacity of high temperature sorbents is an intensive area of research. Even more so, CO₂ uptake capacity of waste-derived sorbents also needs to be further enhanced as the capacity is usually less than that of pure sorbents. Therefore, there is a strong need to investigate different waste materials that could be developed into high temperature CO₂ sorbents. As a general guide, the CO₂ uptake capacity of waste-derived high temperature solid sorbents needs to at least correspond to the commercially available solvents e.g. MEA (176 mg CO₂/g sorbent).

Despite various studies on pure Li₄SiO₄ sorbents, there are limited studies on the development of high temperature Li₄SiO₄ sorbents derived from low-cost solid wastes. These solid wastes have thus far included coal-derived and biomass-derived waste materials, such as pulverised fuel ash and rice husk ash, respectively (Olivares-Marin et al., 2010; Wang et al., 2011). For example, Olivares-Marin et al. (2010) investigated Colombian and Russian coals derived fly ashes that was obtained from coal-fired power plants, while Wang et al. (2011) used ashes deriving from rice husks that was obtained from a rice mill in Wuhan, China (Olivares-Marin et al., 2010; Wang et al., 2011).

Another potential material to be developed as CO₂ sorbents is palm oil mill boiler ash (POMBA). POMBA is a by-product of combustion process in a self-sustainable mill plants, also posed similar environmental and health concerns as other known solid wastes. This material has not been known to be used for producing CO₂ sorbents. In addition, the potential of POMBA as a precursor for high temperature
sorbents has not been reported. Many published studies on biomass-derived sorbents such as oil palm solid waste, durian shell and olive stones are that of low sorption temperatures ranging from 25 to 100 °C (Nasri et al., 2013; Chandra et al., 2009; Roman et al., 2008).

Consequently, studies on effect of CO₂ concentrations, sorption temperature and regeneration of waste-derived Li₄SiO₄ sorbents on the CO₂ uptake are needed to understand the performance of proposed waste-derived sorbents. Previous works reported that these are some of the crucial parameters in determining the performance of CO₂ sorbents. For example, Essaki et al. (2005) reported significant changes in the CO₂ uptake capacity of pure Li₄SiO₄ sorbents in a 15% (280 mg CO₂/g sorbent) compared to a 5% CO₂ (30 mg CO₂/g sorbent) sorption environment (Essaki et al., 2005).

1.3. Research aim and objectives

The aim of this study is to develop high temperature CO₂ sorbents using solid wastes from power generation plants. The materials of interest are hypothesised to be suitable for CO₂ capture at high (500, 600 and 700 °C) sorption temperatures, depending on their chemical and physical characterisation properties. Different methods of synthesising the sorbents and regenerability of the sorbents are hypothesised to affect the sorption capacity. The following research objectives were established to address the hypotheses of this study:
1. To assess the suitability of the materials of interest into solid sorbents by performing chemical and physical characterisations.

2. To synthesise sorbents with CO$_2$ uptake capacities of at least 100 mg CO$_2$/g sorbent for waste-derived Li$_4$SiO$_4$ sorbents at high temperatures via chemical impregnation method.

3. To investigate the influence of different sorption temperatures (500, 600, 700 °C) on CO$_2$ sorption capacity of the sorbents.

4. To study CO$_2$ sorption by sorbents under diluted CO$_2$ environment.

5. To examine the regeneration performance of synthesised sorbents.

In order to address Objective 1, a series of characterisation analyses including particle size distribution, x-ray diffraction, nitrogen adsorption/desorption isotherm and surface area, x-ray fluorescent, scanning electron microscope and fourier transform infrared were carried out on a series of waste materials and their corresponding prepared Li$_4$SiO$_4$ sorbents. The characteristics of waste materials and synthesised sorbents are described in Chapter 4 of this thesis. To address Objective 2, waste materials were subjected to solid state impregnation method. Upon synthesis, the resulting waste-derived sorbents were subjected to thermogravimetric (TG) analysis to determine their CO$_2$ uptake capacities.

To address Objectives 3, 4 and 5, synthesised sorbents were subjected to thermogravimetric analysis under controlled sorption conditions and the subsequent experimental data are discussed in Chapter 5. Chapter 2 discusses the background to this study, including reviews of relevant published works that have
influenced this study. Finally, Chapter 6 concludes the discussions in previous chapters and provides recommendations for future work. There is also a list of references cited at the end of this thesis.
Chapter 2 Literature review

In this chapter, global CO₂ emissions and mitigation strategies, especially for carbon dioxide capture and storage (CCS), are introduced in Section 2.1 and 2.2, respectively. Next, published work on CO₂ capture by solid sorbents is reviewed in Section 2.3. Finally, a review on CO₂ capture by industrial waste materials is presented in Section 2.4.

2.1. CO₂ emissions and mitigation strategies

2.1.1. Global CO₂ emissions

Records have shown that world energy consumption has been escalating since the beginning of 19th century Industrial Revolution (WEC, 2003). In the years between 1971 and 2011, total world energy consumption increased almost two times. The U.S. Energy Information Administration (EIA) has forecasted an increase in world energy consumption of more than 155% from 2010 to 2040 (EIA, 2013). This has caused increasing fossil fuel burning which consequently increases anthropogenic greenhouse gases (GHG), particularly carbon dioxide (CO₂). As a consequence, in 2011, CO₂ emissions to the atmosphere have increased by 40% of those pre-industrial levels (IPCC, 2013).

CO₂ has been identified as the main contributor of anthropogenic GHG emissions, representing about 76% of the total global GHG emission in 2010 (Ecofys, 2013).
In the UK, 82% of the total GHG emission were CO$_2$ in 2012 (DECC, 2014). Anthropogenic CO$_2$ is mainly released into the atmosphere by combustion of fossil fuel such as coal, oil and natural gas, as well as renewable energy sources like biomass; as well as deforestation activities including burning of trees for land clearance; and also industrial and resource extraction processes (IPCC, 2005).

Figure 2.1 shows the increasing CO$_2$ atmospheric concentrations, particularly after the Industrial Revolution. The concentrations were based on the analysis of ice cores obtained from 1987 to 1993 and logged atmospheric CO$_2$ concentrations from 1958 until 2014 (Etheridge et al., 1998; Scripps, 2014). Figure 2.1a shows that CO$_2$ concentrations have never exceeded 280 ppmv for more than 800 years until around 1900, where the concentrations reached 300 ppmv and have been increasing continuously since then at an increasing rate (Figure 2.1b) (Keeling and Whorf, 2005). Constant increase in global energy demanded raised fossil fuel burning to meet this demand and also caused a significant impact on CO$_2$ atmospheric concentrations. In addition, the U.S. National Oceanic and Atmospheric Administration reported that CO$_2$ atmospheric concentration reached 400 ppm on May 2013 for the first time since measurements began in 1958 in Mauna Loa (NOAA, 2013).
Increase in GHG emission is being acknowledged as the main contributor to climate change which is estimated to continue throughout this 21st century (IPCC, 2005; IPCC, 2007). Climate change disturbs balanced nature of the Earth, including elevated global average surface temperature, rising global average sea levels and
extraordinary melting of the ice caps (IPCC, 2007). A significant example of climate change impact can be clearly seen by the rapid melting of the Chacaltaya Glacier in Bolivia, where the initial 0.22 km$^2$ of glacier in 1940 was quickly reduced to 0.01 km$^2$ in 2005 (IPCC, 2007).

Anthropogenic CO$_2$ emissions are largely due to the combustion of fossil fuels for power generation, accounting for 41% of the total emissions (NRC, 2010). Combustion of coal emits more CO$_2$ due to its high carbon content per unit of energy released (about 93 to 99 kg of CO$_2$ per GJ of energy released, depending on the type of coal being burned), as presented in Table 2.1. Among the different types of fossil fuel i.e. coal, liquid fuels and natural gas, coal emits the highest amount of CO$_2$ per GJ of energy released with the highest value of 99 kg CO$_2$/GJ. Liquid fuels emits on average of 69 kg CO$_2$ per GJ of energy released, while the amount of CO$_2$ emission of natural gas is approximately half compared to that of coal.
Table 2.1 Carbon content (in kg CO$_2$ emitted per GJ of energy released) for different types of fuel (EIA, 2012)

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>kg CO$_2$/GJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td></td>
</tr>
<tr>
<td>i. Anthracite</td>
<td>99</td>
</tr>
<tr>
<td>ii. Bituminous</td>
<td>89</td>
</tr>
<tr>
<td>iii. Lignite</td>
<td>93</td>
</tr>
<tr>
<td>iv. Subbituminous</td>
<td>92</td>
</tr>
<tr>
<td>Liquid fuels</td>
<td></td>
</tr>
<tr>
<td>i. Diesel fuel/heating oil</td>
<td>70</td>
</tr>
<tr>
<td>ii. Gasoline</td>
<td>68</td>
</tr>
<tr>
<td>Natural gas</td>
<td>52</td>
</tr>
</tbody>
</table>

However, coal has not always been the main CO$_2$ contributor. In the past, CO$_2$ emissions from coal were less than that of liquid fuels, but quickly exceeded starting from 2004 (11 billion metric tonnes) and coal is likely to remain as leading source of CO$_2$ emissions until 2040 (21 billion metric tonnes), as illustrated in Figure 2.2. The natural gas share of CO$_2$ emissions has been relatively small by comparison at 19% of the total in 1990 and expected to continue the trend at projected 22% of total CO$_2$ emission in 2040 (EIA, 2013).
2.1.2. International regulatory framework

The United Nations Framework Convention on Climate Change (UNFCCC) was agreed in New York on 9 May 1992 as the direct outcome of the Rio Earth Summit in the same year (UNFCCC, 1992). Its main objective was “to achieve stabilisation of GHG concentrations in the atmosphere at level that would prevent dangerous anthropogenic interference with the climate system”. The objective has been the driving force for mitigation initiatives of many GHG, including CO₂, on international levels for years to come since its establishment. The countries of UNFCCC, also known as the Parties, hold annual meetings to discuss feasible methods to achieve this objective.
One of the most important outcomes of the meetings was the Kyoto Protocol. Adopted in Kyoto, Japan on 11 December 1997, it was an international agreement among the Parties to set internationally binding emission reduction targets (UNFCCC, 1998). The Protocol placed heavier burden on developed nations for their current high levels of GHG emissions in the atmosphere as a result of more than 150 years of industrial activities, under the principle of “common but differentiated responsibilities”. The Protocol was open for signature from 16 March 1998 to 15 March 1999 and received 84 signatures within the duration. Currently, there are 191 Parties to the Protocol, with the exception of Canada which revoked its ratification status effective 15 December 2012. Although the United States of America is one of the Annex I Parties, which consist of countries committed themselves in aiming to reduce to their 1990 level of greenhouse gases by the year 2000, it has not ratified the Protocol.

The methods applied in the Protocol included the clean development mechanism (CDM). CDM allows emission bargain projects in developing countries to earn certified emission reduction (CER) credits of which each equivalent to 1 tonne of CO₂. CER can be traded, sold and used by industrialised countries to meet a part of their emission reduction targets under the Protocol. Nevertheless, it was not until 2001 at the Convention’s seventh meeting at Marrakesh (Morocco) that the detailed rules for implementation of the Protocol were adopted. The Protocol officially entered into force on 16 February 2005. The first commitment started on 2008 and ended in 2012. During this commitment period, 37 industrialised
countries along with European Community committed to reduce GHG to an average of 5% against 1990 levels.

The second commitment of the Kyoto Protocol, also known as the Doha amendment of the Kyoto Protocol, began on 1 January 2013 and expected to end on 31 December 2020 (UNFCCC, 2012). Adopted in Doha on 8 December 2012, the amendment also updated the list of GHG along with several articles of the Kyoto Protocol in agreement with the second commitment. During the new commitment period, it is expected that GHG emission levels are to be reduced by at least 18% below 1990 levels despite altered composition of Parties during the first commitment period.

Other notable negotiations that lead to current commitments include the 2007 Bali Action Plan, the 2010 Cancun agreements, the 2011 Durban as well as the 2013 Warsaw Climate Change Conferences. The Bali Action Plan was established as a direct respond to the IPCC 4th Assessment Report that warned about the change in climate system and that delay in reducing emissions significantly inhibited opportunities to achieve lower stabilisation levels and increased the risk of more severe climate change impacts. Consequently, the Bali Action Plan introduced a comprehensive process to enable full implementation of the Convention through long-term cooperative actions with the establishment of the Ad Hoc Working Group on Long-Term Cooperative Action (AWG-LCA). The focus of the working group included to launch actions on mitigation and adaptation of climate change,
technology development and transfer as well as the provision of financial resources to support these actions (UNFCCC, 2007).

The 2010 Cancun agreements highlighted clear objectives for reducing anthropogenic GHG to keep the global average temperature rise of less than 2 °C. These included realising the Bali Action Plan, while additionally urging global protection of forests as the major repository of carbon, encouraging global participation in minimising climate change and ensuring international transparency of these actions (UNFCCC, 2010). Moreover, the Climate Change Conference in Cancun also emphasised in providing for financial and technology development supports to the developing countries in order for them to realise the outlined actions.

The negotiations at the 2011 Durban Climate Change Conference advanced the implementation of Kyoto Protocol, Bali Action Plan and Cancun agreements. The 2011 Durban outcomes were considered to be a turning point in climate change negotiations, where the Parties were clearly more committed to adopt a universal legal agreement on climate change as soon as possible and no later than 2015. The highlight of the outcomes in Durban conference included the roadmap for implementation, consisting of the second commitment period of Kyoto Protocol, or later known as the Doha amendment to Kyoto Protocol, the launch of new platform of negotiations that critically finding ways to further raise the existing level of national and international actions, more transparent emission reduction and limitation plans in addition to provide supports to the developing countries and
global review of the emerging climate challenge to ensure whether there was a need to revise the maximum two-degree global temperature rise limit (UNFCCC, 2011).

The 2013 Warsaw Climate Change Conference was essentially a preparation of the Parties for a universal climate change agreement planned to be held in 2015. The objectives of the 2015 agreement were essentially to further collectively encourage effective global effort to rapidly reduce the climate change consequences while building adaptation capacity. Among key decisions made during this conference there was the establishment of the Green Climate Fund to support developing countries in realising the action plans, finalisation of monitoring, reporting and verification arrangements for domestic actions, mechanism to address loss and damage caused by long-term climate change impacts. Warsaw 2013 also provided showcase for climate change action by business, cities, regions and civil societies and the Parties were convinced that the solutions to climate change had become available via technological options, wealth as well as knowledge.

2.1.3. Mitigation strategies

There is a wide portfolio of technological options to reduce CO₂ emissions, including: i) improving energy efficiency, ii) switching from high carbon intensive fuel such as coal to a less carbon intensive fuels like natural gas, iii) increasing the use of renewable energy sources or nuclear, iv) capturing CO₂ by enhancing the
biological absorption capacity of forests and soils, and vi) capturing and storing CO₂ chemically or physically which is also known as carbon capture and storage or CCS (IPCC, 2005; Plaza et al., 2007).

CCS is a promising choice to reduce the overall mitigation costs and escalating flexibility in reducing GHG emissions. Nonetheless, the extent of application of CCS would depend on technical maturity, costs, overall potential, technology diffusion and transfer to developing nations and their capacity to apply the technology. Social factors such as regulatory aspects, environmental issues and public perception also played important roles to the rate of deployment of the technology (IPCC, 2005).

Positive implications of CCS on CO₂ emission reduction can be explained using the Socolow stabilisation wedges analysis. The analysis derived from CO₂ emission (GtC/year) curves from fossil fuel combustion and cement manufacture which regarded two different scenarios; 1) the business-as-usual (BAU) scenario which assumed zero carbon mitigation initiative and; 2) CO₂ stabilisation at 500 ppm by Wigley, Richels and Edmonds (WRE 500), as shown in Figure 2.3A. The curves are divided into a stabilisation triangle of avoided emissions and continued fossil fuel emissions (Figure 2.3B) which fixed at 7 GtC/year starting 2004 until the WRE500 scenario is ideally applied in 2054. The stabilisation wedges are then referred to as graphical interpretation of activities reducing the rate of carbon build-up in the atmosphere that grows in 50 years at 7 GtC/year (Pacala and Socolow, 2004).
In this analysis, CCS was included as one of the recommended activities in reducing the carbon build-up. The analysis proposed four CCS options; 1) CO$_2$ capture at baseload power plant; 2) CO$_2$ capture at hydrogen plant; 3) CO$_2$ capture at coal-to-synfuels plant and; 4) CO$_2$ storage in geological formations. CCS would be able to reduce CO$_2$ emissions by 1 GtC/year within 50 years of employment.

Figure 2.3 CO$_2$ emission (GtC/year) curves from fossil fuel combustion and cement manufacture with two different scenarios; A) the business-as-usual (BAU) scenario which assumed zero carbon mitigation initiative and; B) CO$_2$ stabilisation at 500 ppm by Wigley, Richels and Edmonds (WRE 500) (Pacala and Socolow, 2004)

This analysis was reaffirmed in 2011 by the author himself and the core messages of the analysis were found to be still valid as they were in 2004 (Socolow, 2011). However, the wedges needed to fill the stabilisation triangle had increased to nine,
instead of seven in 2004 (Figure 2.4). The additional 2-segment global CO₂ emissions trajectory that started in 2011 instead of 2004 added another 50 ppm to the equilibrium concentration. The delayed trajectory also produced approximately 0.5 °C rise in the average surface temperature of the earth. This shows the gravity of consequences when the deployment of appropriate activities to reduce CO₂ emissions is delayed. This is backed up by recent IEA report which stated that unless CCS technology is widely deployed, no more than one-third of proven reserves of fossil fuels can be consumed prior to 2050 if the world is to achieve the 2 °C of average global surface temperature rise (IEA, 2012).

![Stabilisation triangles in 2004 and 2011 (Socolow, 2011)](image)

The IEA introduced the BLUE Map scenario in the 2008 Energy Technology Perspective, in order to project the ability of the world to reduce 50% CO₂ emission by the year 2050 (IEA, 2008). This scenario served as extension of the Baseline scenario in the World Energy Outlook 2007 (also referred to as WEO
2007 450 ppm case), which was projected up to the year 2030. The BLUE Map scenario took into account the adoption of technologies with marginal costs of up to USD 200 per tonne CO₂. Figure 2.5 shows the source of CO₂ savings in the BLUE Map scenario compared to the World energy Outlook 2007 450 ppm case (IEA, 2008). It is apparent that in order to achieve the optimistic 50% reduction of CO₂ emission by the year 2050, more stringent mitigation strategies have to be deployed. These, among others, include the deployment of CCS technologies in industries as well as power generation.

![Figure 2.5 The source of CO₂ savings in the BLUE Map scenario compared to the World Energy Outlook 2007 450 ppm case (IEA, 2008).](image)

### 2.2. Carbon dioxide capture and storage (CCS)

CCS is a technological option to reduce anthropogenic CO₂ emissions. Figure 2.6 provides a general illustration to the CCS chain from the capture plant to geological storage, and including CO₂ transport (GCCSI, 2013a). CO₂ would be captured at large point sources such as coal-fired power plants. Captured CO₂ will be
separated from capture medium, compressed to a high pressure usually at supercritical conditions of approximately more than 200 bar and 250 °C.

The modes of CO₂ transportation can be divided into two, namely offshore and onshore. Offshore transport includes pipelines and ships. Large amounts of CO₂ can be transported predominantly via pipelines due to the readily available millions of kilometres of pipelines worldwide that transport various types of fluids, including CO₂, and thus would appear to be the most economical and practical (Golomb, 1997; Koorneef et al., 2012). Shipment can be an alternative option for many parts of the world. Europe has been involved in shipment of CO₂ on a small scale, where typically 1000 tonnes food-quality CO₂ is shipped from large point sources to coastal distribution terminals. Shipping larger amounts of CO₂, i.e. 10,000 and 40,000 cubic metres, are likely to be similar to that of liquefied petroleum gas (LPG), which expertise has been developed for decades.

Onshore transport can also include pipelines, as well as road tankers and rails. Transports by road tankers and rails are possible for smaller amount of CO₂ being transported over shorter distances compared to transport by pipelines. Nevertheless, it is unlikely for wheeled modes of transportations to be in significant number based on large amount of CO₂ to be transported to storage sites which are more economical and practical using pipelines (Golomb, 1997; GCCSI, 2013a).
Transported CO₂ is then injected and stored in geologic formations (Figueroa et al., 2008; Klara et al., 2003). Figure 2.7 shows different types of CO₂ storage options (IPCC, 2005), where the most common options are saline water-saturated reservoir rocks, oil and gas fields and coal systems. Other options include storage in basalts, oil shales and cavities. CO₂ storage capacity estimates for different geological options are summarised in Table 2.2. These different CO₂ storage options are discussed below.
Saline formations consist of porous sedimentary rocks saturated with formation waters that are considered as unsuitable for human consumption, agricultural or industrial use. Supercritical CO\textsubscript{2} can be stored in deep saline formations due to its ability to retain CO\textsubscript{2} underground at relatively high water formation pressure. Saline formations have been identified as one of the best options for large volume CO\textsubscript{2} storage in geological formation (Bachu, 2000; Bradshaw et al., 2002). Table 2.2 shows the lower estimate of storage capacity in deep saline formations is 1000 Gt CO\textsubscript{2}, while the upper estimate is possibly up to $10^4$ Gt CO\textsubscript{2} (IPCC, 2005). Nevertheless, these formations are commonly less understood in comparison to shallow freshwater aquifers or hydrocarbon bearing reservoirs and any assessment of their CO\textsubscript{2} storage potential typically includes significant uncertainty because of the scarcity of subsurface data. Additionally, the containment potential
of the seal rock is usually untested and there is uncertainty regarding potential for undiscovered natural resources (CO2CRC, 2008).

CO₂ can be stored in depleted and oil and gas reservoirs. These types of storage are estimated to be between 675 and 900 Gt CO₂ worldwide, as shown in Table 2.2 (IPCC, 2005). CO₂ is also used in still producing oil and gas reservoirs to enhance oil or gas recovery (EOR/EGR) by miscible or immiscible flooding, therefore providing an economic benefit and storing CO₂ at the same time. Storing CO₂ in this way provides an advantage of proven potential containment by retention of hydrocarbon for millions of years. Geological and engineering data for detailed site characterisation are also widely available (Holloway & Savage, 1993; IPCC, 2005). However, possible disadvantages include limited potential storage capacity due to the physical size of the fields, potential leak point caused by the presence of existing oil wells and timing of availability of depleted fields with regards to source of CO₂ (CO2CRC, 2008).

CO₂ storage in coal seams is different from that of other geological formations due to its storage mechanism by adsorption process. Gaseous CO₂ is used in coal seams, instead of pumping liquid CO₂ in other geological formations, and injected into coal micropore surfaces resulting in displacement of the existing methane (CH₄) since coal has higher affinity to CO₂ than CH₄ (Gunter et al., 1997; Bradshaw & Rigg, 2011; IPCC, 2005). Because of the displacement of CH₄ and its higher greenhouse radiative effect than CO₂, CO₂ storage in coal seams is done in conjunction with enhanced coal bed methane recovery (ECBM). Challenges in
storing CO₂ in coal seams include feasibility of injecting CO₂ due to typically low permeability of the coal cleat system, especially with increasing depth. This may compromise the economic viability of ECBM caused by large number of wells that may need to be drilled to overcome injecting issues relating to low permeability. Subsequently, storing CO₂ in unmineable coal seams was deemed to have the smallest storage capacity, as shown in Table 2.2 (IPCC, 2005).

**Table 2.2 CO₂ storage capacity estimates for different geological options worldwide (IPCC, 2005).**

<table>
<thead>
<tr>
<th>Reservoir type</th>
<th>Lower estimate of storage capacity (Gt CO₂)</th>
<th>Upper estimate of storage capacity (Gt CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil and gas fields</td>
<td>675*</td>
<td>900*</td>
</tr>
<tr>
<td>Unmineable coal seams (ECSM)</td>
<td>3 – 15</td>
<td>200</td>
</tr>
<tr>
<td>Deep saline formations</td>
<td>1000</td>
<td>Uncertain, but possibly 10⁴</td>
</tr>
</tbody>
</table>

* These numbers would increase by 25% if “undiscovered” oil and gas fields were included in this assessment.

The total CO₂ storage capacity in the European countries was estimated to be approximately 360,000 Mt, with most of that capacity (326,000 Mt) in deep saline aquifers, 32,000 Mt in depleted hydrocarbon fields (EOR/EGR included) and 2000 Mt in unmineable coal (ECBM included) beds (GeoCapacity Consortium, 2009).
About 68% (244,000 Mt) of the total storage capacity is located offshore, while the remaining 32% (116,000 Mt) is onshore (GeoCapacity Consortium, 2009).

Table 2.3 shows the highest CO₂ storage capacity estimates amongst the European countries. Norway shows the highest CO₂ storage capacity in deep saline aquifers and depleted hydrocarbon fields with 29,188 Mt of total capacity. The decreasing order is then followed by Germany (17,080 Mt), United Kingdom (14,400 Mt), Spain (14,179 Mt) and Romania (9,000 Mt) as the top five European countries with the highest CO₂ storage capacity estimates. With the exception of United Kingdom, most of these countries have the largest estimated CO₂ storage capacity in deep saline formations than in depleted hydrocarbon fields.

Table 2.3 Selected CO₂ storage capacity estimates in metric tonnes (Mt) in European countries (GeoCapacity Consortium, 2009). Note that depleted hydrocarbon fields included EOR/EGR and unmineable coal fields included ECBM.

<table>
<thead>
<tr>
<th>Country</th>
<th>CO₂ storage capacity (Mt)</th>
<th></th>
<th></th>
<th></th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Deep saline aquifers</td>
<td>Depleted hydrocarbon fields</td>
<td>Unmineable coal fields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td>26031</td>
<td>3157</td>
<td>-</td>
<td></td>
<td>29188</td>
</tr>
<tr>
<td>Germany</td>
<td>14900</td>
<td>2180</td>
<td>-</td>
<td></td>
<td>17080</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>7100</td>
<td>7300</td>
<td>-</td>
<td></td>
<td>14400</td>
</tr>
<tr>
<td>Spain</td>
<td>14000</td>
<td>34</td>
<td>145</td>
<td></td>
<td>14179</td>
</tr>
<tr>
<td>Romania</td>
<td>7500</td>
<td>1500</td>
<td>-</td>
<td></td>
<td>9000</td>
</tr>
</tbody>
</table>
2.2.1. Costs of CCS

The costs of CCS can be divided into three components, namely capture (including separation and compression of captured CO$_2$), transport and storage (including measurement, monitoring and verification). The cost of capture dominates the cost of employing full CCS system for electricity generation from fossil-fired power plants. High cost of capture comprises the cost of separating captured CO$_2$ and compressing it to a high pressure suitable for pipelines, the most common and usually the most economical way to transport CO$_2$. Compression process of any gas, including CO$_2$, is a notably energy-consuming process which contributes to high cost of capture (Herzog, 2011).

Table 2.4 shows an estimation of additional electricity cost after CCS employment by CCS components. The cost of capture technology in a pulverised coal-fired (PC) power plant would add approximately 1.8 to 3.4 US$ct/kWh to the cost of electricity without CO$_2$ capture, 0.9 to 2.2 US$ct/kWh for an integrated gasification combined cycle (IGCC) power plant and 1.2 to 2.4 US$ct/kWh for a natural gas combined cycle (NGCC) power plant. The negative costs shown in the table are coupled with assumed offset revenues from CO$_2$ storage in EOR or ECSM projects (IPCC, 2005).
Table 2.4 Estimation of additional electricity cost after CCS employment by CCS components (IPCC, 2005)

<table>
<thead>
<tr>
<th>CCS components</th>
<th>Power plant system</th>
<th>Additional electricity cost after CCS employment (US$ct/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capture</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>1.8 – 3.4</td>
<td></td>
</tr>
<tr>
<td>IGCC</td>
<td>0.9 – 2.2</td>
<td></td>
</tr>
<tr>
<td>NGCC</td>
<td>1.2 – 2.4</td>
<td></td>
</tr>
<tr>
<td>Transport and storage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>-1 – 1</td>
<td></td>
</tr>
<tr>
<td>IGCC</td>
<td>-0.5 – 0.5</td>
<td></td>
</tr>
<tr>
<td>NGCC</td>
<td>-0.5 – 0.5</td>
<td></td>
</tr>
</tbody>
</table>

Costs of CCS per tonne of CO₂ vary widely according to CO₂ sources, as shown in Table 2.5. CO₂ capture presents the highest costs of the whole CCS chain. CO₂ capture cost for fossil fuel-fired power plants range from 15 to 75 US$/tCO₂ captured, while hydrogen and ammonia production as well as gas processing plants range from 5 to 55 US$/tCO₂ captured. Other industrial activities capture cost range from 25 to 115 US$/tCO₂ captured, which require the highest cost to employ capture technology among other major CO₂ sources. CO₂ transport require the lowest cost of the entire CCS system with cost range between 1 and 8 US$/tCO₂ transported. The cost for geological storage of CO₂ is generally small with the exception of mineral carbonation which range between 50 and 100 US$/tCO₂ mineralised. These figures were estimated based on assumptions that natural gas prices between 2.8 and 4.4 US$/GJ and coal prices range from 1 to 1.5 US$/GJ (IPCC, 2005).
The cost of capture could be lower by 20 to 30% over the next decade, along with the costs of transport and storage as a result of technology maturity (IPCC, 2005; DECC, 2012). In the meantime, the UK Department of Energy and Climate Change (DECC) outlined drivers for CCS cost reduction (DECC, 2012). The drivers are chosen based on a report by Rubin et al. on “Prospect for improved carbon capture technology” in 2010 which include; 1) technology enhancement in process design and materials; 2) optimisation of construction logistics; 3) economies of scale which justify larger scale units would typically results in reduced costs per unit of capacity; 4) design margins reduction; 5) product standardisation; 6) increased competition; 7) reduction in key input price such as construction labour and services, materials and components; and 8) system integration and optimisation in terms of thermodynamic efficiency and design optimisation (Rubin et al., 2010; DECC, 2012).
Table 2.5 CCS cost range for industrial activities by CCS components (IPCC, 2005).

<table>
<thead>
<tr>
<th>CCS components</th>
<th>Cost range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capture</td>
<td></td>
</tr>
<tr>
<td>• Fossil fuel-fired power plants</td>
<td>15 – 75 US$/tCO₂ captured</td>
</tr>
<tr>
<td>• Hydrogen and ammonia production/gas processing plants</td>
<td>5 – 55 US$/tCO₂ captured</td>
</tr>
<tr>
<td>• Other industrial sources</td>
<td>25 – 115 US$/tCO₂ captured</td>
</tr>
<tr>
<td>Transport</td>
<td>1 – 8 US$/tCO₂ transported</td>
</tr>
<tr>
<td>Geological storage</td>
<td>0.5 – 8 US$/tCO₂ stored</td>
</tr>
<tr>
<td>• Monitoring and verification</td>
<td>0.1 – 0.3 US$/tCO₂ stored</td>
</tr>
<tr>
<td>• Ocean storage</td>
<td>5 – 30 US$/tCO₂ stored</td>
</tr>
<tr>
<td>• Mineral carbonation</td>
<td>50 – 100 US$/tCO₂ mineralised</td>
</tr>
</tbody>
</table>

2.2.2. Current CCS demonstration projects worldwide

As of 2013, the Global CCS Institute (GCCSI) has identified 65 active large-scale integrated projects (LSIP) worldwide (GCCSI, 2013b). LSIPs are defined as projects that involve all CCS components at a scale of at least 0.8 MtCO₂/yr for a coal-based power plant or 0.4 MtCO₂/yr for other emission-intensive facilities. There were 20 LSIPs operating or under construction stage with total CO₂ capture capacity of more than 37 MtCO₂/yr and 44 LSIPs in planning stages of development with potential capture capacity of approximately 78.5 MtCO₂/yr.
In comparison with previous years, the total number of LSIPs that were in planning stage in 2013 of 45 has decreased from 59 in 2010, as shown in Figure 2.8. However, the opposite trend can be observed in the total number of LSIPs in operating or under construction stages of development where 12 were in active stages in 2010 increased to 22 in 2013, with additional 4 operating LSIPs in 2013. The contrary trend is due to some of the planned LSIPs in earlier years have positively passed the financial investment decision (FID), as well as execution phase and commenced the consecutive active stages of development.

![Figure 2.8 Annual comparisons of LSIPs at different stages of development (GCCSI, 2013b)](image)

Despite the increasing number of total LSIPs entering the operating stage in 2013, the total potential mass of CO$_2$ captured and stored in all stages of development
have decreased over the years beginning in 2010 from 162 MtCO$_2$ to 140 MtCO$_2$, as shown in Figure 2.9 (GCCSI, 2013b). This is due to the change of status of LSIPs to either being cancelled or put on-hold. On the other hand, the volumes of CO$_2$ captured and stored have increased since 2010 from 12 MtCO$_2$/yr to 17.18 MtCO$_2$/yr in 2013. These values correspond with total volume of CO$_2$ captured and stored by eleven operating LSIPs around the world, as shown in Table 2.6. The operating LSIPs are dominated by developed nations, particularly in North America and Europe. Technology-wise, most of the operating LSIPs are applying pre-combustion capture and transporting the CO$_2$ via pipelines with the exception of two direct injection projects, namely, Sleipner CO$_2$ Injection project in Norway and Petrobras Lula Oil Field CCS Project in Brazil. Two apparent storage types used are deep saline formations and enhanced oil recovery (EOR).

![Figure 2.9 Annual comparisons of mass of CO$_2$ captured and stored from 2010 until 2013 (GCCSI, 2013b)](image-url)
Table 2.6 Operating LSIPs worldwide (GCCSI, 2014).

<table>
<thead>
<tr>
<th>Project Name</th>
<th>Volume CO₂ (MtCO₂/yr)</th>
<th>Capture Type</th>
<th>Transport Type</th>
<th>Storage Type</th>
<th>Operation Year</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Val Verde Natural Gas Plants</td>
<td>1.3</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced Oil Recovery</td>
<td>1972</td>
<td>United States</td>
</tr>
<tr>
<td>Enid Fertilizer CO₂-EOR Project</td>
<td>0.68</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced Oil Recovery</td>
<td>1982</td>
<td>United States</td>
</tr>
<tr>
<td>Shute Creek Gas Processing Facility</td>
<td>7</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced Oil Recovery</td>
<td>1986</td>
<td>United States</td>
</tr>
<tr>
<td>Sleipner CO₂ Injection</td>
<td>1</td>
<td>Pre-Combustion</td>
<td>Direct injection</td>
<td>Offshore Deep Saline Formations</td>
<td>1996</td>
<td>Norway</td>
</tr>
<tr>
<td>Great Plains Synfuel Plant and Weyburn-Midale Project</td>
<td>3</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced Oil Recovery</td>
<td>2000</td>
<td>Canada</td>
</tr>
<tr>
<td>In Salah CO₂ Storage</td>
<td>1*</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Onshore Deep Saline Formations</td>
<td>2004</td>
<td>Algeria</td>
</tr>
<tr>
<td>Snøhvit CO₂ Injection</td>
<td>0.7</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Offshore Deep Saline Formations</td>
<td>2008</td>
<td>Norway</td>
</tr>
<tr>
<td>Century Plant</td>
<td>8.4</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced Oil Recovery</td>
<td>2010</td>
<td>United States</td>
</tr>
<tr>
<td>Air Products Steam Methane Reformer EOR Project</td>
<td>1.0</td>
<td>Pre-Combustion</td>
<td>Pipeline</td>
<td>Enhanced oil recovery</td>
<td>2013</td>
<td>United States</td>
</tr>
<tr>
<td>Coffeyville Gasification Plant</td>
<td>1.0</td>
<td>Industrial separation</td>
<td>Pipeline</td>
<td>Enhanced oil recovery</td>
<td>2013</td>
<td>United States</td>
</tr>
<tr>
<td>Lost Cabin Gas Plant</td>
<td>0.8-1.0</td>
<td>Pre-combustion</td>
<td>Pipeline</td>
<td>Enhanced oil recovery</td>
<td>2013</td>
<td>United States</td>
</tr>
<tr>
<td>Petrobras Lula Oil Field CCS Project</td>
<td>0.7</td>
<td>Pre-combustion</td>
<td>Direct injection</td>
<td>Enhanced oil recovery</td>
<td>2013</td>
<td>Brazil</td>
</tr>
</tbody>
</table>

* Injection suspended, future injection strategy under review (GCCSI, 2014).
2.3. CO$_2$ capture

There are mainly three sources to capture CO$_2$ from, namely at i) stationary large point sources such as fossil fuel power generation plants, fuel and industrial processing plants; 2) smaller and mobile sources in the transportation, residential and building sectors and; 3) ambient air. However, the concentration of CO$_2$ in these sources determines the feasibility of capturing CO$_2$ since higher concentration would provide greater driving force in separating the gases. The highest CO$_2$ concentration is found in stationary large point sources mentioned earlier and could provide the most feasible profile of technologies. Lower CO$_2$ concentrations found in small and mobile sources as well as in ambient air would increase the complexity of the separation process and the associated costs required to manufacture such technology (IPCC, 2005).

The capture of CO$_2$ can be accomplished by three different routes, namely post-combustion, pre-combustion and oxy-combustion, as shown in Figure 2.10 (Figueroa et al., 2008). Post-combustion separates CO$_2$ from flue gases and can occur anywhere along the product processing stream from combustor to effluent exhaust, where the CO$_2$ concentration in flue gases is normally between 3 to 15 vol%. The pre-combustion route involves CO$_2$ capture after the gasification process and prior to the combustion step (IPCC, 2001). The most common configuration involves gasification with air or oxygen. The products undergo a water-gas shift to a high-concentration stream of CO$_2$ and H$_2$. The CO$_2$ is then captured and the H$_2$ is reacted with air. Finally, in oxy-combustion, pure oxygen substitutes air as
combustion gas producing a stream concentrated with CO₂ and H₂O (GCEP, 2005). However, partial oxygen concentration is also possible to be used in practice due to low resistance of boiler material against high temperature associated with combustion using pure oxygen (Li et al., 2013).

![Block diagrams illustrating post-combustion, pre-combustion, and oxy-combustion systems (Figueroa et al., 2008)](image)

There are several technology options for CO₂ capture that are being researched including liquid absorption, solid absorption, cryogenics, membranes,
microbial/algal systems and adsorption, as shown in Figure 2.11 (Rao and Rubin, 2002). Under these categories, there are more specific methods like chemical and physical liquid absorption processes, adsorber beds and regeneration solid adsorption methods, as well as gas separation/absorption and ceramic based systems for membranes.

![Diagram of CO₂ Separation and Capture](image_url)

**Figure 2.11 Technology options for CO₂ separation and capture (Rao & Rubin, 2002)**

Both absorption and adsorption can be divided into two types of processes i.e. physical and chemical. Physical sorption process, also known as physisorption, uses sorbents to trap as much CO₂ molecules as possible by intermolecular forces, without any chemical reaction assisting the process (IUPAC, 1997). This process occurs at low to medium sorption temperatures ranging from 25 °C to 100 °C. Chemical sorption process, or chemisorption, utilises strong chemical bonds between sorbents and CO₂ molecules with the help of high sorption temperatures, usually ranging from 500 °C to 700 °C. Chemical reactions that occur generate strong chemical bonds on the surface of adsorbent that bind the CO₂ molecules.
However, both processes can occur in parallel or alternately at some point in the sorption process.

In cryogenic separation, CO₂ is separated from the flue gas stream by condensation which at atmospheric pressure, CO₂ condenses at −56.6 °C. Taking refrigeration costs into consideration, this kind of separation process is most effective in gas streams with high CO₂ concentrations (Wang et al., 2011). Membranes separate CO₂ from gas mixture stream based on the relative rates at which constituent species permeates. Membranes usually are made of polymeric films of which permeation rates would differ based on the relative sizes of the molecules or diffusion coefficients in the membrane material. The difference in partial pressure of the gases at either side of the membrane is the driving force of the separation process. Microbial/algae are microscopic organisms that usually grow suspended in water and feed on CO₂ to produce O₂, much the same as in photosynthetic process adopted by plants. However, factors like availability of light, pH, O₂ removal, suitable design of the photobioreactor, culture density and proper agitation of the reactor that will affect the process significantly (Kumar et al., 2011).

2.3.1. CO₂ sorption by solid sorbents

Solid sorbents have become an increasing popular area of research, although liquid sorbents are considered as the more mature CO₂ capture technology, going back to the capture of CO₂ for enhanced oil recovery (EOR) operations in the 1970s (Rao
and Rubin, 2002). However, liquid solvents like monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) have been found to have problems of scale and performance stability (Munoz et al., 2009). Furthermore, liquid sorbents are prone to degradation and oxidation resulting in products that are corrosive and may require hazardous material handling procedures (Islam et al., 2011).

These problems can be resolved using solid sorbents. Additionally, the energy required for regeneration and moving liquid solvents is reduced by more than 30% with solid sorbents, if high (more than 132 g CO₂/kg sorbent) CO₂ uptake capacity of the sorbent is achieved (Gray et al., 2008). Furthermore, solid sorbents produce no liquid wastes and offer much wider temperature range applications between 25 and 700 °C (Choi et al., 2009; Olivares-Marin & Maroto-Valer, 2012). Because of these reasons, CO₂ adsorption on solid sorbents has become an increasingly interesting option for many industries for various benefits. The following section discusses CO₂ capture at high (over 400 °C) sorption temperatures, where chemisorption is the dominant sorption process (Wang et al., 2011).

2.3.2. CO₂ capture by lithium-based sorbents

In recent years, Li₄SiO₄ has been developed as a potential solid sorbent for CO₂ capture due to its high CO₂ capacity and sorption kinetics, especially at high sorption temperatures. Li₄SiO₄ reacts with CO₂ to produce lithium carbonate (Li₂CO₃) and silicon dioxide (SiO₂), as shown in equation (2.1), with a theoretical
maximum uptake capacity of 735 mg CO$_2$/g. However, practically, reaction products i.e. Li$_2$SiO$_3$ restrict the sorption process. Therefore, the reaction advances according to equation (2.2) instead, which yields the limited CO$_2$ adsorption of 367 mg CO$_2$/g sorbent (Yamaguchi et al., 2007).

\[
\text{Li}_4\text{SiO}_4 + 2\text{CO}_2 \rightarrow 2\text{Li}_2\text{CO}_3 + \text{SiO}_2 \quad (2.1)
\]

\[
\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_3 \quad (2.2)
\]

There are a number of studies on pure Li$_4$SiO$_4$ sorbents for CO$_2$ capture at high temperatures (Essaki et al., 2005; Kato et al., 2005; Yamaguchi et al., 2007). Essaki et al. (2005) revealed most CO$_2$ uptake occurred at 500 °C (220 mg CO$_2$/g sorbent) for CO$_2$ concentration of 5 vol% and 600 °C for 10 vol% (220 mg CO$_2$/g sorbent) and 15 vol% (270 mg CO$_2$/g sorbent) of CO$_2$. During later parts of their study, an attempt was made to express the variation in sorption with temperature more clearly by evaluating using a wider temperature range from 400 to 700 °C with a smaller temperature interval for every 50 °C for only 10 vol% of CO$_2$. These results agreed with the first study, which showed the fastest and highest uptake at 600 °C with the same amount of CO$_2$ uptake. This showed that CO$_2$ sorption by Li$_4$SiO$_4$ is strongly affected by the sorption temperature and the initial rate-determining step changed depending on the CO$_2$ concentration.

Kato et al. (2005) investigated CO$_2$ capture using lithium-containing oxides, including Li$_4$SiO$_4$ and Li$_2$ZrO$_3$. Cylindrical Li$_4$SiO$_4$ pellet type sample with added
lithium zirconate (Li$_2$ZrO$_3$) was placed in a packed bed reactor before subjected to CO$_2$ flow. Li$_2$ZrO$_3$ was added to suppress degradation of the absorption capacity during regeneration cycle as well as to control grain growth in order to maintain high surface area.

The samples were firstly subjected to pure CO$_2$ flow at 700 °C in order to examine the pure reaction between Li$_4$SiO$_4$ as well as Li$_2$ZrO$_3$ and CO$_2$. It was found that the reaction between Li$_4$SiO$_4$ and CO$_2$ was 50% larger (350 mg CO$_2$/g) and reached equilibrium much faster than the reaction between Li$_2$ZrO$_3$ and CO$_2$. They then studied the adsorption process at 500 °C under 20% CO$_2$ flow, and found that CO$_2$ uptake was also about 50% greater (250 mg CO$_2$/g) than that of Li$_2$ZrO$_3$ (150 mg CO$_2$/g). The same adsorption temperature was then experimented on 2% CO$_2$ flow, and the result showed that there were still significant amount of CO$_2$ adsorbed by Li$_4$SiO$_4$ (250 mg CO$_2$/g), whereas Li$_2$ZrO$_3$ showed no clear CO$_2$ uptake.

Cyclic tests were conducted using 20% CO$_2$ gas flow at a rate of 300 ml/min at 600 °C for adsorption and followed by 800 °C for regeneration for 1 hour for each process. The tests were repeated 1, 10, 20 and 50 times. Also, 2 mass% and 5 mass% of Li$_2$ZrO$_3$ was added to the samples. The results showed initial sorption rate of 280 mg CO$_2$/g per hour and decreasing with the increment of time and number of cycles, which is an expected pattern. Different amounts of Li$_2$ZrO$_3$ addition also played an important role to the regeneration cycles. It was found that the 5 mass% addition of Li$_2$ZrO$_3$ improved the most on the reproducibility of
CO₂ sorption/desorption, by maintaining the sorption rate of more than 90% even after 50 cycles.

Yamaguchi et al. (2007) discussed CO₂ separation using Li₄SiO₄-based powder and membrane sorbents. Firstly, CO₂ uptake on Li₄SiO₄ powder samples was investigated. The samples were heat-treated at 700 and 1000 °C. Then, sorption tests on powder samples were conducted at 700 °C under pure CO₂ flow. The results showed that the sample heat-treated at 700 °C had faster sorption rate and more CO₂ uptake (330 mg CO₂/g within 2 minutes) than the one that was heat-treated at 1000 °C.

A membrane was then produced using the synthesised Li₄SiO₄ powder. The results proved CO₂/N₂ selectivity between 4 and 6 in the temperature range of 525 – 625 °C. According to the authors, CO₂ transport mechanism through the membrane was possibly assisted by carrier transport of CO₃²⁻ and O²⁻ by the Li₂CO₃ and Li₂SiO₃ electrolytes. Although this experiment was conducted under pure CO₂ flow which most probably be the reason of high sorption rate compared to previous studies, this clearly showed the great potential for Li₄SiO₄ to be used as solid sorbent for carbon capture compared to other lithium-based, for example Li₂ZrO₃.

Despite various studies on pure Li₄SiO₄ sorbents, there are only two published studies on the development of Li₄SiO₄ sorbents derived from low-cost precursors, as shown in Table 2.7. The highest CO₂ capacity was 324 mg CO₂/g sorbent by sorbent derived from rice husk ash (Wang et al., 2011), while the fly ash derived
Li$_4$SiO$_4$ sorbents were able to capture about 20 mg CO$_2$/g sorbent (Olivares-Marin et al., 2010). In terms of regenerability of both rice husk and fly ash derived sorbents, the CO$_2$ uptake capacities remained almost unchanged even after 10 cycles.

Table 2.7 Li$_4$SiO$_4$-based sorbents using low-cost precursors for CO$_2$ adsorption at high sorption temperatures (modified from Olivares-Marin & Maroto-Valer, 2012)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Synthesis conditions</th>
<th>Modifications</th>
<th>Maximum CO$_2$ capacity</th>
<th>Regenerability</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash (Coal by-product)</td>
<td>Solid state calcination with Li$_2$CO$_3$ at 950 °C for 8h</td>
<td>K$_2$CO$_3$ addition.</td>
<td>Up to 107 mg CO$_2$/g sorbent at 600 °C</td>
<td>Sorbents can maintain their sorption capacities after 10 cycles</td>
<td>Olivares-Marin et al. (2010)</td>
</tr>
<tr>
<td>Rice husk ash (Biomass by-product)</td>
<td>Solid state calcination with Li$_2$CO$_3$ at 800 °C for 4h</td>
<td>Not evaluated.</td>
<td>Up to 324 mg CO$_2$/g sorbent at 700 °C</td>
<td>CO$_2$ uptake in samples remained almost unchanged even after 15 cycles.</td>
<td>Wang et al. (2011)</td>
</tr>
</tbody>
</table>

2.4. Solid wastes from power generating plants

Coal fly ash, or better known as pulverised fuel ash (PFA) in the UK, is a by-product of combustion process at temperature range between 1200 and 1700 °C in coal-fired boilers in power generation plants. The by-product indicates the presence of various refractory mineral matters in the feed coal and some components of the
fuel (Sear, 2001). Fly ash consists of fine particles and usually captured by electrostatic precipitators or other types of particle filtration equipment. Depending on the origin of the coal used in the combustion process, the characteristics of the resulting fly ash vary considerably, although unburned carbon, silica (SiO$_2$), alumina (Al$_2$O$_3$) and calcium oxide (CaO) are commonly found in fly ash.

Blissette and Rowson (2012) estimated that world annual production of fly ash is approximately 750 million tonnes and is expected to increase. Currently, a mere 25% of total fly ash produced is being utilised worldwide with most of the remaining ended up in landfills by storing it in huge fly ash lagoons or dumped into the sea (Wang, 2008). Disposing fly ash in this manner can create major environmental concerns due to the potential leaching of metals and organic compounds and their migration into groundwater or nearby surface water (Blisette and Rowson, 2012). Furthermore, fly ash lagoons have been known to breach and affect human health through direct inhalation of particulates from fly ash. Consequently, it has caused substantial distress to the local community (Wang, 2008).

Amongst 25% of the utilised portion, fly ash is popularly used in the cement industry for their low loss-on-ignition (LOI) value which makes it suitable for cement production under the ASTM C618 specification. However, the modification to low-NOx burners (LNB) have significantly increase the values of LOI in resulting fly ash, making it a less desirable choice in the cement industry (Srivastava et al.,
This reduces the percentage of fly ash being utilised, increases the amount of fly ash being disposed of and consequently leads to a strong need to explore other possibilities of utilising fly ash. One way of doing this is to use fly ash as a precursor in the development of CO$_2$ sorbents.

Another type of solid waste from power generation plants includes oil palm ash, or also known as palm oil mill boiler ash (POMBA). POMBA is a by-product of combustion process in biomass-fired boilers in palm oil mills for self-sustained energy in the mill. The biomass includes the fibres and shells of oil palm, which are the residue of palm oil extraction. Silica (SiO$_2$), alumina (Al$_2$O$_3$), iron oxide (Fe$_2$O$_3$) and calcium oxide (CaO) are among compounds commonly found in POMBA. Although, the varieties of proportion of irrigated area, geographical conditions, fertilizers used, climatic variation, soil chemistry, timeliness of production and agronomic practices in the oil palm growth process affect the chemical composition of POMBA greatly (Foo & Hameed, 2009).

The production of POMBA is heavily concentrated in Southeast Asia as many countries in this region are big exporters of palm oil, such as Malaysia. Malaysia is currently the world's largest palm oil producing country and there are 426 operating palm oil mills present in this country in 2011 with POMBA production rate of more than 4 million tonnes per year (MPOB, 2011; Mohamed et al., 2005). This figure is predicted to escalate due to the rapid increase in worldwide demand of palm oil which in turn, increasing the amount of POMBA generated by palm oil mills (Chong et al., 2009). Current ash disposal cost, either in landfills or ash
ponds, at $5 per tonne in developing countries and $50 per tonne in developed countries have further accentuated the urgency of transforming the residue into a more valuable end product (Foo & Hameed, 2009).

2.4.1. Use of solid wastes for development of CO$_2$ sorbents

Development of sorbents for CO$_2$ capture from waste materials has been widely investigated and a review has been recently published by Olivares-Marin and Maroto-Valer (2012). Solid sorbents of wide range of sorption temperatures were developed according to physical and chemical characteristics of waste materials. For example, carbonaceous waste materials were used as precursors of carbon-based sorbents for CO$_2$ capture at low temperature range between 25 and 75 °C. Wastes containing high amounts of silica and alumina such as fly ashes were converted into zeolite-based materials, mesoporous silica-based materials and lithium-based sorbents for capture at medium (70 – 100 °C) and high (100 – 750 °C) temperatures, subject to the specific precursor and the route of synthesis and surface modifications.

In this section, only the development of Li$_4$SiO$_4$ sorbents deriving from solid waste materials from power generating plant is discussed. Olivares-Marin et al. (2010) studied CO$_2$ capture using lithium-based sorbents from fly ashes at high temperatures ranging from 450°C to 700°C. The lithium-based (Li$_4$SiO$_4$) sorbents were prepared by subjecting three different sources of fly ash samples which contain between 24 to 27 wt% content of silica to calcination process at 950°C in
the presence of lithium carbonate (Li$_2$CO$_3$). For reference purposes, pure lithium silicate, indicated by P-Li$_4$SiO$_4$ was also synthesised and used in this work. Potassium carbonate (K$_2$CO$_3$) was also added to the sorbents as it has been reported to improve sorption capacity, as K$_2$CO$_3$ is believed to form eutectic melt during CO$_2$ sorption on Li$_4$SiO$_4$. The molten carbonate shell significantly increased the diffusivity of CO$_2$ molecules through the Li$_2$CO$_3$ shell to the bulk of Li$_4$SiO$_4$ particle, and therefore, increasing the CO$_2$ uptake capacity of the sorbents.

According to their findings, the sorption temperature also strongly affected the CO$_2$ sorption capacity for the sorbents prepared from fly ashes. When the sorption temperature rises up to 600$^\circ$C, the sorption capacity increased. The capture capacity also increased with increased amount of K$_2$CO$_3$ added to the fly ash sorbent, but not the P-Li$_4$SiO$_4$. At experimental conditions of 600$^\circ$C and addition of 40 mol% of K$_2$CO$_3$, the maximum CO$_2$ sorption capacity for the lithium-based sorbent was 107 mg CO$_2$/g.

In order to study the sorbents performance, multiple CO$_2$ sorption/desorption cycles were carried out. Results showed that the Li$_4$SiO$_4$-based fly ash sorbent can maintain its original capacity during 10 cycle processes and reached equilibrium capture capacity within 15 minutes, while P-Li$_4$SiO$_4$ demonstrated a continual upward tendency for the 15 minute of the capture step and attained no equilibrium capacity during the experiment time. This is because the P-Li$_4$SiO$_4$ with 20 mol% K$_2$CO$_3$ addition has maximum capacity of 244 mg CO$_2$/g, thus, will
show continual upward tendency for the 15 minute of the capture step until it has captured the maximum capacity of 244 mg CO₂/g.

To the best of the author’s knowledge, this is the only study that has been published on the development of Li₄SiO₄-based sorbents using solid waste materials from power generating plants. Thus, this research is aimed to further explore the development of Li₄SiO₄ and sorbent derived from low-cost precursors, including the effects of different waste materials, preparation methods, sorption temperature, CO₂ concentration and regeneration of sorbents.
Chapter 3 Experimental methodology

This chapter describes the parent waste materials and methodology used in the experimental studies. The experimental work is divided into three main tasks, namely, procurement and characterisation of parent waste materials, preparation and characterisation of sorbents and CO$_2$ capture by developed sorbents. Figure 3.1 shows the flowchart for this study. In the first task, waste materials were selected based on their chemical compositions i.e. high silica (SiO$_2$) content and subjected to characterisation analyses including particle size distribution and XRD analyses, to name a few.

Then, sorbents were developed via dry or wet chemical impregnation methods. Developed sorbents were also characterised using a variety of analyses such as particle size distribution and x-ray diffraction analyses. Finally, the prepared sorbents were used to capture CO$_2$ in varying sorption conditions, for example, CO$_2$ concentrations and sorption temperatures. Regeneration performance of the developed sorbents was also investigated.
Sorbents were developed from waste materials including fly and bottom ashes collected from a number of coal-fired power plants and a palm oil mill boiler, as detailed in the following Section 3.1. Lithium- and sodium-based high temperature sorbents from high SiO₂ content ashes were developed using dry and wet synthesis methods, namely solid state (SS) and suspended impregnation (SI), which will be detailed in subsequent sections.

3.1. Procurement and characterisation of waste materials

3.1.1. Waste materials procurement

A preliminary selection of waste materials which were readily available in sample stock was chosen for chemical composition analysis. This step was conducted to categorise the amount of SiO₂ content in every sample tested. Subsequently,
samples with the highest amount of SiO$_2$ content were chosen to proceed with further characterisation analyses e.g. particle size distribution analysis and surface area analysis. Table 3.1 shows the waste materials used in this study including two pulverised fuel ash samples (C- and R-PFA) and two bottom ash samples, namely furnace bottom ash (FBA) and palm oil mill boiler ash (POMBA). The feedstock and nomenclatures of every sample are also presented in Table 3.1.

**Table 3.1 Waste materials used in this study.**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Feedstock</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulverised Fuel Ash</td>
<td>Coal</td>
<td>C-PFA</td>
</tr>
<tr>
<td>Furnace Bottom Ash</td>
<td>Coal</td>
<td>FBA</td>
</tr>
<tr>
<td>Palm Oil Mill Boiler Ash</td>
<td>Oil Palm</td>
<td>POMBA</td>
</tr>
</tbody>
</table>

3.1.2. **Characterisation of waste materials**

Following the procurement of waste materials, characterisation analyses were carried out. This included particle size distribution analysis using laser diffraction, x-ray fluorescent analysis for chemical composition determination, nitrogen adsorption/desorption for pore size and surface area analysis, as well as x-ray diffraction analysis for mineralogical study. These characterisation analyses are discussed in subsequent subsections.
It should be noted that the chemical impregnation preparation of all waste-derived Li$_4$SiO$_4$ sorbents were carried out entirely by the author. The author appreciates the assistance of experimental officers for their support in operating some of the analytical instruments. These instruments include the 1050 XRD Philips Analytical with a Hilton Brooks 3 kW X-ray generator attachment (operated by Dr. Georgina Rosair at School of Engineering and Physical Sciences in Heriot-Watt University), PANalytical Axios-Advanced XRF spectrometer (operated by Mr. Nick Marsh at the Department of Geology in University of Leicester) and FEI Quanta SEM (operated by Mr. Mark Leonard at School of Engineering and Physical Sciences in Heriot-Watt University).

\textbf{3.1.2.1. Particle size distribution analysis}

\textbf{3.1.2.1.1. Background of laser diffraction for particle size distribution analysis}

Laser diffraction was used to analyse particle size distribution of the waste materials. It measures particle size distributions by calculating the angular variation in intensity of light scattered, collected by an array of detectors positioned perpendicular to the optical axis as a laser beam passes through a dispersed particulate sample (Richardson et al., 2002). Figure 3.2 shows the schematic of the optical system for a reverse Fourier lens arrangement laser diffraction with a liquid flow cell. A light source emits a laser through the beam expander. The expanded laser then passes through the flow cell sensing zone and scatters at an angle and intensity that are dependent on sizes of the particles in the zone. Smaller particles scatter light at relatively low intensity to wide angles, while
larger particles scatter more strongly at narrow angles. Next, high and low angle detectors capture scattered laser patterns accordingly and convert them into particle size distribution using an appropriate model of light behaviour.

Figure 3.2 Schematic of the optical system for a typical laser diffraction analyser with a liquid flow cell (Hackley et al., 2004).

3.1.2.1.2. Experimental procedures of laser diffraction for particle size distribution analysis

Particle size analyses were conducted by the author using a Malvern Mastersizer 2000E producing a 4 mW He-Ne laser source of 632.8 nm in wavelength and attached to a Hydro 2000SM small volume manual sample dispersion unit. The Mastersizer 2000 software controlled the system for measurement and data
analysis. Particle size range for this instrument was between 0.1 and 1000 µm. Prior to analysis, the flow cell sensing zone was filled with 99.5% propanol as the dispersion medium for the samples via the dispersion unit and the machine was left for 10 to 20 minutes to allow thermal equilibrium to take place.

Propanol was used as the suspension medium due to its ability to suspend and disperse the studied waste materials. This is important to ensure the laser was diffracted by a singular particulate of waste material rather than an agglomeration of particles which would strongly affect the analysis outcome. The instrument then automatically aligned so that the incident path of the laser was in line with the optical arrays. The cleanliness of the system was checked and a background reading recorded. The sample was gradually added into the dispersion unit until ideal concentration was achieved which was approximately 1 g of sample per 1 litre of dispersion medium. The instrument collected and analysed the scattering data to calculate a particle size distribution. The analysis was carried out in triplicates and the error calculated was 1.05%.

3.1.2.2. X-ray Diffraction (XRD) analysis

3.1.2.2.1. Background of XRD analysis

XRD is a non-destructive and versatile technique used to obtained information about the crystallographic structure of materials by comparing the analysed data against a wide set of database. The schematic of an XRD is illustrated in Figure 3.3
A solid or powder sample is placed in the diffractometer and bombarded with X-rays generated by copper X-ray tube. The diffracted X-rays are then collected by a detector and sent to a computer. The computer then converts them to digital data and produces the diffraction pattern of the sample. The computer also matches the pattern against a database using specialised identification software (Jenkins and Snyder, 1996).

![Schematic of an XRD](image)

**Figure 3.3 Schematic of an XRD** (Morris et al., 2012).

### 3.1.2.2.2. Experimental procedures of XRD analysis

XRD analyses were carried out by the instrument operator in the School of Engineering and Physical Sciences in Heriot-Watt University using a 1050 XRD Philips Analytical attached to a 3 kW X-ray generator Hilton Brooks. The X-ray generator produced copper kα radiation with wavelength of 0.15418 nm. Samples were ground using an agate mortar and pestle to fine powder. About 500 mg of sample was packed into an aluminium holder and subsequently placed in a magazine. The analysis was conducted at angle range of 5 to 65° with continuous...
scanning rate at 1.2°/min. Diffraction patterns were analysed using EVA, a software package used for the qualification of crystalline compounds. The error range of XRD measurements was between 2 to 3%.

### 3.1.2.3. X-ray fluorescent (XRF) analysis

#### 3.1.2.3.1. Background of XRF analysis

XRF is a non-destructive technique to qualitatively and quantitatively analyse elemental composition of a sample. Similar to XRD, X-ray is used in this analysis to irradiate on the sample. As a result of the irradiation step, x-ray fluorescence is generated which possess energy characteristic to each element in the sample. The x-ray fluorescence is then collected by a detector before converted into digital signals. The digital signal is then amplified to be analysed of its elemental composition using spectrometry analysis software. The schematic of an XRF is shown in Figure 3.4.

![Figure 3.4 Schematic of an XRF (PANalytical, 2014)](image-url)
3.1.2.3.2. Experimental procedures of XRF analysis

XRF analyses of waste materials were carried out to quantify the elemental composition and were performed by the instrument operator in the Department of Geology at University of Leicester using a PANalytical Axios-Advanced XRF spectrometer. Firstly, approximately 1 g of parent waste material was ground using agate mortar and pestle to fine powder. The fine powder was then ignited at 1100 °C and the subsequent ignited powder was mixed with lithium metaborate and lithium tetraborate flux. The mixture was fused at the same temperature in the furnace which was then used in the XRF spectrometer to determine their quantitative elemental composition in the form of oxides. The standard error for XRF analysis was 1.8% and the analysis was carried out in duplicates.

3.1.2.4. Scanning electron microscope (SEM) analysis
3.1.2.4.1. Background of SEM analysis

Scanning electron microscope (SEM) utilises electron beams to resolve a greatly magnified image of a sample. As shown in Figure 3.5, a SEM comprises basic parts of an electron gun, vacuum chamber containing anode plate, lenses, samples chamber and detectors. To enable control and viewing of the microscopic images generated, a computer is connected to the instrument. In the initial stage of scanning a sample using a SEM, a beam of electrons is first generated. This is done by the electron gun, usually of the thermionic type, is heated up by high voltage. When there is sufficient heat produced, electrons are emitted, resulting a strong
electric force between the electron gun and the anode plate in the vacuum chamber. This produces a beam of electrons which then follows a vertical path down the microscope column, then through the lenses and onto the sample in the sample chamber.

Upon impact with the electron beam, secondary electrons are displaced from the surface of the sample. A secondary electron detector collects the disseminated electrons to record levels of brightness of the sample's image. Backscatter and x-ray detectors gather electrons that reflected off (also known as backscattered electrons) and x-rays emitted from the surface of the sample, respectively, and subsequently producing an image on the computer monitor.
3.1.2.4.2. Experimental procedures of SEM analysis

SEM analyses were performed by the author with the assistance from a technician in the School of Engineering and Physical Sciences using a FEI Quanta SEM. Firstly, an aluminium sample holder stub was prepared by attaching a double sticky carbon tape onto it. Then, the sample (about 3 mg) was evenly adhered to the carbon tape and any excess powder was tapped off to ensure no loose particles will be released inside the SEM chamber. The vacuum was then vented prior to the mounting of the sample onto the sample stage in the SEM chamber. It should be
noted that the controlling of the instrument, including the venting, was done via the instrument software on a computer.

After the sample was mounted onto the sample holder, the chamber door was manually closed and automatically fastened to prevent room air from entering the chamber. Next, air in the SEM chamber was pumped out until it achieved sufficient vacuum for the system to open the column valve and establish an electron beam via the filament. Following the initiation of electron beam, the sample stage was moved to inspection location, which was approximately 10 mm from the end of the column. The positioning of the sample stage was done on the computer and assisted by a video camera located inside the chamber, allowing real-time observation of the stage movement. Inspection of sample was then performed by moving the sample stage and capturing SEM images. Images were captured based on their surface characteristics and image magnification.

3.2. Preparation and characterisation of developed sorbents

3.2.1. Preparation of lithium-based CO₂ sorbents

Lithium-based CO₂ sorbents were developed into i.e. waste-derived Li₄SiO₄ and pure Li₄SiO₄ sorbents. The preparation methods of both types of sorbents are described in the following subsections.
3.2.1.1. Preparation of waste-derived Li₄SiO₄ sorbents

All waste materials were developed into Li₄SiO₄-based CO₂ sorbents via dry preparation method i.e. solid state (SS) impregnation. The sorbents were prepared by mixing Li₂CO₃ powder with the studied waste materials using a Fritsch Pulverisette 2 mortar grinder until the solid mixture achieved homogeneity. Homogeneity of the solid mixture was considered achieved when there was no visible difference in the colour of both solids. The mixing time varied (3 to 5 min) with the type of waste materials used e.g. finer particle size fly ash samples (C- and R-PFA) taking shorter time to achieve homogeneity compared to significantly larger particle size bottom ash samples (FBA and POMBA).

Stoichiometric amount of Li₂CO₃ was used according to equation 3.1, where 2 mol of Li₂CO₃ reacts with 1 mol of SiO₂ to yield 1 mol of Li₄SiO₄ and 2 mol of gaseous CO₂. It is worthy to note that all waste-derived Li₄SiO₄ sorbents were prepared with 0, 5, 10 and 20% excess lithium.

\[
2Li_2CO_3(s) + SiO_2(s) \rightarrow Li_4SiO_4(s) + 2CO_2(g)
\]  

(3.1)

Hence, calculating the amount of Li₂CO₃ needed;

\[
1 \text{ mol of } Li_2CO_3 = [(6.94 \times 2) + (12.01 \times 1) + (16 \times 3)] \frac{g}{mol} Li_2CO_3
\]
\[ 1 \text{ mol of } Li_2CO_3 = 73.89 \frac{g}{mol} Li_2CO_3 \]

\[ 1 \text{ mol of } Li_2CO_3 = 73.89 \, g \, Li_2CO_3 \]

\[ 2 \text{ mol of } Li_2CO_3 = [73.89 \times 2] \, g \, Li_2CO_3 \]

\[ \therefore 2 \text{ mol of } Li_2CO_3 = 147.78 \, g \, Li_2CO_3 \]

Similarly, calculating the amount of SiO\textsubscript{2} needed;

\[ 1 \text{ mol of } SiO_2 = [(28.09 \times 1) + (16 \times 2)] \frac{g}{mol} SiO_2 \]

\[ 1 \text{ mol of } SiO_2 = 60.09 \frac{g}{mol} SiO_2 \]

\[ \therefore 1 \text{ mol of } SiO_2 = 60.09 \, g \, SiO_2 \]

Due to the varied amount of SiO\textsubscript{2} content in parent waste materials, the amount of waste samples was calculated according to the amount of SiO\textsubscript{2} needed. For example, there was 49.81 wt\% of SiO\textsubscript{2} found in RPFA. Hence, the amount of RPFA needed for a 0\% excess Li is as follows;
\[
\text{Amount of RPFA needed} = \frac{\text{Amount of } \text{SiO}_2 \text{ needed}}{\text{Weight percentage of SiO}_2 \text{ content in RPFA}}
\]

\[
= \frac{60.09 \text{ g}}{49.81} \times 100
\]

\[
\therefore \text{Amount of RPFA needed} = 120.63 \text{ g}
\]

The amount of excess lithium was calculated by adding 5, 10 and 20 wt% of Li\(_2\)CO\(_3\). For example:

\[
5 \text{ wt}\% \text{ excess of } \text{Li}_2\text{CO}_3 = 147.78 \text{ g Li}_2\text{CO}_3 \times \frac{5}{100}
\]

\[
\therefore 5 \text{ wt}\% \text{ excess of } \text{Li}_2\text{CO}_3 = 7.39 \text{ g Li}_2\text{CO}_3
\]

Thus, the total amount of Li\(_2\)CO\(_3\) needed to calcine Li\(_4\)SiO\(_4\) sorbent with 5% excess Li:

\[
5 \text{ wt}\% \text{ excess of } \text{Li}_2\text{CO}_3 = 14.78 \text{ g } + 0.74 \text{ g} = 15.52 \text{ g Li}_2\text{CO}_3
\]

Due to the limited availability of waste materials, only 10% of the total calculated amount of parent waste materials, Li\(_2\)CO\(_3\), SiO\(_2\) and excess Li were used during preparation method, as summarised in Table 3.2.
Table 3.2 Amount of starting materials required for waste-derived Li$_4$SiO$_4$ sorbents preparation. The amounts of parent waste materials needed were calculated according to the amount of SiO$_2$ contents in each waste material. Fixed amounts of parent waste materials were mixed with varying amounts of Li$_2$CO$_3$, depending on excess lithium.

<table>
<thead>
<tr>
<th>Starting materials</th>
<th>Amount of starting materials needed (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No excess</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>14.8</td>
</tr>
<tr>
<td>5%</td>
<td>-</td>
</tr>
<tr>
<td>10%</td>
<td>-</td>
</tr>
<tr>
<td>20%</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$ sources</td>
<td></td>
</tr>
<tr>
<td>Pure SiO$_2$</td>
<td>6.01</td>
</tr>
<tr>
<td>CPFA (55.3% SiO$_2$)</td>
<td>10.9</td>
</tr>
<tr>
<td>RPFA (49.8% SiO$_2$)</td>
<td>12.1</td>
</tr>
<tr>
<td>FBA (47.8% SiO$_2$)</td>
<td>12.6</td>
</tr>
<tr>
<td>POMBA (66.3% SiO$_2$)</td>
<td>9.06</td>
</tr>
</tbody>
</table>

The mixed powder was weighed (5 g) then calcined in an alumina crucible in a muffle furnace at 800 °C in air for 8 h. During this stage, the SiO$_2$ component of the waste materials reacted with Li$_2$CO$_3$, yielding Li$_4$SiO$_4$-based sorbents (Olivares-Marín et al., 2010). After calcination, the resulting products were homogenised using the same grinder. Subsequently, the waste-derived Li$_4$SiO$_4$ sorbents were analysed of their CO$_2$ uptake capacity using procedures as described in Section 3.2.3. Different amounts of excess lithium (5, 10 and 20 wt%) were added to the samples due to the high tendency of lithium to sublimate (Pfeifer and Knowles, 2004; Avalos-Rendon et al., 2010). These amounts of excess lithium were chosen...
so that there are sufficiently excess amount of lithium, without significantly exceeding the stoichiometric ratio, as this would produce a completely different substance following the heat treatment.

Following the solid state impregnation method, the effect of different sorbent preparation methods was also investigated. However, only POMBA was used for this purpose due to the highest CO$_2$ uptake by its corresponding SS-B-Li$_4$SiO$_4$ sorbents, as reported in Chapter 5. A wet preparation method (henceforth will be identified as the suspended impregnation (SI) method) was adopted from Chang et al. (2001), where the solid SiO$_2$ precursor (in this case, POMBA) suspended in a solution of lithium salt before subjecting it to thermal treatment (Chang et al., 2001). A detailed procedure on the calcination of waste-derived Li$_4$SiO$_4$ sorbent using SI method is explained below.

A desired amount of lithium nitrate (LiNO$_3$) was dissolved into deionised (DI) water. The amount of LiNO$_3$ used was determined by the stoichiometric ratio of Li:Si of Li$_4$SiO$_4$. Once the clear solution of LiNO$_3$ was prepared, the required amount of POMBA was added to the solution. After 20 minutes of stirring and mixing, the mixed solution was subjected to rotary evaporation at a pressure of 600 mbar at 140 °C for 1 hour, followed by a pressure of 100 mbar at the same temperature for 2 hours. The prepared powders were then subjected to heat treatment at 500 °C for 2 hours.
3.2.1.2. **Preparation of pure sorbents (P-Li₄SiO₄)**

Pure Li₄SiO₄ sorbents were prepared for comparison with the waste-derived sorbents, where pure SiO₂ powder was used and reacted with Li₂CO₃ powder to produce pure Li₄SiO₄ sorbents. Similar to the preparation of waste-derived sorbents, pure SiO₂ was mixed with Li₂CO₃ powder using a Fritsch Pulverisette 2 mortar grinder until the solid mixture achieved homogeneity. The mixed powder (approximately 5g) was then calcined in an alumina crucible in a muffle furnace at 800 °C in atmospheric air for 8h. After calcination, the resulting products were homogenised in the same grinder to ensure there was no agglomeration in the end product.

3.2.2. **CO₂ capture by sorbents**

3.2.2.1. **CO₂ capture by sorbents in pure CO₂ environment**

CO₂ capture analyses were conducted using a TA Instruments Q500 Thermogravimetric Analyser (TGA) in a controlled gas flowing environment. Initial weight (about 15 mg) of the sorbents was recorded. Prior to CO₂ sorption testing, the sorbents were preconditioned and dried in flowing N₂ at 5 ml/min. The sorption temperature was elevated and held at the target temperature (500, 600 or 700 °C) for 30 minutes at atmospheric pressure.

Then, the flowing gas was changed to 100% CO₂ gas at 100 ml/min to allow determination of CO₂ sorption capacity. The weight increase due to CO₂ sorption
was measured as a function of time at constant temperature and concentration of CO\textsubscript{2} at atmospheric pressure. The analysis continued for 120 minutes to allow sufficient time for the sorption process to occur. The flowing gas was then changed back to N\textsubscript{2} to allow desorption of CO\textsubscript{2} to take place. It is worthy to note that while this type of CO\textsubscript{2} desorption procedure may not necessarily represent the actual technique applied at an industrial scale, it is considered an established practice in a laboratory-scaled analysis, as reported in published work (Kato et al., 2005; Olivares-Marín et al., 2010). Finally, the sorbents were subjected to N\textsubscript{2} for another 120 minutes to ensure adequate time was provided for CO\textsubscript{2} desorption.

### 3.2.2.2. CO\textsubscript{2} capture by sorbents in CO\textsubscript{2}/N\textsubscript{2} environment

Similar to CO\textsubscript{2} capture by sorbents in pure CO\textsubscript{2} environment, initial weight (about 15 mg) of the sorbents was recorded. Prior to CO\textsubscript{2} sorption testing, the sorbents were preconditioned and dried in flowing N\textsubscript{2} at 5 ml/min. The sorption temperature was elevated and held at the targeted reaction temperature (500, 600 or 700 °C) for 30 minutes at atmospheric pressure.

Then, the flowing gas changed to 14 vol\% CO\textsubscript{2} with balance N\textsubscript{2} at 100 ml/min to allow reaction and determination of CO\textsubscript{2} sorption capacity. This particular composition of reaction gas was chosen to simulate the volumetric concentration of CO\textsubscript{2} in a typical flue gas composition which could be somewhere in between 10 and 15 vol\% for a coal-fired power plant (GCCSI, 2012). It should be noted that the reaction gas for this part of the analysis was supplied by a gas cylinder of pre-
mixed gases. The weight increase due to CO$_2$ sorption was measured as a function of time at constant temperature and concentration of CO$_2$ at atmospheric pressure. The analysis continued for 120 minutes to allow sufficient time for the sorption process to occur. The flowing gas was then changed back to N$_2$ to allow desorption of CO$_2$ to take place. The sorbents were subjected to N$_2$ for another 120 minutes to ensure enough time for CO$_2$ desorption.

### 3.2.2.3. Regeneration studies of sorbents

To examine the sorbents durability, CO$_2$ capture analyses were followed by regeneration steps. The same procedures as for single cycle (Subsection 3.2.1.1) were followed up until the desorption step, where 30 minutes of desorption time was used instead of 120 minutes. Shorter desorption time was employed to allow adequate CO$_2$ desorption and at the same time the analysis duration did not get excessively prolonged. The sorption/desorption cycles were repeated 9 more times to represent 10 cycles of regeneration steps. Parameters for analysis include number of cycles before the impregnated samples lose their ability to adsorb further CO$_2$ as well as the percentage of sorption decay rate of the samples.

### 3.2.2.4. Devolatilisation of parent waste materials

Devolatilisation of parent waste materials was determined in a TA Instruments Q500 Thermogravimetric Analyser. The procedures followed that of CO$_2$ capture in pure environment (Section 3.2.2.1), with the exception of the flowing gas.
Instead of pure CO$_2$, this analysis was conducted in pure N$_2$ environment. Other parameters such as operating temperatures (500, 600 and 700 °C) and analysis duration (120 minutes) remained the same. The analysis came to an end once the 120-minute analysis duration was completed.
Chapter 4 Characterisation of waste materials and Li$_4$SiO$_4$ sorbents

This chapter discusses the characterisation studies of the parent waste materials used in this research (Section 4.1) and the developed waste-derived Li$_4$SiO$_4$ sorbents (Section 4.2). Finally, Section 4.3 summarises the characterisation studies of all the materials investigated and also the potential performance of proposed CO$_2$ sorbents on the basis of physico-chemical properties.

4.1. Characterisation of parent waste materials

Four waste materials were selected as precursors for the development of high temperature sorbents, including two fly ash samples (CPFA and RPFA), one furnace bottom ash sample (FBA) and one palm oil mill boiler ash sample (POMBA), as listed in Table 3.1 in Chapter 3. These waste materials were selected from a large suite of samples based on their chemical compositions, in particular, high silica (SiO$_2$) content, as the sorbents developed from these precursors are Li$_4$SiO$_4$-based.

4.1.1. Particle size distribution

The particle size distributions of as-received CPFA, RPFA, FBA and POMBA samples were analysed using laser diffraction method, as described in Section 3.1.2.1. The D(0.1), D(0.5), D(0.8) and D(0.98) values presented in Table 4.1 indicate that 10%,
50%, 80% and 98% of the particles measured were less than or equal to the size stated in the table, respectively. CPFA contained the smallest particle sizes with $D(0.1)$, $D(0.5)$ and $D(0.98)$ values of 2.75, 13.14, 31.67 and 102.32 µm, respectively. The sequence is then followed by RPFA (4.52, 41.89 and 103.32 µm, respectively), FBA (57.68, 181.72 and 697.89 µm, respectively) and POMBA (86.35, 239.41 and 718.76 µm, respectively). As expected, the bottom ash sample FBA contains larger particle sizes compared to fly ash samples CPFA and RPFA, as bottom ash consists of particles that are too large to be carried in the flue gases and impact on the furnace walls or fall through open grates to an ash hopper at the bottom of the furnace.

In industrial applications, POMBA is produced by burning palm oil shells and husks in palm oil mills to produce steam for electricity generation, which is essential in extracting crude palm oil. For best performance and also considering environmental pollution control, 80% palm husk and 20% palm shell are typical proportion used in a steam boiler for electricity generation in a palm oil mill (Borhan et al., 2010). Hence, the particle sizes of the resulting ash determined by the size of the disintegration of the raw materials fed into the boiler. Consequently, there are significant differences between particle sizes of POMBA and its coal-derived ash CPFA, RPFA and FBA samples.
Table 4.1 D(0.1), D(0.5), D(0.8) and D(0.98) values of particle size distribution of waste materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D(0.1) (µm)</td>
</tr>
<tr>
<td>CPFA</td>
<td>2.75</td>
</tr>
<tr>
<td>RPFA</td>
<td>4.52</td>
</tr>
<tr>
<td>FBA</td>
<td>57.68</td>
</tr>
<tr>
<td>POMBA</td>
<td>86.35</td>
</tr>
</tbody>
</table>

Comparing the particle size distribution shown in Table 4.1 and other similar samples found in published studies proved to be in good agreement. Olivares-Marin et al. (2010) reported similar particle size distribution of coal-derived fly ash samples, where 98% of the particles measured were less than or equal to 250 µm (Olivares-Marin et al., 2010). Consoli et al., (2007) reported similar particle size distribution of their coal bottom ash sample having average diameter D(0.5) value of 144 µm (Consoli et al., 2007). However, the particle size distribution values of palm oil boiler ash reported in other studies varied significantly. Chong et al., (2009) reported particle size distribution of oil palm ash within the range of 75 to 2000 µm, with 35% of the particles measured were larger than 1000 µm, 59% of the particles measured were in between 100 and 1000 µm and the remaining of the sample volume having less than 100 µm in size (Chong et al., 2009).
4.1.2. Loss-on-ignition (LOI) and major oxides composition analysis

Table 4.2 shows the LOI values and major elements presented as their oxides form for the parent waste materials. LOI value is a measure of unburnt carbon in the waste materials and can also be used as an indicator for the efficiency of the combustion process (Levandowski and Kalkreuth, 2009). Some differences are immediately evident, although in general LOI values of waste materials were found to be relatively low with the largest value reported for FBA (8.47 wt%), followed by POMBA (8.12 wt%), RPFA (4.09 wt%) and CPFA (4.00 wt%). These values are in good agreement with values found in literatures of similar materials, where the LOI values for coal-derived PFA samples were reported to be lower than their bottom ash counterparts (Vassilev et al., 2005; Levandowski and Kalkreuth, 2009; Dai et al., 2010). The LOI value of the biomass-derived POMBA sample was also in good agreement with published literature of 7.3 wt% (Zainudin et al., 2005). Higher LOI values of biomass-derived ashes in comparison to that of coal-derived ash samples were also reported in published studies, where LOI values of 28 and 15 wt% for wood- and wheat straw-derived biomass ashes were reported (Thy et al., 2006).

The SiO$_2$ contents of the parent waste materials were of particular interest, as high concentration of SiO$_2$ is essential in order to ensure maximal amount of Li$_4$SiO$_4$ was generated using the waste materials, and therefore, maximising the amount of CO$_2$ uptake by the sorbents. As shown in Table 4.2, all waste materials contain significant amounts of SiO$_2$. The highest concentration of SiO$_2$ was found in
POMBA (66.30 wt%), followed by CPFA (55.29 wt%), RPFA (49.81 wt%) and FBA (47.77 wt%). Table 4.2 also shows that apart from SiO$_2$, there are considerable amounts of Al$_2$O$_3$ in all waste materials, with the highest Al$_2$O$_3$ amount found in RPFA (23.05 wt%), followed by FBA (21.55 wt%), CPFA (20.73 wt%) and the lowest amount in POMBA (1.34 wt%).

Table 4.2 Major elements analysis of the waste materials.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CPFA</td>
</tr>
<tr>
<td>LOI</td>
<td>4.00</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>55.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>20.7</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.23</td>
</tr>
<tr>
<td>CaO</td>
<td>4.04</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.21</td>
</tr>
<tr>
<td>MgO</td>
<td>1.79</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.04</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.92</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.84</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.61</td>
</tr>
<tr>
<td>MnO</td>
<td>0.13</td>
</tr>
</tbody>
</table>

In addition, relatively lower amounts of other elements such as iron, calcium, potassium, magnesium and phosphorus can also be found in all parent waste materials. Comparatively high concentrations of Fe$_2$O$_3$ were found in the coal-derived waste materials, with the highest found in FBA (10.47 wt%), followed by RPFA (7.13 wt%) and CPFA (6.23 wt%), while the biomass-derived waste material POMBA contained comparatively low Fe$_2$O$_3$ at 2.35 wt%. In contrast, highest
concentration of CaO was found in POMBA (6.46 wt%), whereas similar concentrations found in RPFA (4.90 wt%), FBA (4.83 wt%) and CPFA (4.04 wt%). Similar trends can be seen for K$_2$O, MgO and P$_2$O$_5$, where the highest concentrations of these elements (6.80, 3.78 and 3.09 wt%, respectively) were found in POMBA compared to the rest of the waste materials. Significant amount of potassium and phosphorus are expected in biomass, especially in oil palm-derived waste materials as these are essential elements used in fertilizers (Yin et al, 2008).

Variances in concentrations of elements across waste materials are expected, since they are highly dependent on the type and origin of the feedstock used during combustion process (Vassilev et al., 2005). However, major oxides compositions of coal-derived waste materials CPFA, RPFA and FBA are in good agreement with published values, where four of the highest amount of oxides are in the order of SiO$_2$>Al$_2$O$_3$>Fe$_2$O$_3$>CaO (Medina et al., 2010). In addition, major oxides compositions of biomass-derived waste material POMBA also are in good agreement with previously published studies, where SiO$_2$ was identified as the main component (Zainudin et al., 2005; Ooi et al., 2013). Furthermore, relatively higher concentrations of K$_2$O, CaO and MgO in POMBA compared to coal-derived ashes are also found in other biomass-derived ashes, where similar values reported in published studies (Thy et al., 2006; Borhan et al., 2010). Nonetheless, the key chemical compositions (SiO$_2$) of all waste materials were significant enough to be deemed suitable for the development of Li$_4$SiO$_4$-based sorbents at the beginning stage of this research.
While SiO$_2$ content in waste materials is important in order to maximize the amount of Li$_4$SiO$_4$, the unavoidable presence of other oxides in the parent waste materials is expected to affect the performance of CO$_2$ uptake by waste-derived Li$_4$SiO$_4$ sorbents. Gauer and Heschel (2006) reported the effect of hetero elements, such as Fe and Al doping of pure Li$_4$SiO$_4$ sorbents on CO$_2$ uptake performance (Gauer and Heschel, 2006). The authors adopted the concept of designing solid state ion conductors to improve ion mobility, which could be achieved by introducing defects into crystalline Li$_4$SiO$_4$ through appropriate doping of foreign elements such as Al and Fe.

Subsequently, they found that by doping Li$_4$SiO$_4$ with either Al or Fe improved the reactivity performance of Li$_4$SiO$_4$ in capturing CO$_2$ at temperatures above 500 °C. However, Li$_4$SiO$_4$ doped with Fe presented further improvement in releasing captured CO$_2$ compared to Al. The authors explained the less negative Gibbs energy of formation of Fe$_2$O$_3$ (-742 kJ/mol) compared to SiO$_2$ (-856 kJ/mol) might have caused the oxygen bonds in Li$_4$SiO$_4$ to be weakened and therefore the detachment of O$^{2-}$ is eased. On the contrary, oxygen bonds might be strengthened by Al doping due to the higher negative Gibbs energy of formation of Al$_2$O$_3$ (-1582 kJ/mol) (Gauer and Heschel, 2006).

The weight percentages of dopant Al$_2$O$_3$ and Fe$_2$O$_3$ (maximum of 2.53 and 3.90 wt%, respectively) used were significantly lesser than that in most of the parent waste materials (with the exception of POMBA) used in the current research. Therefore, the CO$_2$ sorption reactivity performance of POMBA-derived Li$_4$SiO$_4$
sorbent is expected to be similar to the findings of Gauer and Heschel (2006). In contrast, due to the extra amount of Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} found in the rest of the parent waste materials, the reactivity performance of their corresponding Li\textsubscript{4}SiO\textsubscript{4} sorbents are predicted to be further improved.

In another study conducted by Mejio-Trejo et al. (2008), the authors found that CO\textsubscript{2} uptake improved up to 7\% compared to Li\textsubscript{4}SiO\textsubscript{4} sorbent by doping pure Li\textsubscript{4}SiO\textsubscript{4} with Na in small quantity of up to 0.15 mol, which is equivalent to approximately 4.05 wt\% of Na\textsubscript{2}O (Mejio-Trejo et al., 2008). They also found that Na was located on the surface of Li\textsubscript{4}SiO\textsubscript{4} particles, and thus, aiding the CO\textsubscript{2} chemisorption process and subsequently increasing the CO\textsubscript{2} uptake capacity of Na-doped Li\textsubscript{4}SiO\textsubscript{4} sorbent. It is then expected that the CO\textsubscript{2} uptake performance of waste-derived Li\textsubscript{4}SiO\textsubscript{4}-based sorbents will be positively affected by the small amounts of Na found in the parent waste materials.

4.1.3. Phase composition analysis of waste materials

Figures 4.1 to 4.4 show the x-ray diffractograms of waste materials CPFA, RPFA, FBA and POMBA, respectively. As expected, the main crystalline phase was quartz (SiO\textsubscript{2}) in all coal-derived waste materials (CPFA, RPFA and FBA). The identification of crystalline phase of SiO\textsubscript{2} as quartz contributes to produce a good high temperature Li\textsubscript{4}SiO\textsubscript{4}-based CO\textsubscript{2} sorbent, according to Seggiani et al. (2011). The authors reported that quartz produced porous and small (less than 1 µm) Li\textsubscript{4}SiO\textsubscript{4} particle sizes which provide large contact area for CO\textsubscript{2} molecules to react
with (Seggiani et al., 2011). On the contrary, amorphous silica produced dense and larger Li$_4$SiO$_4$ particles (average of 80 µm), resulting in lower surface area (Seggiani et al., 2011). In addition to quartz, aluminosilicate crystalline phases of mullite (Al$_6$Si$_2$O$_{13}$) and sillimanite (Al$_2$SiO$_5$) were also identified in all coal-derived waste materials.

Amorphous peaks (2θ ranging from about 15 to 35° for C- and RPFA; about 15 to 25° and 55 to 65° for FBA) can also be identified in these diffractograms, indicating coexistence of amorphous constituents in the waste materials. It is thought that amorphous phase of aluminosilicate constituents was also found in the sample, as suggested by previously published study on mineral phases in coal fly ash samples (Kumar et al., 2001). Also as seen in Figures 4.1 to 4.3, there were various unidentified peaks on the diffractograms of the coal-derived waste materials. This is because coal is comprised of various other minerals such as lime and magnetite in addition to high amount of carbon (Levandowski et al., 2009; Vassilev et al., 2005), and therefore, by-products of coal combustion process are expected to contain traces of various minerals.
Figure 4.1 XRD diffractogram of CPFA.

Figure 4.2 XRD diffractogram of RPFA.

Q = Quartz (SiO$_2$)
M = Mullite (Al$_6$Si$_2$O$_{13}$)
S = Sillimanite (Al$_2$SiO$_3$)
Similar to its coal-derived waste materials counterparts, quartz was also identified as the main crystalline phase of the biomass-derived waste material POMBA, as shown in Figure 4.4. In contrast to the coal-derived waste materials CPFA, RPFA and FBA, the absence of amorphous peak in POMBA indicates that there is no significant coexistence of amorphous constituents in the biomass-derived waste material. Consequently according to observations previously discussed by Seggiani et al. (2011), it is expected that Li$_4$SiO$_4$ sorbents deriving from this parent waste material would exhibit porous textural characteristics and smaller in particle size than the rest of the waste materials, and therefore, have the ability to capture more CO$_2$ (Seggiani et al., 2011). Moreover, peaks of crystalline potassium aluminium bis(tetraoxidosulphate) dodecahydrate (KAl(SO$_4$)$_2$.12H$_2$O) and jadeite (Al$_{0.52}$Ca$_{0.47}$Fe$_{0.48}$Na$_{0.53}$Si$_2$O$_8$) were also identified.
4.1.4. Nitrogen adsorption/desorption isotherm profiles and surface areas

The porous texture of the parent waste materials was also analysed by nitrogen adsorption and desorption isotherms conducted at 77 K and the resulting isotherm profiles are shown in Figures 4.5 to 4.8. All of the materials exhibit similar convex isotherms to the $P/P_0$ axis over its entire range which corresponds to type II isotherm according to the IUPAC classification (IUPAC, 1985). These type II isotherms are associated with non-porous or macroporous adsorbents with unobstructed monolayer/multilayer adsorption and indicated by a distinctive point in the isotherms labelled as Point B at the beginning of the almost linear middle section. At this point, the monolayer coverage is complete and multilayer adsorption begins (IUPAC, 1985). This textural characteristic explains the low
volume of nitrogen adsorbed by the parent waste materials, ranging from maximum volume adsorbed of 3.330 to 6.318 cm$^3$/g STP (Table 4.3).

In addition, all waste materials isotherm profiles exhibit hysteresis loops which are associated with capillary condensation taking place in mesopores (IUPAC, 1985). Specifically, the hysteresis loops are of type H3 according to IUPAC classification and correspond to adsorption and desorption branches almost vertical and nearly parallel over a wide range of $P/P_\infty$. Also, this type of hysteresis loop does not have limiting uptake over a range of high relative pressure $P/P_\infty$. Taking into consideration that type II isotherm profiles were exhibited by all materials, it can be deduced that all parent waste materials exhibit a combination of macroporosity and mesoporosity. Furthermore, the POMBA isotherm profile shows low pressure hysteresis which can be recognised by the extended loop to the lowest attainable pressure, as shown in Figure 4.8. This phenomenon may be related to the swelling of a non-rigid porous structure exist in the waste material (IUPAC, 1985).
Figure 4.5 Nitrogen adsorption/desorption isotherm at 77 K of CPFA.

Figure 4.6 Nitrogen adsorption/desorption isotherm at 77 K of RPFA.
Figure 4.7 Nitrogen adsorption/desorption isotherm at 77 K of FBA.

Figure 4.8 Nitrogen adsorption/desorption isotherm at 77 K of POMBA.
Surface area values of all parent waste materials can be found in Table 4.3. It is observed that surface area values of all waste materials were relatively low and follow the descending order of CPFA (4.74 m$^2$/g), followed by RPFA (4.10 m$^2$/g), FBA (3.77 m$^2$/g) and POMBA (2.82 m$^2$/g). The order of surface area values of the parent waste materials inversely correlates with that of the particle size values: CPFA>RPFA>FBA>POMBA, as presented in Table 4.1.

Comparing the surface area of parent waste materials in this study with that of published data, the surface area values of the fly ashes CPFA and RPFA are comparable to that of reported by Medina et al. (2010) (4.73 m$^2$/g) (Medina et al., 2010). However, there is a slight difference on BET surface area of oil palm ash reported by Zainuddin et al. (2005), where 10.2 m$^2$/g of surface area was obtained (Zainuddin et al., 2005). The difference could be due to different geological origins of the biomass obtained in the study, as this affects the chemical compositions of the biomass and subsequently affecting the amount of organic matter burn-off of the materials. This then affects the textural characteristics and surface area of the materials.

Table 4.3 also shows total pore volume and pore diameter of waste materials calculated using the Barrett-Joyner-Halenda (BJH) method. In general, the total pore volumes of the waste materials were relatively low and could be explained by the equally low calculated surface areas. The total pore volumes of all waste materials were highest for the fly ash samples RPFA and CPFA with volumes of 0.0079 and 0.0077 cm$^3$/g, respectively. Total pore volume of POMBA was the
lowest value compared to other waste materials with 0.0034 cm$^3$/g, while FBA contained 0.0069 cm$^3$/g of total pore volume. All waste materials contained pore diameter larger than 2 nm but smaller than 50 nm which categorised them as having mesopore type of porosity according to the IUPAC classification (IUPAC, 1985).

Table 4.3 BET surface area, BJH total pore volume and pore diameter of waste materials.

<table>
<thead>
<tr>
<th>Waste material</th>
<th>BET surface area (m$^2$/g)</th>
<th>BJH total pore volume x 10$^{-3}$ (cm$^3$/g)</th>
<th>BJH pore diameter (nm)</th>
<th>Volume adsorbed (cm$^3$/g STP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPFA</td>
<td>4.74</td>
<td>7.71</td>
<td>6.02</td>
<td>6.32</td>
</tr>
<tr>
<td>RPFA</td>
<td>4.10</td>
<td>7.93</td>
<td>2.42</td>
<td>4.77</td>
</tr>
<tr>
<td>FBA</td>
<td>3.77</td>
<td>6.92</td>
<td>3.08</td>
<td>4.46</td>
</tr>
<tr>
<td>POMBA</td>
<td>2.82</td>
<td>3.44</td>
<td>20.2</td>
<td>3.33</td>
</tr>
</tbody>
</table>

4.1.5. Scanning electron microscope analysis

Figures 4.9 to 4.12 show SEM micrographs of the parent waste materials at 5000 times magnification. There are two classified differences that can be identified between the PFA (Figures 4.9 and 4.10) and bottom ash (Figures 4.11 and 4.12) samples. As seen from Figures 4.9 and 4.10, the PFA samples had no obvious porosity on the surface of the particles. Additionally, the samples consist of spherical particles and agglomerates of various particle sizes (1 – 10 µm) that correspond to inorganic constituents caused by high temperature burning of coal during combustion process (Rubio et al., 2008).
On the other hand, FBA and POMBA samples consist of polyhedral and non-porous particles as well as agglomerates, as shown in Figures 4.11 and 4.12. The particle sizes were also considerably larger than CPFA and RPFA for these samples (2 – 15 µm), considering the images were taken at the same degree of magnification as CPFA and RPFA samples. The particle sizes shown in Figures 4.11 and 4.12 are also in good agreement with the particle sizes described in subsection 4.1.1, where much larger particle sizes are observed in bottom ash samples FBA and POMBA compared to fly ash samples CPFA and RPFA.

SEM micrographs of waste materials confirm the textural analysis data discussed previously. Nitrogen adsorption/desorption isotherm profiles of waste materials exhibit type II isotherm that associated with non-porous adsorbents, as shown in Figures 4.9 to 4.12. These characteristics of waste materials contribute to the relatively low volume of nitrogen adsorbed, as reported in the previous section. They also confirm the type H3 hysteresis loop that associated with assemblage of plate-like particles which are loosely coherent that caused the aggregates to develop slit-shaped pores.
Figure 4.9 SEM micrograph of CPFA.

Figure 4.10 SEM micrograph of RPFA.
Figure 4.11 SEM micrograph of FBA.

Figure 4.12 SEM micrograph of POMBA.
4.2. Characterisation of waste-derived Li$_4$SiO$_4$ sorbents

In this section, the characterisation of Li$_4$SiO$_4$-based sorbents is discussed. As described in Chapter 3, the sorbents were developed using solid state method by mixing stoichiometric amounts of the waste materials with powder Li$_2$CO$_3$ homogeneously before being subjected to heat treatment at 800 °C for 8h. It should be noted that sorbents were prepared with different amounts of excess lithium (0, 5, 10, 20 wt%).

Prepared sorbents are labelled in the form of W-X-Y-Z, where W represents preparation method of the sorbent (SS for solid state; SI for suspended impregnation), X indicates waste material that was used to develop the sorbent (C, R, F or B for CPFA, RPFA, FBA or POMBA, respectively), while Y symbolises the type of sorbent (Li$_4$SiO$_4$ in this chapter) and Z indicates the amount (in wt%) of excess lithium. For example, SS-B-Li$_4$SiO$_4$-10 denotes a POMBA-based Li$_4$SiO$_4$ sorbent prepared using solid state method with 10 wt% excess lithium.

There are five types of Li$_4$SiO$_4$-based sorbents developed in this research, deriving from CPFA, RPFA, FBA and POMBA (identified henceforward in this thesis as SS-C-Li$_4$SiO$_4$, SS-R-Li$_4$SiO$_4$, SS-F-Li$_4$SiO$_4$ and SS-B-Li$_4$SiO$_4$, respectively) samples as well as a pure-Li$_4$SiO$_4$ (SS-P-Li$_4$SiO$_4$) sorbent developed using a commercial SiO$_2$ powder for comparison purposes.
A series of physical and chemical characterisation analyses were carried out to examine the features of the sorbents, including X-ray diffraction (XRD) to ascertain the mineral phases present, especially that of crystalline Li$_4$SiO$_4$; Fourier transform infrared (FTIR) analysis to investigate the chemical bonds of the functional groups which could also support the outcome provided by XRD analysis; scanning electron microscope (SEM) analysis to observe the textural characteristics as well as the particle size of sorbents; and nitrogen adsorption/desorption isotherms to determine BET surface area and porous texture of sorbents.

### 4.2.1. Phase composition analysis of Li$_4$SiO$_4$ sorbents

Phase composition analysis was performed on all sorbents and the resulting diffractograms were compared with Joint Committee on Powder Diffraction Standards (JCPDS) database to determine the mineral phases present. Figure 4.13 shows x-ray diffractograms of SS-P-Li$_4$SiO$_4$ with different amounts of excess lithium a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10; d) SS-P-Li$_4$SiO$_4$-20. As shown, the sorbents exhibit sharp diffraction peaks labelled by (*) attributed to Li$_4$SiO$_4$ and the variance in peak intensities can be attributed to different crystal sizes as well as the strain within the crystallites (Venegas et al., 2007). As provided by the JCPDS standard, the crystal structure of Li$_4$SiO$_4$ found in SS-P-Li$_4$SiO$_4$ sorbents were all monoclinic with space group P2$_1$/m and lattice parameters of $a = 11.532$ Å, $b = 6.075$ Å, $c = 16.678$ Å, $\beta = 99.04^\circ$. 
Comparing across sorbents with different amounts of excess lithium, there are some SiO₂ present in SS-P-Li₄SiO₄-0, whereas no SiO₂ was detected in subsequent excess of lithium addition SS-P-Li₄SiO₄-5, SS-P-Li₄SiO₄-10 and SS-P-Li₄SiO₄-20. This suggests a more complete Li₄SiO₄ synthesis with at least 5 wt% excess lithium under synthesis conditions at 800 °C for 8h. Lithium sublimation is thought to be the reason of this occurrence, as previously reported (Antolini and Ferretti, 1995; Pfeiffer and Knowles, 2004). Loss of lithium during Li₄SiO₄ synthesis occurs as Li₂CO₃ melts and decomposes to evolve into CO₂ and Li₂O at temperature higher than 710 °C (Lu and Lee, 2000). Therefore, excess amount of lithium in Li₄SiO₄ synthesis was regarded to be a reasonable step to implement in order to increase the amount of Li₄SiO₄ produced.
Figure 4.13 XRD diffractograms of pure Li₄SiO₄ with different amounts of excess lithium a) SS-P-Li₄SiO₄-0; b) SS-P-Li₄SiO₄-5; c) SS-P-Li₄SiO₄-10; d) SS-P-Li₄SiO₄-20.
Figure 4.14 shows the X-ray diffractograms of SS-C-Li_4SiO_4 with different amounts of excess lithium a) SS-C-Li_4SiO_4-0; b) SS-C-Li_4SiO_4-5; c) SS-C-Li_4SiO_4-10; d) SS-C-Li_4SiO_4-20. As shown, the waste-derived sorbents exhibit relatively sharp peaks compared to SS-P-Li_4SiO_4 sorbents, albeit slightly amorphous based on amorphous peaks detected at 2θ value range about 30 – 35 °. The crystal structure of Li_4SiO_4 found in SS-C-Li_4SiO_4 was also monoclinic with the same space group and lattice parameters as found in SS-P-Li_4SiO_4.

Unsurprisingly, Li_4SiO_4 was not the only crystalline phase present, as other crystal constituents were also detected in all SS-C-Li_4SiO_4 sorbents, including Li_2SiO_3, LiAlO_2 and LiAlSiO_4. The presence of crystal constituents other than Li_4SiO_4 and Li_2SiO_3 in the waste-derived sorbents was due to various compounds other than SiO_2 identified in its parent sample CPFA, as shown in Table 4.2 (Section 4.1). Since aluminosilicates like mullite (Al_6Si_2O_13) and sillimanite (Al_2SiO_5) were found in CPFA, it is expected that the resulting sorbents produced other lithium compounds deriving from these aluminosilicate crystals.

The addition of different amounts of excess lithium used in preparing the sorbents does seem to affect the intensities of Li_4SiO_4 peaks. This could be contributed by two possibilities, with one of them being due to lithium sublimation of Li_2CO_3 during synthesis, and therefore, requiring more lithium than is stoichiometrically needed. Another possibility is that, Li_2CO_3 may have reacted with other available compounds in CPFA such as the aluminosilicates, reducing the amount of Li_2CO_3 to
react with SiO$_2$ in the parent sample CPFA, and therefore, producing the other lithium crystals in resulting SS-C-Li$_4$SiO$_4$ sorbents.

Comparing with diffractograms of the waste material in Figure 4.1, it is expected that the chemical phase composition of CPFA has changed following the addition of Li$_2$CO$_3$ and subsequent heat treatment at 800 °C for 8h. Figure 4.8 also shows that there were no peaks that associated with Li$_2$CO$_3$ and SiO$_2$ in SS-C-Li$_4$SiO$_4$ sorbents, and therefore, indicating that both compounds have completely reacted during the synthesis process. The absence of peaks associated with aluminosilicates, such as mullite and sillimanite, in Figure 4.14 indicates that these mineral phases have reacted with Li$_2$CO$_3$ addition during preparation process and produced the various lithium aluminate crystals, as previously reported.

Some amorphous peaks (at approximately $2\theta$ values of 23, 35, 45 and 50) were also detected, indicating amorphous constituents in SS-C-Li$_4$SiO$_4$ sorbents. Amorphous constituents present in the waste-derived sorbents could be advantageous to CO$_2$ uptake performance due to the versatility of amorphous structure to hold CO$_2$ molecules, and therefore, increasing the CO$_2$ uptake capacity of the sorbents. Furthermore, the diffusion of CO$_2$ molecules into amorphous structure is faster than that in crystalline due to the atomic disorder (Sadoway, 2010), and therefore, increasing the rate of CO$_2$ sorption of the sorbents.
Figure 4.14 XRD diffractograms of CPFA-derived Li$_4$SiO$_4$ with different amounts of excess lithium: a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10; d) SS-C-Li$_4$SiO$_4$-20.
Similar diffractograms can also be observed for sorbents derived from RPFA and FBA waste materials, as can be seen in Figures 4.15 and 4.16. The main crystal phase present in the sorbents was Li$_4$SiO$_4$, as expected from reaction between Li$_2$CO$_3$ and significant presence of SiO$_2$ in the waste materials. Also, the presence of Li$_2$SiO$_3$, LiAlO$_2$ and LiAlSiO$_4$ was also detected resulting from reaction between Li$_2$CO$_3$ and other elements already exist in the parent waste materials such as the aluminosilicates. Similar observations in the diffractogram patterns of these sorbents are expected as all three parent waste materials originated from coal and have similar chemical compositions, as reported in Table 4.2.

There are also several amorphous peaks detected in SS-R-Li$_4$SiO$_4$ and SS-F-Li$_4$SiO$_4$ sorbents, as shown in Figures 4.15 and 4.16 at roughly the same 2θ values as in Figure 4.14. This indicates the coexistence of amorphous constituents, such as Li$_4$SiO$_4$ and lithium aluminosilicate derivatives, in the waste-derived sorbents. The coexistence of amorphous constituents is expected to be found in waste-derived Li$_4$SiO$_4$ sorbents, as there were amorphous peaks detected in parent waste materials RPFA and FBA. In addition, amorphous components might have existed in waste-derived Li$_4$SiO$_4$ sorbents due to the incomplete crystallisation of Li$_4$SiO$_4$. 

Figure 4.15 XRD diffractograms of RPFA-derived Li$_4$SiO$_4$ with different amounts of excess lithium a) SS-R-Li$_4$SiO$_4$-0; b) SS-R-Li$_4$SiO$_4$-5; c) SS-R-Li$_4$SiO$_4$-10; d) SS-R-Li$_4$SiO$_4$-20.
Figure 4.16 XRD diffractograms of FBA-derived Li₄SiO₄ with different amounts of excess lithium a) SS-F-Li₄SiO₄-0; b) SS-F-Li₄SiO₄-5; c) SS-F-Li₄SiO₄-10; d) SS-F-Li₄SiO₄-20.
Figure 4.17 shows the XRD diffractograms of SS-B-Li$_4$SiO$_4$ with different amounts of excess lithium a) SS-B-Li$_4$SiO$_4$-0; b) SS-B-Li$_4$SiO$_4$-5; c) SS-B-Li$_4$SiO$_4$-10; d) SS-B-Li$_4$SiO$_4$-20. The waste-derived sorbents exhibit sharp peaks comparable to SS-P-Li$_4$SiO$_4$ sorbents and more defined peaks compared to the rest of coal-derived SS-C-Li$_4$SiO$_4$, SS-R-Li$_4$SiO$_4$ and SS-F-Li$_4$SiO$_4$ sorbents. Nevertheless, the crystal structure of Li$_4$SiO$_4$ found in SS-B-Li$_4$SiO$_4$ was also monoclinic with the same space group and lattice parameters, as found in SS-P-Li$_4$SiO$_4$.

Similar to other waste-derived sorbents discussed previously, Li$_4$SiO$_4$ was not the only crystalline phase present, as other crystals were also detected in SS-B-Li$_4$SiO$_4$ sorbents including SiO$_2$, Li$_2$SiO$_3$ and LiAlSiO$_4$. A similar observation was seen for SS-P-Li$_4$SiO$_4$ sorbents, where the peaks associated with SiO$_2$ crystals in the waste-derived sorbents can also be observed (Figure 4.17), which is probably due to lithium sublimation occurred in Li$_2$CO$_3$ during synthesis process.

On the other hand, there is no SiO$_2$ detected in SS-B-Li$_4$SiO$_4$-5, SS-B-Li$_4$SiO$_4$-10 and SS-B-Li$_4$SiO$_4$-20 which indicates a more complete Li$_4$SiO$_4$ synthesis under synthesis conditions at 800 °C for 8h. It is thought that the already limited amount of SiO$_2$ present in POMBA had completely reacted with Li$_2$CO$_3$ to produce the equally limited amount of SS-B-Li$_4$SiO$_4$. Excess Li$_2$CO$_3$ is then believed to react with next available compounds in POMBA, such as calcium to produce other unidentified lithium crystals in SS-B-Li$_4$SiO$_4$, which a combination of these compounds is possible.
Comparing with the diffractogram obtained for the parent material (Figure 4.4), it is obvious that the chemical phase composition of POMBA has changed following the addition of Li$_2$CO$_3$ and heat treatment at 800 °C for 8h during synthesis of SS-B-Li$_4$SiO$_4$ sorbents. The coexistence of Li$_2$SiO$_3$ in SS-B-Li$_4$SiO$_4$ sorbents is expected, as this proved that the reaction between Li$_2$CO$_3$ and the SiO$_2$ in POMBA advanced according to equation 2.2 (Section 2.3.2).

Also, it should be noted that while there are more peaks associated with lithium aluminosilicate crystals detected in other waste-derived Li$_4$SiO$_4$ sorbents, there was only LiAlSiO$_4$ found in SS-B-Li$_4$SiO$_4$ sorbents. This is due to substantially low Al$_2$O$_3$ (1.34 wt%) found in the parent waste material POMBA. In addition, there was no potassium-containing crystal detected in Figure 4.17, suggesting that the potassium could be lost in some way, as it has been reported that potassium in potassium zirconates are not very stable and decompose at temperature as low as 570 up to 750 °C which are lower than synthesis temperature used in this study at 800 °C (Dash et al., 1996).
Figure 4.17 XRD diffractograms of POMBA-derived Li$_4$SiO$_4$ with different amounts of excess lithium a) SS-B-Li$_4$SiO$_4$-0; b) SS-B-Li$_4$SiO$_4$-5; c) SS-B-Li$_4$SiO$_4$-10; d) SS-B-Li$_4$SiO$_4$-20.
4.2.2. **Fourier transform infrared (FTIR) analysis of Li₄SiO₄ sorbents**

FTIR analyses were conducted to characterise chemical functional groups present, based on the characteristics of vibrational and rotational energies of different molecular bonds. Figure 4.18 shows the FTIR spectra of SS-P-Li₄SiO₄ sorbents with different amounts of excess lithium a) SS-P-Li₄SiO₄-0; b) SS-P-Li₄SiO₄-5; c) SS-P-Li₄SiO₄-10; d) SS-P-Li₄SiO₄-20. In general, all SS-P-Li₄SiO₄ sorbents exhibit similar spectra patterns with slight differences in the intensity of infrared absorption bands.

Upon closer observations, strong presence of absorption bands can be detected in all sorbents in the wavenumber regions between 600 and 1000 cm⁻¹ as well as between 1400 and 1600 cm⁻¹. The earlier may be attributed to vibration bands of different metal-oxygen bonds, including Si-O- (807 cm⁻¹) in SiO₄ tetrahedral which exist in Li₄SiO₄ (Humphreys and Hatherly, 1995; Shokri et al., 2009) and Li-O- at 964 cm⁻¹ (Ortiz-Landeros et al., 2011). However, the latter may be associated with -C=O (between 1443 and 1588 cm⁻¹) vibration bands in CO₂ of Li₂CO₃ (Hwang et al., 2007; Zhang et al., 2008). Table 4.4 summarises the absorption bands identification of SS-P-Li₄SiO₄ sorbents.
Figure 4.18 FTIR spectra of SS-P-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10; d) SS-P-Li$_4$SiO$_4$-20.
Table 4.4 Absorption bands identification of SS-P-Li$_4$SiO$_4$ sorbents.

<table>
<thead>
<tr>
<th>Absorption bands of sorbents (cm$^{-1}$)</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>1475</td>
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<tr>
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</tr>
<tr>
<td>1247</td>
<td>Si$_2$O</td>
</tr>
<tr>
<td>1194</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>950</td>
<td>Li-O$^-$</td>
</tr>
<tr>
<td>915</td>
<td></td>
</tr>
<tr>
<td>871</td>
<td>Si-O$^-$ in SiO$_2$ tetrahedral</td>
</tr>
<tr>
<td>826</td>
<td></td>
</tr>
<tr>
<td>806</td>
<td></td>
</tr>
<tr>
<td>739</td>
<td>SiO$_3^{2-}$ (mesasilicate)</td>
</tr>
<tr>
<td>684</td>
<td></td>
</tr>
</tbody>
</table>

Comparing spectra patterns across sorbents with different amounts of excess lithium, the absorption bands associated with carbonates in Li$_2$CO$_3$ (between 1443 and 1588 cm$^{-1}$) were present in all SS-P-Li$_4$SiO$_4$ sorbents. It is assumed that there are still remaining Li$_2$CO$_3$ present in all sorbents and could be a direct result of excess lithium added during the preparation process.
Figure 4.19 shows the FTIR spectra of SS-C-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10; d) SS-C-Li$_4$SiO$_4$-20. In general, SS-C-Li$_4$SiO$_4$ revealed similar spectral patterns to that of SS-P-Li$_4$SiO$_4$, with absorption bands observed in two different wavenumber regions, namely 1400 and 1500 cm$^{-1}$ and 800 and 1000 cm$^{-1}$. Absorption bands in the earlier region are identified to be associated with -C=O (between 1434 and 1522 cm$^{-1}$) vibration bands in CO$_2$ of Li$_2$CO$_3$, similar to the pure SS-P-Li$_4$SiO$_4$ sorbents. However, absorption bands in the latter region are slightly different, having only three distinctive and more intense absorption bands compared to that of SS-P-Li$_4$SiO$_4$ which presented substantially more in terms of quantity yet lower intensity absorption bands. Upon closer observations, absorption bands between 800 and 1000 cm$^{-1}$ also identified to be associated with Li$_4$SiO$_4$ at wavenumbers 834, 882 and 956 cm$^{-1}$. Table 4.5 summarises the absorption bands identification of SS-C-Li$_4$SiO$_4$ sorbents.
Figure 4.19 FTIR spectra of SS-C-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium
a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10; d) SS-C-Li$_4$SiO$_4$-20.
Table 4.5 Absorption bands identification of SS-C-Li$_4$SiO$_4$ sorbents.

<table>
<thead>
<tr>
<th>Absorption bands of sorbents (cm$^{-1}$)</th>
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<td>823</td>
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</tr>
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</table>

FTIR spectra obtained for SS-R-Li$_4$SiO$_4$ and SS-F-Li$_4$SiO$_4$ sorbents showed similar patterns to that of SS-C-Li$_4$SiO$_4$ sorbents, and are included in the Appendix section at the end of this thesis (Figures A4.1 and A4.2).

Figure 4.20 shows FTIR spectra of SS-B-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium a) SS-B-Li$_4$SiO$_4$-0; b) SS-B-Li$_4$SiO$_4$-5; c) SS-B-Li$_4$SiO$_4$-10; d) SS-B-Li$_4$SiO$_4$-20. Again, similar absorption bands in two different wavenumber regions can be observed in all sorbents, indicating presence of metal-oxygen bonds including Li-O- associated with Li$_4$SiO$_4$ at wavenumbers 834, 882 and 956 cm$^{-1}$. As
mentioned earlier, the presence of Li₂CO₃ in all sorbents could be the result of excess amounts of unreacted Li₂CO₃ added during the preparation process.

Interestingly, more intense absorption bands in the wavenumber region of 1400 and 1500 cm⁻¹ are observed in SS-B-Li₄SiO₄-5, SS-B-Li₄SiO₄-10 and SS-B-Li₄SiO₄-20 sorbents (Figures 4.20b, 4.20c and 4.20d, respectively) compared to that of SS-B-Li₄SiO₄-0, as seen in Figure 4.20a. Vibration bands of -C=O (between 1443 and 1588 cm⁻¹) in CO₂ of Li₂CO₃ is thought to be the reason for the strong absorption, but Figure 4.20 also shows additional presence of other absorption bands. Table 4.6 summarises the absorption bands identification of SS-B-Li₄SiO₄ sorbents.
Figure 4.20 FTIR spectra of SS-B-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium a) SS-B-Li$_4$SiO$_4$-0; b) SS-B-Li$_4$SiO$_4$-5; c) SS-B-Li$_4$SiO$_4$-10; d) SS-B-Li$_4$SiO$_4$-20.
Table 4.6 Absorption bands identification of SS-B-Li$_4$SiO$_4$ sorbents.

<table>
<thead>
<tr>
<th>Absorption bands of sorbents (cm$^{-1}$)</th>
<th>Identification</th>
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111
4.2.3. Nitrogen adsorption/desorption isotherm profiles and surface areas of Li$_4$SiO$_4$ sorbents

Figure 4.21 presents the nitrogen adsorption/desorption isotherm profiles at 77 K for a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10 and d) SS-P-Li$_4$SiO$_4$-20. SS-P-Li$_4$SiO$_4$ sorbents exhibit isotherm profiles correlated to type II according to the IUPAC classification (IUPAC, 1985). Type II isotherm profiles are associated with non-porous or macroporous adsorbents with unobstructed monolayer/multilayer adsorption and indicated by a distinctive point in the isotherms labelled as Point B at the beginning of almost linear middle section. At this point, the monolayer coverage is complete and multilayer adsorption begins (IUPAC, 1985). The maximum volume nitrogen adsorbed by SS-P-Li$_4$SiO$_4$ sorbents ranging from 16.7 to 33.5 cm$^3$/g STP (Table 4.7).

The isotherm profiles of SS-P-Li$_4$SiO$_4$ also exhibit hysteresis loops type H3, which associated with assemblage of plate-like particles which are loosely coherent that caused the aggregates to develop slit-shaped pores (IUPAC, 1985). This type of hysteresis loops correspond to adsorption and desorption branches almost vertical and nearly parallel over a wide range of P/P$_o$ and do not exhibit any limiting adsorption at high P/P$_o$. The resulting surface areas of the sorbents seemed to decrease with increased amounts of excess lithium, where the calculated values of BET surface areas were 8.57, 5.77, 3.14 and 1.79 m$^2$/g for SS-P-Li$_4$SiO$_4$-0, SS-P-Li$_4$SiO$_4$-5, SS-P-Li$_4$SiO$_4$-10 and SS-P-Li$_4$SiO$_4$-20, respectively. Similar inverse correlation between Li/Si ratio and the resulting BET surface area of sorbents has
also been reported in literature (Tang et al., 2009) and attributed to the agglomeration of individual particles causing the decrease in the overall surface area of the sorbents (Tang et al., 2009).

**Figure 4.21** Nitrogen adsorption/desorption isotherms at 77 K for a) SS-P-Li₄SiO₄-0; b) SS-P-Li₄SiO₄-5; c) SS-P-Li₄SiO₄-10; d) SS-P-Li₄SiO₄-20.

Figure 4.22 shows the nitrogen adsorption/desorption isotherm profiles at 77 K for a) SS-C-Li₄SiO₄-0; b) SS-C-Li₄SiO₄-5; c) SS-C-Li₄SiO₄-10; d) SS-C-Li₄SiO₄-20.
Similar to SS-P-Li₄SiO₄ sorbents, SS-C-Li₄SiO₄-0 sorbent (Figure 4.22a) exhibit isotherm profile correlated to type II isotherm according to the IUPAC classification (IUPAC, 1985). Hence, it is deduced that this sorbent also is made up of non-porous or macroporous particles with unobstructed monolayer/multilayer adsorption, as indicated by a Point B at the beginning of the almost linear middle section. On the other hand, SS-C-Li₄SiO₄-5, SS-C-Li₄SiO₄-10 and SS-C-Li₄SiO₄-20 sorbents show the most prominent Point B and could indicate the least porous sorbent compared to the rest of SS-C-Li₄SiO₄ sorbents. The lack of porosity could be the reason to the low volume of nitrogen adsorbed by the sorbents, ranging from maximum volume adsorbed of 2.28 to 9.13 cm³/g STP (Table 4.7).

The isotherm profiles of SS-C-Li₄SiO₄ sorbents also exhibit hysteresis loops type H3 which are associated with aggregates of plate-like particles developing slit-shaped pores (IUPAC, 1985). Additionally, SS-C-Li₄SiO₄-5 and SS-C-Li₄SiO₄-10 sorbents isotherm profiles show low pressure hysteresis, recognised by the extended loop to the lowest attainable pressure, as shown in Figures 4.22b and 4.22c. This phenomenon may be related to the swelling of a non-rigid porous structure exist in the waste material (IUPAC, 1985).

The resulting surface areas of the sorbents seemed to decrease with increased amounts of excess lithium, where the calculated values of surface areas were 6.2371, 0.5475, 0.9984 and 1.4558 m²/g for SS-C-Li₄SiO₄-0, SS-C-Li₄SiO₄-5, SS-C-Li₄SiO₄-10 and SS-C-Li₄SiO₄-20, respectively (Table 4.7). As previously stated, similar inverse correlation between Li/Si ratio and the resulting surface area of
sorbents has also been reported in literature, suggesting that increase in Li/Si ratio promotes $\text{Li}_4\text{SiO}_4$ grain growth (Tang et al., 2009).

Contrasting SS-C-$\text{Li}_4\text{SiO}_4$ sorbents with the parent waste material CPFA, the textural characteristics have changed significantly following the addition of $\text{Li}_2\text{CO}_3$ and thermal treatment at 800 °C for 8h. Interestingly, the surface area of CPFA was temporarily improved following the addition of $\text{Li}_2\text{CO}_3$ and thermal treatment, but then it quickly decreased as the Li/Si ratio increased. The increase in surface area is expected, since the CPFA-$\text{Li}_2\text{CO}_3$ mixture was subjected to high temperature (800 °C) that may have contributed to the devolatilisation of organic constituents in CPFA that contributed to the increase in surface area. The devolatilisation of organic constituents that is believed to contribute to the increase in surface area of SS-C-$\text{Li}_4\text{SiO}_4$-0 sorbent supports the LOI value (4 wt%) of CPFA reported previously in section 4.1.2, confirming organic matters content in the parent waste material may cause devolatilisation.
Table 4.7 BET surface area, total pore volume and pore diameter of SS-P-Li₄SiO₄ and SS-C-Li₄SiO₄ sorbents

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume x 10⁻³ (cm³/g)</th>
<th>Pore diameter (nm)</th>
<th>Volume adsorbed (cm³/g STP)</th>
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</thead>
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<tr>
<td>SS-P-Li₄SiO₄-0</td>
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<td>11.1</td>
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Figure 4.22 Nitrogen adsorption/desorption isotherms at 77 K for a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10; d) SS-C-Li$_4$SiO$_4$-20.
4.2.4. *Scanning electron microscope analysis of Li$_4$SiO$_4$ sorbents*

Scanning electron microscope analyses were also performed to study morphological characteristics of pure and waste derived Li$_4$SiO$_4$ sorbents. Figure 4.23 shows pure SS-P-Li$_4$SiO$_4$-0 and SS-P-Li$_4$SiO$_4$-5 sorbents at 1000 and 5000 (inset figure) times magnifications. In general, the particles presented dense polyhedral morphology due to the sintering effect during the long heating process implied during preparation of the sorbents (Rodriguez-Mosqueda and Pfeiffer, 2013), having smooth surface (Figure 4.23a inset) with an average particle size of at least 5 µm, as can be observed in Figure 4.23a. These particles formed large agglomerates of around 10 µm or larger. Similar morphological descriptions of pure Li$_4$SiO$_4$ sorbents also prepared by solid state method were reported in literatures, relating the characteristics to high temperature used during the thermal treatment (Veliz-Enriquez et al., 2007; Qi et al., 2012; Seggiani et al., 2013).

Figure 4.23b shows SEM micrograph of SS-P-Li$_4$SiO$_4$-5 sorbent, in order to observe the effect of excess lithium on the texture of Li$_4$SiO$_4$ sorbent. Comparing SS-P-Li$_4$SiO$_4$-0 (Figure 4.23a) with SS-P-Li$_4$SiO$_4$-5 (Figure 4.23b), dense polyhedral particle shape can still be observed. However, the surface of pure Li$_4$SiO$_4$ sorbent with 5% excess lithium seems to exhibit surface with coarser texture than that of SS-P-Li$_4$SiO$_4$-0. This may be due to the melting of excess Li$_2$CO$_3$ with boiling point lower (628 °C) than that of synthesis temperature used in this study (800 °C).
Similar morphological characteristics to that of SS-P-Li$_4$SiO$_4$-0 sorbent can be observed in waste derived SS-C-Li$_4$SiO$_4$-0, SS-R-Li$_4$SiO$_4$-0, SS-F-Li$_4$SiO$_4$-0 and SS-B-Li$_4$SiO$_4$-0, as shown in figures 4.24a, 4.25a, 4.26a and 4.27a, respectively. All sorbents showed dense polyhedral morphology with smooth surface (insets in figures) and average particle sizes between 5 to 10 µm forming agglomerates of around 20 µm or larger. These values are larger than that of SS-P-Li$_4$SiO$_4$-0, perhaps due to the considerably smaller precursors were used in the preparation of SS-P-Li$_4$SiO$_4$-0, with SiO$_2$ average particle size between 5 and 15 nm.

Excess lithium added during preparation of coal-derived SS-C-Li$_4$SiO$_4$-5, SS-R-Li$_4$SiO$_4$-5 and SS-F-Li$_4$SiO$_4$-5 sorbents (Figures 4.24b, 4.25b and 4.26b, respectively) also showed coarser surface texture compared to their non-excess lithium counterparts. Again, it is believed that the excess amount of Li$_2$CO$_3$ during preparation of the sorbents melted and subsequently formed coverings of molten Li$_2$CO$_3$ on the surface of the waste-derived Li$_4$SiO$_4$ sorbents upon cooling. On the
other hand, a slightly different surface texture was observed in SS-B-Li₄SiO₄-5 sorbent (Figure 4.27b), where thread-like texture can be seen on the surface of the particles.

The particle size of resulting Li₄SiO₄ sorbents was reported to be directly related to the particle size of starting SiO₂ used in the preparation stage as SiO₂ particles remained in solid state during calcination temperature at 800 °C due to its high melting point at 1726 °C (Seggiani et al., 2013). For this reason, SiO₂ particles are strongly believed to act as cores to control the particle size of resulting Li₄SiO₄ sorbents.

![SEM micrographs](image)

Figure 4.24 SEM micrographs of a) SS-C-Li₄SiO₄-0 and b) SS-C-Li₄SiO₄-5 sorbents.
Figure 4.25 SEM micrographs of a) SS-R-Li$_4$SiO$_4$-0 and b) SS-R-Li$_4$SiO$_4$-5 sorbents.

Figure 4.26 SEM micrographs of a) SS-F-Li$_4$SiO$_4$-0 and b) SS-F-Li$_4$SiO$_4$-5 sorbents.
4.3. Summary

In summary, Chapter 4 discussed the characterisation of the parent waste materials, namely, CPFA, RPFA, FBA and POMBA, used in this study (Section 4.1) and their corresponding high temperature Li₄SiO₄ sorbents (Section 4.2). A number of analytical techniques were conducted in order to study the contributing characteristics of parent waste materials and their corresponding Li₄SiO₄ sorbents that could produce high-efficient CO₂ sorbents at high sorption temperatures.

Five of these analytical techniques were conducted on four aforementioned samples of parent waste materials, including particle size distribution, major oxides composition and loss-on-ignition, phase composition, nitrogen adsorption/desorption and surface area as well as scanning electron microscopic analyses. On the other hand, four characterisation analyses were carried out on the
corresponding waste-derived Li$_4$SiO$_4$ sorbents, including mineral phase composition by XRD, Fourier transform infrared, nitrogen adsorption/desorption and surface area and scanning electron microscopic analyses.

Particle size distribution analysis of the parent waste materials revealed varying particle sizes across samples, although they can be classified according to their apparent difference in particle sizes i.e. fly ash CPFA and RPFA samples having average diameter between 13 and 41 µm, and bottom ash FBA and POMBA samples having average size (D(0.5) value) between 182 and 240 µm. Small particle sizes of parent waste materials could have an advantage over larger ones due to larger surface area can be provided for the resulting Li$_4$SiO$_4$ sorbents for the CO$_2$ sorption to take place.

Nevertheless, particle sizes of precursors alone cannot be used to predict CO$_2$ capture performance. The chemical composition and the loss-on-ignition (LOI) values of the materials also need to be taken into consideration. The samples followed decreasing order of LOI value as follows: FBA (8.47 wt%) > POMBA (8.12 wt%) > RPFA (4.09 wt%) > CPFA (4 wt%). Although the LOI values of the parent waste materials may not directly correlate with the CO$_2$ uptake performance of the resulting Li$_4$SiO$_4$ sorbents, they could affect the production performance of the
sorbents due to the preparation of the sorbents requires calcination at 800 °C (Section 3.2.1).

In addition, the chemical compositions of the parent waste materials also need to be taken into consideration. X-ray fluorescence analyses were carried out on all parent waste materials to identify their chemical compositions. The results showed that all materials used in this study contain significant amounts of component of interest, SiO$_2$, where its content exceeding 47 wt% in all samples. High amount of SiO$_2$ in waste materials is essential in order to ensure maximum possible content of Li$_4$SiO$_4$ was calcined using the waste materials and therefore, maximising the amount of CO$_2$ uptake by the sorbents. At least 47 wt% of SiO$_2$ content found in all parent waste materials was deemed to be suitable for a development of high temperature Li$_4$SiO$_4$-base sorbents.

The unavoidable presence of other oxides in the parent waste materials is expected to affect the performance of CO$_2$ uptake by waste-derived Li$_4$SiO$_4$ sorbents. As previously explained in subsection 4.1.2, the presence of other elements, such as Al, Fe and Na, into Li$_4$SiO$_4$-based sorbents could affect their CO$_2$ uptake performances. Based on the amounts of these elements found in their oxides form in the parent waste materials, it is expected that the reactivity
performance of CO₂ capture by the Li₄SiO₄-based sorbents developed using these materials would be improved, in comparison to the pure Li₄SiO₄ sorbents.

Phase composition analyses (subsection 4.1.3) were carried out on all parent waste materials as well as the resulting waste-derived Li₄SiO₄ sorbents. It was found that quartz was the main phase of SiO₂ in all coal-derived ash samples, in addition to aluminosilicates such as mullite and sillimanite. Moreover, there were also some amorphous phases detected in the diffractograms, indicating coexistence of amorphous constituents, such as the aluminosilicates, in parent waste materials. In the waste-derived Li₄SiO₄ sorbents (subsection 4.2.1), these crystalline and amorphous constituents were converted into mainly Li₄SiO₄ crystals, following the addition of Li₂CO₃ during calcination process. Other constituents also found in the sorbents including LiAlO₂, Li₂SiO₃ and LiAlSiO₄, resulting from the aluminosilicates discovered in the parent waste materials.

There were still some amorphous peaks detected in the waste-derived Li₄SiO₄ sorbents, compared to none found in the pure Li₄SiO₄ sorbents. The amorphous phase found in the waste-derived Li₄SiO₄ sorbents could be advantageously affecting the CO₂ uptake performance of the sorbents, due to the versatility of amorphous structure in capturing CO₂ molecules. In comparison to the more ordered structure of its crystalline counterpart which is predominantly found in pure Li₄SiO₄ sorbents, the coexistence of amorphous Li₄SiO₄ could increase the CO₂
sorption capacity of the waste-derived sorbents (Sadoway, 2010). Furthermore, the diffusion of molecules into amorphous structure is faster than that in crystalline due to the atomic disorder (Sadoway, 2010), and therefore, potentially increasing the rate of CO$_2$ sorption of the sorbents.
Chapter 5 CO₂ capture by waste-derived Li₄SiO₄ sorbents

This chapter discusses the CO₂ capture studies of parent waste materials and waste-derived Li₄SiO₄ sorbents at different sorption temperatures (500, 600, 700 °C). Firstly, section 5.1 examines the relative CO₂ uptake capacities by parent waste materials in pure (100 vol%) CO₂ environment. Section 5.2 discusses the CO₂ uptake capacities by waste-derived Li₄SiO₄ sorbents in pure and diluted (14 vol%, balance N₂) CO₂ environments. Subsequently, section 5.3 presents the regeneration studies of the sorbents in multiple cycles, also in pure and diluted CO₂ environments. Finally, section 5.4 summarises the CO₂ capture studies for all materials and correlates their capacities with the physico-chemical characteristics of the sorbents reported in Chapter 4.

5.1. CO₂ uptake by parent waste materials

Thermogravimetric analyses (TGA) were conducted on all as-received parent waste materials in pure (100 vol%) CO₂ environment at 500, 600 and 700 °C for 120 minutes. As previously mentioned in Chapter 3, the analysis duration of 120 minutes was conducted to allow sufficient time for CO₂ sorption to take place. It is also worthy to note that the parent waste materials were not subjected to any pre-treatment method before the CO₂ uptake analysis. This provides ‘raw’ CO₂ uptake capacity of waste materials prior to calcination process and also serves as the benchmark values for the progress of subsequent modification of the materials.
Figure 5.1 shows TGA weight change profiles of CPFA at 500, 600 and 700 °C in CO₂ environment. In general, the weight of the parent waste material CPFA is observed to be progressively increasing with temperature, depending on the residence time. At 500 °C, the weight gradually increased until it reached the end of analysis. On the other hand at 600 °C, the weight change profile presents a peak at approximately between 50 and 90 minutes into the analysis, before rapidly decreasing afterwards. Similar trend can be observed at 700 °C, where a sharper peak is observed at about 55th minute of analysis duration and the decrease is faster than that observed at 600 °C.

![Figure 5.1 Isothermal weight uptake profiles of CPFA at 500, 600 and 700 °C in pure CO₂ environment.](image)

The peaking behaviour shown by CPFA is believed to be caused by the instability of the material when it is being subjected to high sorption temperatures, as shown in
Figure 5.1. In order to verify this theory, additional experiments were carried out under N$_2$ flow in isothermal conditions at 500, 600 and 700 °C (Figure 5.2). It is apparent that the decrease in weight percentage of the material became more pronounced as the temperature increased. This indicates that the degree of instability of the material is strongly affected by the temperatures investigated in this study. This observation corroborates the peaking behaviour (Figure 5.1), where the weight of CPFA was observed to have the most prominent decrease at 700 °C.

![Figure 5.2 Thermal stability of CPFA in N$_2$ environment at isothermal conditions (500, 600 and 700 °C).](image)

Figure 5.3 shows TGA weight change profiles of RPFA at 500, 600 and 700 °C in CO$_2$ environment. It is observed that the weight change profiles of RPFA progressively increasing with temperature throughout the analysis duration. At 500 °C, the weight gradually increased until it reached the end of analysis. Similar trend is observed at 600 °C with an increased in overall weight change. However
at 700 °C, a mild peaking behaviour is detected approximately between 50 and 75 minutes into the analysis.

![Graph showing weight change profiles of RPFA at 500, 600 and 700 °C in pure CO2 environment.]

Figure 5.3 Isothermal weight change profiles of RPFA at 500, 600 and 700 °C in pure CO2 environment.

Again, it is believed that the peaking behaviour was caused by the instability of the material at high temperatures. Therefore, additional experiments were carried out under N2 flow in isothermal conditions at 500, 600 and 700 °C (Figure 5.4). A similar profile to CPFA (Figure 5.2) was also observed in RPFA (Figure 5.4), where the weight of the parent waste material decreased as the temperature increased. This observation corroborates the peaking behaviour (Figure 5.3), where the weight of RPFA was observed to have the most prominent decrease at 700 °C.
In order to determine the overall amount of CO\textsubscript{2} uptake by the parent waste materials, weight change due to the instability of the material needs to be accounted for by subtracting the weight change of the material under N\textsubscript{2} flow from that of CO\textsubscript{2} analysis. The overall amount of CO\textsubscript{2} uptake by all parent waste materials at isothermal conditions are summarised in Table 5.1.
Table 5.1 Weight changes in pure CO\textsubscript{2} and N\textsubscript{2}, as well as overall CO\textsubscript{2} sorption of parent waste materials at 500, 600 and 700 °C. The overall CO\textsubscript{2} sorption was calculated by subtracting the weight decrease in N\textsubscript{2} from the weight uptake in pure CO\textsubscript{2}. The overall CO\textsubscript{2} uptake values are also converted into mg/g for ease of comparison in later discussions.

<table>
<thead>
<tr>
<th>Waste material</th>
<th>Temperature (°C)</th>
<th>Weight uptake in CO\textsubscript{2} (wt%)</th>
<th>Weight decrease in N\textsubscript{2} (wt%)</th>
<th>Overall CO\textsubscript{2} uptake (wt%)</th>
<th>Overall CO\textsubscript{2} uptake (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPFA</td>
<td>500</td>
<td>0.34</td>
<td>0.07</td>
<td>0.27</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.30</td>
<td>0.13</td>
<td>0.17</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.29</td>
<td>0.16</td>
<td>0.13</td>
<td>1.30</td>
</tr>
<tr>
<td>RPFA</td>
<td>500</td>
<td>0.39</td>
<td>0.12</td>
<td>0.27</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.46</td>
<td>0.19</td>
<td>0.27</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.48</td>
<td>0.34</td>
<td>0.14</td>
<td>1.40</td>
</tr>
<tr>
<td>FBA</td>
<td>500</td>
<td>0.30</td>
<td>0.21</td>
<td>0.09</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.52</td>
<td>0.27</td>
<td>0.25</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.66</td>
<td>0.29</td>
<td>0.37</td>
<td>3.70</td>
</tr>
<tr>
<td>POMBA</td>
<td>500</td>
<td>0.32</td>
<td>0.23</td>
<td>0.08</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>0.53</td>
<td>0.27</td>
<td>0.26</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.58</td>
<td>0.26</td>
<td>0.32</td>
<td>3.20</td>
</tr>
</tbody>
</table>

In general, overall CO\textsubscript{2} uptake capacities are all less than 4 mg CO\textsubscript{2}/g sorbent. The CO\textsubscript{2} uptake values by waste materials are significantly lower than that of commercially available solvents (approximately 176 mg CO\textsubscript{2}/g sorbent) (Samanta et al., 2012). This proves unsuitability of the waste materials as CO\textsubscript{2} sorbents if they were to be used without any treatment.

Most of the parent waste materials (RPFA, FBA and POMBA) show an increasing uptake with increased sorption temperatures during the 120 minutes of analysis. After taking into account the instability factor of the parent waste materials, FBA
showed the highest overall CO$_2$ uptake capacity of 3.70 mg CO$_2$/g sorbent at 700 °C. This is then followed by POMBA, with maximum overall CO$_2$ uptake capacity of 3.20 mg CO$_2$/g sorbent, also at 700 °C. RPFA showed similar trend of increasing weight uptake capacity in CO$_2$ environment, analogous to FBA and POMBA. However, the trend changed after taking into account the instability factor of the parent waste material in N$_2$ environment. The maximum overall CO$_2$ uptake capacity of RPFA was calculated to be 2.70 mg CO$_2$/g sorbent at 500 °C.

On the other hand, CPFA shows inverse correlations between CO$_2$ uptake capacity and sorption temperature before and after taking into account the instability factor, with highest overall CO$_2$ uptake capacity of 2.70 mg CO$_2$/g sorbent at 500 °C. The maximum CO$_2$ uptake capacities of parent waste materials exhibited a direct correlation with LOI values, as showed previously in Table 4.2 (8.47 wt% for FBA, 8.12 wt% for POMBA, 4.09 wt% for RPFA and 4.00 wt% for CPFA). The amounts of maximum CO$_2$ capacities decreased with decreasing LOI values of the materials, according to descending order of LOI values: FBA>POMBA>RPA>CPFA.

Analysing the results from a wider point of view, several factors could contribute to the generally low CO$_2$ uptake by parent waste materials. These include low surface area due to dense textural characteristics, as discussed in Chapter 4. There is also the possibility that the CO$_2$ uptake capacity of parent waste materials is contributed by the reaction between CO$_2$ molecules and metal oxides present on the surface of the waste materials. Pure metal oxides such as MgO and CaO are known to chemically absorb CO$_2$ at elevated temperatures of higher than 400 °C.
(Martavaltzi and Lemonidou, 2008; Hassanzadeh and Abbasion, 2010) producing MgCO$_3$ and CaCO$_3$, respectively. Significantly low concentrations (<10 wt%) of these metal oxides in waste materials, also as reported in Chapter 4, is deemed to be key reason for the low CO$_2$ uptake.

Table 5.2 shows the correlations between the maximum CO$_2$ uptake capacities by waste materials and their total concentrations of CaO and MgO at 500, 600 and 700 °C. At 500 °C, the CO$_2$ uptake capacities of fly ashes CPFA and RPFA decreased with decreasing amounts of CaO and MgO. Interestingly, it does not seem to be the case for the bottom ashes FBA and POMBA, where the CO$_2$ uptake capacities decreased with increasing amounts of CaO and MgO. While it is expected that the CO$_2$ uptake capacities of the waste materials to have a direct correlation with the amount of CaO and MgO because of their ability to chemically absorb CO$_2$ at high temperatures, it is not expected for these two parameters to have an inverse correlation. A possible explanation for this observation could be contributed by the significantly larger particle sizes of the bottom ash waste materials compared to the fly ash ones, causing less CO$_2$ captured by FBA and POMBA within the same analysis duration of 120 minutes. Higher sorption temperature could improve CO$_2$ uptake by FBA and POMBA, since CO$_2$ sorption of CaO and MgO chemically motivate on thermal energy.

However at 600 °C, an increasing trend of this correlation is observed, where the CO$_2$ uptake capacity increased as a function of MgO and CaO concentrations in the waste materials. The descending order of CO$_2$ uptake capacities by the waste
materials corresponds well with the descending order of CaO and MgO amounts, to follow POMBA>FBA>RPGA>CPFA order. It is also observed that the amount of CO$_2$ captured by waste materials increased compared to that at 500 °C. This observation seems to verify the suggestion that an increase in sorption temperature was needed to further promote the chemical sorption of CO$_2$ by the waste materials.

This is particularly valid when there is a significant amount of unburnt carbon present in the waste materials. Activation process is performed on waste materials to further increase their surface areas in order to provide more areas for CO$_2$ capture via physical adsorption, while the surface of the sorbents is chemically modified to increase the attraction of the surface of the sorbents to the CO$_2$ molecules, and therefore, improving the overall uptake. These low temperature sorbents are known to have higher (69.5 mg CO$_2$/g sorbent) CO$_2$ uptake at much lower sorption temperatures (30 °C) (Maroto-Valer et al., 2008). This is heavily influenced by their ability to perform physical adsorption at lower temperature rather than chemical absorption at higher temperatures.
Table 5.2 Correlations between the amounts of CaO + MgO and CO₂ uptake capacities by waste materials at 500, 600 and 700 °C.

<table>
<thead>
<tr>
<th></th>
<th>Maximum CO₂ uptake capacity (mg CO₂/g sorbent)</th>
<th>CaO + MgO (wt%)</th>
<th>Waste materials</th>
<th>LOI values (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>500 °C</strong></td>
<td>3.94 &gt; 3.41 &gt; 2.98 &gt; 2.31</td>
<td>7.04 &gt; 5.83 &lt; 7.21 &lt; 10.24</td>
<td>RPFA &gt; CPFA &lt; FBA &lt; POMBA</td>
<td>(4.09) (4.00) (8.47) (8.12)</td>
</tr>
<tr>
<td><strong>600 °C</strong></td>
<td>5.26 &gt; 5.18 &gt; 4.60 &gt; 3.00</td>
<td>10.24 &gt; 7.21 &gt; 7.04 &gt; 5.83</td>
<td>POMBA &gt; FBA &gt; RPFA &gt; CPFA</td>
<td>(8.12) (8.47) (4.09) (4.00)</td>
</tr>
<tr>
<td><strong>700 °C</strong></td>
<td>6.61 &gt; 5.76 &gt; 4.79 &gt; 2.96</td>
<td>7.21 &lt; 10.24 &gt; 7.04 &gt; 5.83</td>
<td>FBA &lt; POMBA &gt; RPFA &gt; CPFA</td>
<td>(8.47) (8.12) (4.09) (4.00)</td>
</tr>
</tbody>
</table>

5.2. CO₂ uptake by waste-derived Li₄SiO₄ sorbents

This section investigates the CO₂ uptake capacities by sorbents under pure and diluted CO₂ environments by studying the weight change of the sorbents in a thermogravimetric analyser. CO₂ uptake capacities by sorbents are presented as curves of weight of CO₂ captured in mg per unit g of sorbent versus the analysis duration of 120 minutes. As mentioned in Section 3.2, all of waste-derived Li₄SiO₄ sorbents were prepared with excess amount of lithium due to the tendency of lithium to sublimate at temperatures higher than 710 °C during calcination of the sorbents (Lu and Wei-Cheng, 2000).
However, there is no published study on the specific amount of excess lithium recommended, as well as the effect of excess lithium on CO$_2$ uptake capacity of Li$_4$SiO$_4$ sorbents. Therefore, all sorbents synthesised in this research were prepared with different amounts of excess lithium (5%, 10%, and 20%) in order to study its effect on CO$_2$ uptake capacities of sorbents. Excess lithium is the amount of additional lithium added to the stoichiometric ratio of Li$_4$SiO$_4$. Li$_4$SiO$_4$ sorbents with no excess lithium (0%) were also prepared to establish benchmark sorption performance of the sorbents for comparison purposes.

5.2.2. CO$_2$ uptake by sorbents in pure CO$_2$ environment

Figure 5.5 shows the isothermal CO$_2$ uptake profiles of a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10; d) SS-P-Li$_4$SiO$_4$-20 sorbents in pure CO$_2$ environment. There appears to be a direct correlation between the CO$_2$ uptake performance by the sorbents and the sorption temperatures throughout the duration of analysis. All sorbents captured the lowest amount of CO$_2$ at 500 °C and the highest at 700 °C, with intermediate amount of captured CO$_2$ at 600 °C.

The direct correlation between the amount of CO$_2$ uptake and sorption temperature can be explained using the double shell mechanism (Figure 5.6), whereby superficial chemical sorption occurs between CO$_2$ and Li$^+$ and O$_2^-$ ions to form external Li$_2$CO$_3$ and Li$_2$SiO$_3$ shells over Li$_4$SiO$_4$ particles at lower temperature (500 °C) (Essaki et al., 2005; Duran-Munoz et al., 2013). Diffusion is then promoted as the sorption temperature increases, allowing Li$^+$ and O$_2^-$ ions on the
bulk of Li$_4$SiO$_4$ particle to diffuse through the double shells and react with more CO$_2$ molecules (Essaki et al., 2005; Duran-Munoz et al., 2013). The direct correlation between CO$_2$ uptake capacity of waste-derived Li$_4$SiO$_4$ sorbents and sorption temperature is also in good agreement with previous studies which reported similar trend (Olivares-Marin et al., 2010; Wang et al., 2011).

Figure 5.5 also shows an increase in sorption rate as the sorption temperature increased, as indicated by the slope of the CO$_2$ uptake capacity at the beginning of analysis duration. This could be explained again due to increased diffusion, resulting in faster sorption rate compared to that at lower sorption temperature. The CO$_2$ uptake capacity of SS-P-Li$_4$SiO$_4$ sorbents did not reach sorption equilibrium in all cases, indicating substantially longer sorption time (>120 minutes) is needed by SS-P-Li$_4$SiO$_4$ sorbents to achieve sorption equilibrium.
Figure 5.5 Isothermal CO$_2$ uptake profiles of a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10; d) SS-P-Li$_4$SiO$_4$-20 sorbents in pure CO$_2$ environment.
Table 5.3 shows the CO$_2$ uptake capacity of SS-P-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at sorption temperatures 500, 600 and 700 °C in pure CO$_2$ environment at different times (30 and 120 minutes) during the analysis. It is observed that the CO$_2$ uptake capacity of SS-P-Li$_4$SiO$_4$ sorbents peaks at sorption temperature of 700 °C (135.8 mg CO$_2$/g sorbent) by SS-P-Li$_4$SiO$_4$-20 sorbent, while the lowest uptake capacity was observed by SS-P-Li$_4$SiO$_4$-0 sorbent at 500 °C with 24.47 mg CO$_2$/g sorbent captured. At 500 °C, the CO$_2$ uptake capacity of SS-P-Li$_4$SiO$_4$ sorbents decreased with increasing amounts of excess lithium. However at 600°C, an increasing trend of overall maximum CO$_2$ uptake capacity of sorbents...
can be observed. Similarly, increased amount of maximum CO$_2$ uptake capacity as a function of amounts of excess lithium is observed at 700 °C.

The addition of excess amounts of lithium seems to inhibit CO$_2$ uptake by SS-P-Li$_4$SiO$_4$-0 sorbent at lower sorption temperature (500 °C) (Table 5.3). It is assumed that there is insufficient thermal energy provided at this temperature to fully activate the diffusion of CO$_2$ through the bulk of Li$_4$SiO$_4$ particles, and therefore, the addition of excess lithium inhibits the overall sorption process. A chemical reaction can be determined if it is thermodynamically favourable by obtaining the Gibbs free energy change (ΔG) of that particular process. ΔG of a reaction is factored in by the heat of reaction (ΔH) and the multiplication product of temperature and entropy (ΔS) in the following relationship ΔG = ΔH – TΔS. This shows that the temperature directly affects the thermodynamic spontaneity of that chemical reaction, which is measured by the negativity of ΔG value. Essaki et al. (2006) reported ΔG value for CO$_2$ absorption by Li$_4$SiO$_4$ sorbent to have negative values up to 720 °C, when ΔG values start to show positive values, indicating desorption of CO$_2$ occurs (Essaki et al., 2006).

Hence, additional thermal energy provided at sorption temperature higher than 500 °C causes the ΔG value of CO$_2$ sorption on Li$_4$SiO$_4$ to be smaller (more negative) than at 500 °C, and therefore, permitting Li$_4$SiO$_4$ to capture more CO$_2$. As the sorption temperature increased to 600 and 700 °C, it is assumed that there is enough thermal energy to completely activate the diffusion process. The subsequent addition of excess amounts of lithium that previously acted as inhibitor
now facilitates the sorption process instead, resulting in an increase in CO$_2$ uptake capacities by sorbents.

Comparing the amount of CO$_2$ uptake by SS-P-Li$_4$SiO$_4$ sorbents with that of published studies, Olivares-Marín et al, (2010) reported higher capacity of a pure Li$_4$SiO$_4$ sorbent. For example at 500 °C, a pure Li$_4$SiO$_4$ sorbent captured approximately 50 mg CO$_2$/g sorbent in analysis duration of 60 minutes (Olivares-Marín et al., 2010). It is worthy to note that although solid-state reaction was applied, excess amount of lithium was not added during the preparation of pure Li$_4$SiO$_4$ sorbent in that study (Olivares-Marín et al., 2010). The CO$_2$ uptake capacity obtained in that study was two times higher than the amount of CO$_2$ captured by SS-P-Li$_4$SiO$_4$-0 sorbent at the same sorption temperature in longer sorption time (120 minutes). In addition, the sorbent was calcined at 950 °C for 8h (Olivares-Marín et al., 2010), as opposed to 800 °C for 8h in this study. Hence, the difference in sorbent calcination conditions and preparation method was believed to be the reason for the discrepancy in the amount of CO$_2$ uptake capacities of pure Li$_4$SiO$_4$ sorbents in both studies.
Table 5.3 CO₂ uptake capacity by SS-P-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions in pure CO₂ environment.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO₂ uptake capacity (mg CO₂/g sorbent)</th>
</tr>
</thead>
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</tr>
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</tr>
<tr>
<td>20</td>
<td></td>
<td>96.76</td>
</tr>
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</table>

Figure 5.7 presents the isothermal CO₂ uptake profiles of a) SS-C-Li₄SiO₄-0; b) SS-C-Li₄SiO₄-5; c) SS-C-Li₄SiO₄-10 and d) SS-C-Li₄SiO₄-20 sorbents in pure CO₂ environment. Generally, CO₂ uptake profiles of SS-C-Li₄SiO₄ exhibit similar trend as that of SS-P-Li₄SiO₄, where the uptake capacity increased as a function of sorption temperature. All sorbents captured the lowest amount of CO₂ at 500 °C and the highest at 700 °C, with intermediate amount of captured CO₂ at 600 °C.

The CO₂ uptake profile of SS-C-Li₄SiO₄-0 at 700 °C displays a horizontal line of uptake from minute 15 until the end of analysis duration, indicating that the sorbent is saturated with CO₂ and has reached sorption equilibrium. CO₂ uptake capacities by other SS-C-Li₄SiO₄ sorbents did not display sorption equilibrium.
during analysis duration, probably due to the incomplete diffusion process, as indicated by the slower sorption rate towards the end of the analysis duration. Therefore, longer time is needed for the sorbents to reach saturation. Also similar to SS-P-Li₄SiO₄ sorbents, different amounts of excess lithium added during preparation stage did not seem to affect the sorption temperature at which the CO₂ uptake capacity of SS-C-Li₄SiO₄ sorbents is optimal i.e. at 700 °C.

Comparing the CO₂ uptake trend of the waste-derived SS-C-Li₄SiO₄ sorbents prepared in this study with that published by Wang et al. (2011), it can be seen that the samples presented a similar trend, where the CO₂ uptake of a rice husk-derived RHA1-Li₄SiO₄ sorbent increased with sorption temperatures (Wang et al., 2011). It is worthy to note that during preparation of the sorbent, excess amount of lithium (10%) was added in the solid-state reaction preparation method before being subjected to thermal treatment at 800 °C for 4h. Evaluating the CO₂ uptake trend by SS-C-Li₄SiO₄-10 with that of RHA1-Li₄SiO₄ sorbent, a similar trend is observed, where no sorption equilibrium was achieved at sorption temperatures of 500 and 600 °C (Wang et al., 2011). CO₂ uptake capacity analysis by RHA1-Li₄SiO₄ sorbent was not reported isothermally at 700 °C, and therefore, the uptake trend could not be compared with that of SS-C-Li₄SiO₄-10 sorbent in this study.
Figure 5.7 Isothermal CO$_2$ uptake profiles by a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10; d) SS-C-Li$_4$SiO$_4$-20 sorbents in pure CO$_2$ environment.
The CO₂ uptake capacity of SS-C-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions are shown in Table 5.4. In general, the CO₂ uptake capacity of sorbents increased with sorption temperature, with the highest CO₂ uptake capacity of 263.4 mg CO₂/g sorbent at 700 °C, while the lowest 34.52 mg CO₂/g sorbent at 500 °C. In addition, sorption rate of the sorbents also increased with sorption temperature. This is indicated by the increased amount of CO₂ captured by sorbents at 30 minutes into the analysis at each sorption temperature.

Evidently, there are two different uptake trends of the sorbents with different amounts of excess lithium, where one (at 700 °C) shows increased CO₂ uptake capacity, while the others (at 500 and 600 °C) show the opposite trend of decreasing amount of CO₂ captured with increasing amount of excess lithium. Similar to previously observed in SS-P-Li₄SiO₄ sorbents, it is thought that the addition of excess lithium inhibits SS-C-Li₄SiO₄ sorbents at lower sorption temperatures (500 and 600 °C) are due to insufficient thermal energy to encourage the reaction between the sorbents and CO₂ molecules, resulting in decreasing amount of CO₂ uptake capacity with increasing amount of excess lithium.

At 700 °C, the thermal energy is supposed to be more than enough to contribute to the negativity of ΔG value and causing the sorbents to capture more CO₂ even with increasing amount of excess lithium. Therefore, the reaction only completely activated at 700 °C for SS-C-Li₄SiO₄ sorbents, as opposed to 600 °C for SS-P-Li₄SiO₄ sorbents. Other impurities found in the parent waste material CPFA could be the
reason for the inhibition of the overall reaction process by SS-C-Li₄SiO₄ sorbents. This will be further discussed at the end of this section.

Table 5.4 Table CO₂ uptake capacity of SS-C-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions in pure CO₂ environment.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO₂ uptake capacity (mg CO₂/g sorbent)</th>
<th>30 min</th>
<th>120 min</th>
</tr>
</thead>
<tbody>
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<td>184.9</td>
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</table>

Figure 5.8 presents the isothermal CO₂ uptake profiles of a) SS-R-Li₄SiO₄-0; b) SS-R-Li₄SiO₄-5; c) SS-R-Li₄SiO₄-10 and d) SS-R-Li₄SiO₄-20 in pure CO₂ environment. It is observed that the uptake profile of the sorbents increased as a function of sorption temperature, similar to SS-P-Li₄SiO₄ and SS-C-Li₄SiO₄ sorbents. In addition, CO₂ uptake profile of all SS-R-Li₄SiO₄ sorbents reached sorption equilibrium during the duration of analysis at 700 °C.
Figure 5.8 Isothermal CO$_2$ uptake profiles of a) SS-R-Li$_4$SiO$_4$-0; b) SS-R-Li$_4$SiO$_4$-5; c) SS-R-Li$_4$SiO$_4$-10 and d) SS-R-Li$_4$SiO$_4$-20 in pure CO$_2$ environment.
The CO\textsubscript{2} uptake capacity of SS-R-Li\textsubscript{4}SiO\textsubscript{4} sorbents with different amounts of excess lithium at isothermal sorption conditions are tabulated in Table 5.5. In general, the CO\textsubscript{2} uptake capacity of sorbents increased with sorption temperature. It is observed that the highest CO\textsubscript{2} uptake capacity for the entire duration of analysis was 215.8 mg CO\textsubscript{2}/g sorbent by SS-R-Li\textsubscript{4}SiO\textsubscript{4}-20 sorbent at 700 °C, while the lowest 56.33 mg CO\textsubscript{2}/g sorbent by the same sorbent at 500 °C. Furthermore, sorption rate of the sorbents also increased with sorption temperature. This is indicated by the increased amount of CO\textsubscript{2} captured by sorbents at 30 minutes into the analysis at each sorption temperature.

Comparing the CO\textsubscript{2} uptake capacity of sorbents with increasing amounts of excess lithium at 500 and 600 °C, a familiar decreasing trend to the SS-C-Li\textsubscript{4}SiO\textsubscript{4} sorbents can be observed. On one hand, the highest CO\textsubscript{2} uptakes by the initial SS-R-Li\textsubscript{4}SiO\textsubscript{4}-0 sorbent were 98.27 and 124.5 mg CO\textsubscript{2}/g sorbent at 500 and 600 °C, respectively. As the amount of excess of lithium increased, the CO\textsubscript{2} uptake capacity by SS-R-Li\textsubscript{4}SiO\textsubscript{4}-20 sorbent decreased at 56.33 and 83.09 mg CO\textsubscript{2}/g at 500 and 600 °C, respectively. On the other hand, maximum CO\textsubscript{2} uptake by SS-R-Li\textsubscript{4}SiO\textsubscript{4}-0 sorbent at 700 °C was found to be 177.2 mg CO\textsubscript{2}/g sorbent and keeps increasing with the addition of excess amount of lithium until eventually, the maximum CO\textsubscript{2} uptake by SS-R-Li\textsubscript{4}SiO\textsubscript{4}-20 sorbent reached 215.8 mg CO\textsubscript{2}/g sorbent. The presence of other elements in the parent waste material R-PFA is also thought to affect the degree of inhibition of the reaction between SS-R-Li\textsubscript{4}SiO\textsubscript{4} sorbents and CO\textsubscript{2} molecules. Further discussion on this can be found at the end of this section.
Table 5.5 Maximum CO₂ uptake capacity of SS-R-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions in pure CO₂ environment.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO₂ uptake capacity (mg CO₂/g sorbent)</th>
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</thead>
<tbody>
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<tr>
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</table>

Figure 5.9 presents CO₂ uptake profiles of a) SS-F-Li₄SiO₄-0; b) SS-F-Li₄SiO₄-5; c) SS-F-Li₄SiO₄-10 and d) SS-F-Li₄SiO₄-20 in pure CO₂ environment. Similar to previously discussed sorbents, the CO₂ uptake capacity of SS-F-Li₄SiO₄ sorbents increased as a function of sorption temperature in pure CO₂ environment. The lowest, intermediate and highest amount of CO₂ captured are at 500, 600 and 700 °C, respectively. Interestingly, all SS-F-Li₄SiO₄ sorbents reached sorption equilibrium within 20 minutes of analysis duration at 700 °C. In relation to this, it is assumed that the diffusion of ions in Li₄SiO₄ were completely activated at 700 °C for all SS-F-Li₄SiO₄ sorbents. The addition of excess lithium on each sorbent did not seem to affect the dependency of CO₂ uptake capacity on sorption temperatures, although the excess amount of lithium slightly improved the overall CO₂ uptake capacity of the sorbent.
Figure 5.9 Isothermal CO$_2$ uptake profiles of a) SS-F-Li$_4$SiO$_4$-0; b) SS-F-Li$_4$SiO$_4$-5; c) SS-F-Li$_4$SiO$_4$-10 and d) SS-F-Li$_4$SiO$_4$-20 in pure CO$_2$ environment.
The CO₂ uptake capacity of SS-F-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions are shown in Table 5.6. The highest CO₂ uptake for the complete duration of analysis is captured by SS-F-Li₄SiO₄-20 at 700 °C (199 mg CO₂/g sorbent), while the lowest CO₂ uptake by SS-F-Li₄SiO₄-10 (66.68 mg CO₂/g sorbent) at 500 °C. The highest and lowest amounts of CO₂ captured by SS-F-Li₄SiO₄ sorbents present a direct correlation between the CO₂ uptake capacity and sorption temperature. In addition, an increasing uptake trend as a function of amount of excess lithium is observed at all sorption temperatures. Moreover, sorption rate of sorbents also increased as a function of temperature, as indicated by the increasing amount of CO₂ captured at 30 minutes into the analysis duration.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO₂ uptake capacity (mg CO₂/g sorbent)</th>
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<td></td>
<td>199.0</td>
<td>199.0</td>
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</tr>
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</table>
Figure 5.10 shows the isothermal CO\textsubscript{2} uptake profiles of a) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-0; b) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-5; c) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-10 and d) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-20 in pure CO\textsubscript{2} environment. Evidently, all CO\textsubscript{2} uptake profiles of SS-B-Li\textsubscript{4}SiO\textsubscript{4} sorbents exhibit sorption equilibrium within 15 minutes of analysis duration at 700 °C. Also observed in Figure 5.10 is the continuing trend of increased CO\textsubscript{2} uptake capacity with sorption temperature, where the amount of CO\textsubscript{2} uptake peaks at 700 °C and the lowest at 500 °C. In addition, the CO\textsubscript{2} uptake capacity increased as a function of the amount of excess lithium. Furthermore, the addition of excess lithium during preparation method of sorbents seems to enhance the CO\textsubscript{2} uptake capacity, as can be seen from the increased upper limit of sorption equilibrium with the amount of excess lithium.

Wang et al. (2011) stated that potassium and sodium contents in parent waste materials contributed to the improvement of CO\textsubscript{2} uptake capacities in the resulting waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents (Wang et al., 2011). The authors pointed out that these impurities in the parent waste materials followed reactions represented by equation 5.1, where M represents sodium or potassium and Li\textsubscript{2}−\textsubscript{x}M\textsubscript{x}/\textsubscript{2}CO\textsubscript{3} denotes a mixture of Li\textsubscript{2}CO\textsubscript{3}, K\textsubscript{2}CO\textsubscript{3} and Na\textsubscript{2}CO\textsubscript{3}.

\[
Li_{4-x}M_xSiO_4 + CO_2 \leftrightarrow Li_{2-x}M_{x/2}CO_3 + Li_{2-x}M_{x/2}SiO_3 \tag{5.1}
\]
Figure 5.10 Isothermal CO\textsubscript{2} uptake profiles of a) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-0; b) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-5; c) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-10 and d) SS-B-Li\textsubscript{4}SiO\textsubscript{4}-20 in pure CO\textsubscript{2} environment.
Although there was significantly higher content of $K_2O$ in POMBA (6.80 wt%) compared to the rest of parent waste materials (<2.27 wt%), there was particularly lower content of $Na_2O$ in POMBA (0.03 wt%) compared to other waste materials (up to 0.84 wt%) (Table 4.2). Therefore, it could be concluded that only high content of potassium in POMBA contributed to the significant improvement of CO$_2$ uptake capacity of SS-B-Li$_4$SiO$_4$ sorbents compared to SS-P-Li$_4$SiO$_4$ and other waste derived Li$_4$SiO$_4$ sorbents. Sodium content in parent waste material did not seem to affect CO$_2$ uptake capacity of the resulting waste-derived Li$_4$SiO$_4$ sorbents in current study.

Table 5.7 presents the CO$_2$ uptake capacity of SS-B-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions and different times (30 and 120 minutes) into the analysis. In general, it is observed that SS-B-Li$_4$SiO$_4$ sorbents exhibit an increase in CO$_2$ uptake capacity as a function of excess lithium addition. The lowest CO$_2$ uptake was obtained by SS-B-Li$_4$SiO$_4$-0 sorbent (128.6 mg CO$_2$/g sorbent) at 500 °C, while the highest was obtained by SS-B-Li$_4$SiO$_4$-20 (256.5 mg CO$_2$/g sorbent) at 700 °C. Similar to other waste-derived Li$_4$SiO$_4$ sorbents, the sorption rate of sorbents increased with sorption temperatures. This is indicated by the amount of CO$_2$ captured by sorbents at 30 minutes into the duration of analysis.
Table 5.7 CO$_2$ uptake capacity of SS-B-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions in pure CO$_2$ environment at 30 and 120 minutes into the analysis.

<table>
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<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO$_2$ uptake capacity (mg CO$_2$/g sorbent)</th>
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</tr>
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<tr>
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</tr>
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</table>

As stated in previous studies, the CO$_2$ sorption mechanism by Li$_4$SiO$_4$ sorbents can be explained by two processes i.e. surface chemisorption of CO$_2$ and diffusion of Li$^+$ and O$^{2-}$ ions through the double shells that formed over the bulk of Li$_4$SiO$_4$ particle (Essaki et al., 2005; Duran-Munoz et al., 2013). The diffusion rate is believed to be the limiting step due to the slower reaction rate towards the end of analysis duration, in comparison to the chemisorption step indicated by significantly steeper slope at the beginning of sorption isotherms. If this is the case, then the CO$_2$ sorption by sorbents can be simulated by a double exponential model, as represented by equation (5.2), where $y$ (mg CO$_2$/g sorbent) is the sorption capacity at time $t$. $k_1$ and $k_2$ ($s^{-1}$) represent the exponential rate constants for chemisorption.
and diffusion, respectively, while A and B are the pre-exponential constants and C is the y-intercept.

\[ y = Ae^{(-k_1t)} + Be^{(-k_2t)} + C \]  

(5.2)

In an attempt to corroborate this hypothesis with the data obtained in this study, kinetic analyses were performed on the sorbents with the highest CO\textsubscript{2} sorption capacity (SS-B-Li\textsubscript{4}SiO\textsubscript{4}). Table 5.8 shows the kinetic parameters obtained from SS-B-Li\textsubscript{4}SiO\textsubscript{4} isotherms for chemisorption and diffusion i.e. \( k_1 \) and \( k_2 \), respectively, as well as the \( R^2 \) values indicating the goodness of fit. Generally, \( k_1 \) values are at least 1 order of magnitude higher than those of \( k_2 \) for all SS-B-Li\textsubscript{4}SiO\textsubscript{4} sorbents. This confirms that the diffusion step kinetically limits the overall CO\textsubscript{2} sorption process at sorption temperatures 500, 600 and 700 °C for all SS-B-Li\textsubscript{4}SiO\textsubscript{4} sorbents. It is also observed that both \( k_1 \) and \( k_2 \) values increased with sorption temperatures, confirming that the rate of sorption improved with an increase in sorption temperature. \( k_1 \) and \( k_2 \) values obtained in this study were also found to be in good agreement with published studies. Olivares-Marin et al. (2010) reported similar findings, where \( k_1 \) values were at least 1 magnitude higher than those of \( k_2 \) for fly ash-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents.
Table 5.8 Kinetic parameters and $R^2$ values obtained from SS-B-Li$_4$SiO$_4$ isotherms.

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Sorption temperature (°C)</th>
<th>$k_1$ (s$^{-1}$)</th>
<th>$k_2$ (s$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-B-Li$_4$SiO$_4$-0</td>
<td>500</td>
<td>$5.28 \times 10^{-3}$</td>
<td>$3.14 \times 10^{-4}$</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$6.66 \times 10^{-3}$</td>
<td>$3.70 \times 10^{-4}$</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>$2.52 \times 10^{-2}$</td>
<td>$1.35 \times 10^{-3}$</td>
<td>0.995</td>
</tr>
<tr>
<td>SS-B-Li$_4$SiO$_4$-5</td>
<td>500</td>
<td>$7.12 \times 10^{-3}$</td>
<td>$4.07 \times 10^{-4}$</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$1.03 \times 10^{-2}$</td>
<td>$3.87 \times 10^{-4}$</td>
<td>0.995</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>$2.85 \times 10^{-2}$</td>
<td>$1.93 \times 10^{-3}$</td>
<td>0.992</td>
</tr>
<tr>
<td>SS-B-Li$_4$SiO$_4$-10</td>
<td>500</td>
<td>$1.05 \times 10^{-2}$</td>
<td>$2.95 \times 10^{-4}$</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$1.07 \times 10^{-2}$</td>
<td>$4.16 \times 10^{-4}$</td>
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<tr>
<td></td>
<td>700</td>
<td>$3.03 \times 10^{-2}$</td>
<td>$1.47 \times 10^{-3}$</td>
<td>0.990</td>
</tr>
<tr>
<td>SS-B-Li$_4$SiO$_4$-20</td>
<td>500</td>
<td>$9.60 \times 10^{-3}$</td>
<td>$3.31 \times 10^{-4}$</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>$1.14 \times 10^{-2}$</td>
<td>$4.73 \times 10^{-4}$</td>
<td>0.989</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>$3.17 \times 10^{-2}$</td>
<td>$2.27 \times 10^{-3}$</td>
<td>0.986</td>
</tr>
</tbody>
</table>

The $k$ values were then used to generate the Arrhenius plot, in order to determine the temperature dependence of the reaction rates by obtaining the activation energy ($E_a$) of the reactions. The $E_a$ values were obtained by plotting natural logarithm of the reaction rates, i.e. $\ln k_1$ and $\ln k_2$, versus the inverse of the sorption temperatures in degree Kelvin ($1/T$). The slope of the plot equals to $E_a/RT$, from which $E_a$ value can be calculated (Equation 5.2). Note that $R$ is the gas constant and $\ln A$ is the $y$-intercept.

$$
\ln k = \ln A - \frac{E_a}{RT}
$$

(5.2)

Figures 5.11 to 5.14 show Arrhenius plots of SS-B-Li$_4$SiO$_4$ sorbents with the calculated values of $E_a$ corresponding to $k_1$ and $k_2$ values. Note that $E_{\text{ac}}$ represents the activation energy of the chemisorption step, while $E_{\text{ad}}$ corresponds to
activation energy of the diffusion step. High activation energy denotes reaction rate that is strongly affected by temperature, while low activation energy corresponds to a reaction rate that slightly changes with temperature.

It is found that almost all \( E_{ac} \) values of SS-B-Li\(_4\)SiO\(_4\) sorbents were lower (42.4, 31.9, 36.1 \text{ kJ/mol} \) for SS-B-Li\(_4\)SiO\(_4\)-5, SS-B-Li\(_4\)SiO\(_4\)-10 and SS-B-Li\(_4\)SiO\(_4\)-20, respectively) than those of \( E_{ad} \) (46.5, 49.0, 58.5 \text{ kJ/mol} \) for SS-B-Li\(_4\)SiO\(_4\)-5, SS-B-Li\(_4\)SiO\(_4\)-10 and SS-B-Li\(_4\)SiO\(_4\)-20, respectively), with the exception of SS-B-Li\(_4\)SiO\(_4\)-0, where the \( E_{ac} \) value was higher (47.3 \text{ kJ/mol} \) than \( E_{ad} \) (44.2 \text{ kJ/mol} \). This indicates that the diffusion step of the CO\(_2\) sorption process on SS-B-Li\(_4\)SiO\(_4\)-0 sorbents was slightly affected by sorption temperatures 500, 600 and 700 °C, in comparison to the rest of SS-B-Li\(_4\)SiO\(_4\) sorbents. Furthermore, \( E_{ac} \) values decreased with increasing excess lithium, but at the same time \( E_{ad} \) values increased with the addition of excess lithium. This suggests that the excess lithium enhanced the chemisorption step of CO\(_2\) sorption, but inhibited the diffusion step with addition of excess lithium.
Figure 5.11 Arrhenius plot with $E_a$ values of SS-B-Li$_4$SiO$_4$-0 sorbent at 500, 600 and 700 °C.

Figure 5.12 Arrhenius plot with $E_a$ values of SS-B-Li$_4$SiO$_4$-5 sorbent at 500, 600 and 700 °C.
Figure 5.13 Arrhenius plot with $E_a$ values of SS-B-Li$_4$SiO$_4$-10 sorbent at 500, 600 and 700 °C.

Figure 5.14 Arrhenius plot with $E_a$ values of SS-B-Li$_4$SiO$_4$-20 sorbent at 500, 600 and 700 °C.
Comparing the CO\textsubscript{2} uptake profiles across all five sorbents with various percentages of excess lithium at 500 °C revealed that the CO\textsubscript{2} uptake profiles did not reach equilibrium by the end of the 120-minute analysis time. Interestingly, pure SS-P-Li\textsubscript{4}SiO\textsubscript{4} sorbents captured significantly less CO\textsubscript{2} compared to its waste-derived sorbent counterparts, despite pure SiO\textsubscript{2} was used in the preparation of the sorbent.

As discussed in Section 4.3, the amorphous phase found in the waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents could be contributing to the enhanced CO\textsubscript{2} uptake performance of the sorbents due to the versatility of amorphous structure in capturing CO\textsubscript{2} molecules. In comparison to the more ordered structure of its crystalline counterpart which is predominantly found in SS-P-Li\textsubscript{4}SiO\textsubscript{4} sorbents, the coexistence of amorphous Li\textsubscript{4}SiO\textsubscript{4} is thought to contribute to the increase in CO\textsubscript{2} sorption capacity of the waste-derived sorbents. Faster diffusion of molecules into amorphous structure than that in crystalline due to the atomic disorder (Sadoway, 2010) is also believed to increase the rate of CO\textsubscript{2} sorption of the sorbents.

All five sorbents did not exhibit sorption equilibrium at 600 °C, although the overall CO\textsubscript{2} uptake capacities by all sorbents appeared to be improved with increased sorption temperature by 100 °C except for SS-C-Li\textsubscript{4}SiO\textsubscript{4} and SS-R-Li\textsubscript{4}SiO\textsubscript{4} which showed the opposite trend. This indicates that the increment in sorption temperature has provided enough thermal energy to increase the diffusion of ions in the bulk of Li\textsubscript{4}SiO\textsubscript{4} particles to react with CO\textsubscript{2} molecules, but at the same time not enough for the diffusion to be completely activated that would lead to sorption
equilibrium of sorbents (Duran-Munoz et al., 2013). The overall sorption rate of all sorbents also improved following the increment of sorption temperature from 500 to 600 °C, as indicated by the increase in amount of CO\textsubscript{2} captured by sorbents during the first 30 minutes of analysis.

In addition, SS-P-Li\textsubscript{4}SiO\textsubscript{4} sorbents still showed the lowest amount of CO\textsubscript{2} captured compared to the waste-derived sorbents even at an increased sorption temperature. Among the waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents, the highest CO\textsubscript{2} uptake capacity was obtained by SS-B-Li\textsubscript{4}SiO\textsubscript{4} sorbents at all amounts of excess lithium with highest capacity of up to approximately 197 mg CO\textsubscript{2}/g sorbent by SS-B-Li\textsubscript{4}SiO\textsubscript{4}-20 sorbent. On the other hand, the lowest CO\textsubscript{2} uptake capacity of waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents was obtained by either SS-R-Li\textsubscript{4}SiO\textsubscript{4} or SS-F-Li\textsubscript{4}SiO\textsubscript{4} sorbent, depending on the amount of excess lithium. SS-F-Li\textsubscript{4}SiO\textsubscript{4} sorbents captured more CO\textsubscript{2} (up to 124 mg CO\textsubscript{2}/g sorbent) with the addition of excess lithium, while SS-R-Li\textsubscript{4}SiO\textsubscript{4} sorbents captured more CO\textsubscript{2} (up to 124 mg CO\textsubscript{2}/g sorbent) with less amounts of excess lithium.

Evidently, the CO\textsubscript{2} uptake capacity profiles at 700 °C exhibit a different trend compared to that at 600 °C. Sorption equilibrium was attained at some point depending on the amount of excess lithium by almost all Li\textsubscript{4}SiO\textsubscript{4} sorbents, with the exception of SS-P-Li\textsubscript{4}SiO\textsubscript{4}. Overall CO\textsubscript{2} uptake capacities by all sorbents appeared to be improved at 700 °C. This indicates that the increment in sorption temperature has provided enough thermal energy to completely activate the diffusion of ions in the bulk of Li\textsubscript{4}SiO\textsubscript{4} particles to react with CO\textsubscript{2} molecules that in
turn, lead to sorption equilibrium of sorbents (Duran-Munoz et al., 2013). The overall sorption rate of all sorbents has also substantially improved following the increment of sorption temperature from 600 to 700 °C.

In addition, SS-P-Li$_4$SiO$_4$ sorbents still showed the lowest amount of CO$_2$ captured compared to the waste-derived sorbents even at an increased sorption temperature. It is believed that the impurities in the starting waste materials, e.g., K$_2$O, contributed to the improvement of CO$_2$ uptake capacities of waste-derived Li$_4$SiO$_4$ sorbents, in particular the SS-B-Li$_4$SiO$_4$ sorbents. However, the CO$_2$ uptake capacities of SS-P-Li$_4$SiO$_4$ sorbents have improved significantly at 700 °C of up to 136 mg CO$_2$/g sorbent by SS-P-Li$_4$SiO$_4$-20. Among the waste-derived Li$_4$SiO$_4$ sorbents, the highest CO$_2$ uptake capacity was also obtained by SS-B-Li$_4$SiO$_4$ sorbents at all amounts of excess lithium with highest capacity of up to approximately 257 mg CO$_2$/g sorbent by SS-B-Li$_4$SiO$_4$-20 sorbent at the same sorption temperature. On the other hand, the lowest CO$_2$ uptake capacity of waste-derived Li$_4$SiO$_4$ sorbents was obtained by SS-F-Li$_4$SiO$_4$ sorbent of up to 199 mg CO$_2$/g sorbent by SS-F-Li$_4$SiO$_4$-20.

5.2.3. CO$_2$ uptake by sorbents in diluted CO$_2$ environment

The CO$_2$ uptake capacities for all prepared Li$_4$SiO$_4$ sorbents were determined using diluted CO$_2$ (14 vol% CO$_2$, balance N$_2$) environment. The diluted CO$_2$ concentration is selected specifically at 14 vol% to simulate the CO$_2$ concentration in a flue gas stream exiting the combustion chamber in a coal-fired power plant, containing
from 10 to 15 vol% of CO$_2$ (GCCSI, 2012). It is worthy to note that apart from the concentration of CO$_2$ used in the analysis, other experimental conditions such as sorption temperatures (500, 600 and 700 °C) and duration of analysis (120 minutes) remained constant to that of conditions reported in the previous section.

Isothermal CO$_2$ uptake profiles of SS-P-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium are presented in Figure 5.15. Similar to the outcome reported in previous section (Figure 5.5), the profiles do not exhibit sorption equilibrium at the end of the analysis. Also, the amount of CO$_2$ uptake capacity by sorbents decreased significantly in diluted CO$_2$ environment compared to that in pure one. This observation is in good agreement with a study by Essaki et al. (2005) which reported the CO$_2$ uptake capacity of pure Li$_4$SiO$_4$ pellets decreased significantly (from 27 wt% in 15 vol% CO$_2$ at 600 °C to 2 wt% in 5 vol% CO$_2$) as the partial pressure of CO$_2$ decreased (Essaki et al., 2005).

Additionally, there is a distinctive trend of CO$_2$ uptake profiles in diluted CO$_2$ environment, where the amount of CO$_2$ uptake increased with sorption temperature up to 600 °C before decreasing significantly at 700 °C. The decrease in CO$_2$ uptake capacity is expected due to the substantially low CO$_2$ partial pressure making it harder for the sorbents to capture CO$_2$ efficiently. Seggiani et al. (2013) explained this occurrence to be attributed to the Gibbs free energy changes ($\Delta G$) of the sorption reaction between CO$_2$ and Li$_4$SiO$_4$ (Seggiani et al., 2013). As the CO$_2$ sorption is an exothermic reversible gas-solid reaction with equilibrium constant equivalent to an inverse of CO$_2$ partial pressure, the lower the CO$_2$ concentration
Figure 5.15 Isothermal CO$_2$ uptake profiles of a) SS-P-Li$_4$SiO$_4$-0; b) SS-P-Li$_4$SiO$_4$-5; c) SS-P-Li$_4$SiO$_4$-10 and d) SS-P-Li$_4$SiO$_4$-20 in diluted CO$_2$ (14 vol%) environment.
the lower the equilibrium emission temperature, which is the temperature where CO₂ sorption and regeneration both share the same temperature. Consequently, desorption process was initiated at lower temperature (600 °C) in diluted CO₂ sorption environment compared to the pure one, i.e. at 700 °C (Seggiani et al., 2013).

The CO₂ uptake capacities of SS-P-Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO₂ environment are presented in Table 5.9. It is observed that CO₂ uptake capacity by SS-P-Li₄SiO₄ sorbents in diluted CO₂ environment peaked at sorption temperature of 600 °C with 20 wt% excess lithium (70.32 mg CO₂/g sorbent), while the lowest uptake capacity was observed by SS-P-Li₄SiO₄-0 with 2.08 mg CO₂/g sorbent captured at 700 °C. In addition, the sorption rate of SS-P-Li₄SiO₄ sorbents is observed to increase as a function of sorption temperature of up to 600 °C before it dropped abruptly at 700 °C. This is indicated by the amounts of CO₂ captured at 30 minutes into the analysis duration compared to at the end of the analysis (120 min).

Analysing the CO₂ uptake capacity isothermally and according to increasing amount of excess lithium, SS-P-Li₄SiO₄ sorbents captured less CO₂ with more addition of excess lithium at 500 °C. However at 600 °C, an increasing trend of uptake capacity is observed as the amount of excess lithium is increased. Similar trend was identified at 700 °C despite the sharp decrease in overall CO₂ uptake capacity. The same trend was also observed in pure CO₂ environment (Table 5.3), deducing the same assumption that the excess amounts of lithium inhibits CO₂
uptake by sorbents at lower sorption temperature (500 °C) but not at higher temperatures (600, 700 °C).

Table 5.9 CO$_2$ uptake capacity of SS-P-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO$_2$ environment.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO$_2$ uptake capacity (mg CO$_2$/g sorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30 min</td>
</tr>
<tr>
<td>0</td>
<td>500</td>
<td>15.5716</td>
</tr>
<tr>
<td>5</td>
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<td>9.7643</td>
</tr>
<tr>
<td>10</td>
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<td>5.6585</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>3.0474</td>
</tr>
<tr>
<td>0</td>
<td>600</td>
<td>34.19</td>
</tr>
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<td></td>
<td>44.58</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>49.54</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>53.59</td>
</tr>
<tr>
<td>0</td>
<td>700</td>
<td>1.9285</td>
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<td>5.2617</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>8.0507</td>
</tr>
</tbody>
</table>

Figure 5.16 shows the isothermal CO$_2$ uptake profiles of a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10 and d) SS-C-Li$_4$SiO$_4$-20 in diluted CO$_2$ environment. CO$_2$ uptake capacity profiles by SS-C-Li$_4$SiO$_4$ sorbent do not exhibit sorption equilibrium during the 120-minute analysis, similarly to the profiles in pure CO$_2$ environment. Moreover, the CO$_2$ uptake profiles trend presented in Figure 5.16 is analogous to that of SS-P-Li$_4$SiO$_4$ sorbents in previously discussed Figure 5.15, whereby shifted equilibrium emission temperature to 600 °C in diluted CO$_2$ environment is observed.
The rate of CO\textsubscript{2} sorption by SS-C-Li\textsubscript{4}SiO\textsubscript{4} sorbents increased as the sorption temperature increased from 500 to 600 °C. However, the sorption rate declined abruptly at 700 °C. Additionally, the sorption rate is also noticeably higher than that of SS-P-Li\textsubscript{4}SiO\textsubscript{4}. Furthermore, the amount of excess lithium added during sorbent preparation also seemed to improve the sorption rate, as seen in Figure 5.16.
Figure 5.16 Isothermal CO$_2$ uptake profiles of a) SS-C-Li$_4$SiO$_4$-0; b) SS-C-Li$_4$SiO$_4$-5; c) SS-C-Li$_4$SiO$_4$-10 and d) SS-C-Li$_4$SiO$_4$-20 in diluted CO$_2$ (14 vol%) environment.
Table 5.10 presents maximum CO$_2$ uptake capacity of waste-derived SS-C-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO$_2$ environment. At 500 °C sorption temperature, the overall CO$_2$ uptake exhibits decreasing trend with increasing amount of excess lithium. On the other hand, increasing trend in CO$_2$ uptake as a function of excess lithium at 600 °C was observed, also with slight drop in CO$_2$ uptake by SS-C-Li$_4$SiO$_4$-5 and SS-C-Li$_4$SiO$_4$-20 sorbents. At 700 °C, similar increasing overall trend of CO$_2$ uptake by sorbents with amounts of excess lithium is observed.

Comparing with CO$_2$ uptake in pure environment, there is a change in uptake/amount of excess lithium trend. The highest CO$_2$ uptake was 140.9 mg CO$_2$/g sorbent at 600 °C by SS-C-Li$_4$SiO$_4$-10, whereas the lowest amount of CO$_2$ also captured by SS-C-Li$_4$SiO$_4$-10 sorbent at 700 °C (29.18 mg CO$_2$/g sorbent). The sorption rate of sorbents was also increased up until 600 °C before plummeted at 700 °C, based on the amount of CO$_2$ uptake capacity of sorbents at 30 minutes into the analysis compared to the amount at 120 minutes.
Table 5.10 CO$_2$ uptake capacity of SS-C-Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO$_2$ environment.

<table>
<thead>
<tr>
<th>Amount of excess lithium (%)</th>
<th>Sorption temperature (°C)</th>
<th>CO$_2$ uptake capacity (mg CO$_2$/g sorbent)</th>
<th>30 min</th>
<th>120 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
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<td>75.90</td>
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<td>96.77</td>
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</tr>
<tr>
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<td>600</td>
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<td></td>
</tr>
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<td>105.79</td>
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<td>137.7</td>
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</tr>
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<tr>
<td>0</td>
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<td>43.90</td>
<td>53.77</td>
<td></td>
</tr>
<tr>
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<td>24.51</td>
<td>30.99</td>
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<td>10</td>
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<td>22.31</td>
<td>29.18</td>
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</tr>
<tr>
<td>20</td>
<td></td>
<td>28.07</td>
<td>35.41</td>
<td></td>
</tr>
</tbody>
</table>

Isothermal CO$_2$ uptake profiles of SS-R-Li$_4$SiO$_4$, SS-F-Li$_4$SiO$_4$ and SS-B-Li$_4$SiO$_4$ sorbents in diluted CO$_2$ environment exhibit similar trend to that of SS-C-Li$_4$SiO$_4$ sorbents and therefore, are presented in the Appendix section (Figures A5.3, A5.4 and A5.5) at the end of this thesis.

Table 5.11 lists the CO$_2$ uptake capacity of waste-derived Li$_4$SiO$_4$ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO$_2$ environment at the end of analysis duration. At 500 and 600 °C, overall CO$_2$ uptake trend by SS-R-Li$_4$SiO$_4$ sorbents decreased with increasing amount of excess lithium. However, an inverse trend of CO$_2$ uptake is observed at 700 °C. On the
other hand, a direct correlation between amount of excess lithium and CO₂ uptake was observed by both SS-F-Li₄SiO₄ and SS-B-Li₄SiO₄ sorbents. There is no apparent change when comparing CO₂ uptake trend by all three SS-R-Li₄SiO₄, SS-F-Li₄SiO₄ and SS-B-Li₄SiO₄ sorbents in pure CO₂ environment, although the overall amounts of CO₂ uptake decreased significantly. The decrease in amounts of CO₂ uptake captured by sorbents in diluted CO₂ environment is expected as there is substantially less CO₂ molecules available to react with sorbents.

As mentioned previously, the amount of excess lithium strongly affects the amount of CO₂ uptake by sorbents. In the case of SS-R-Li₄SiO₄ sorbents, the absence of excess lithium produced a sorbent with maximum CO₂ uptake in diluted CO₂ environment at 600 °C (110.1 mg CO₂/g sorbent), while SS-R-Li₄SiO₄-5 captured the lowest amount of CO₂ (27.21 mg CO₂/g sorbent). For both SS-F-Li₄SiO₄ and SS-B-Li₄SiO₄ sorbents, 20% excess lithium enhanced the CO₂ uptake up to 117.3 and 186.1 mg CO₂/g sorbent at 600 °C, respectively. However, the least CO₂ uptake by SS-F-Li₄SiO₄ and SS-B-Li₄SiO₄ sorbents observed by SS-F-Li₄SiO₄-10 (33.73 mg CO₂/g sorbent) and SS-B-Li₄SiO₄-5 (16.35 mg CO₂/g sorbent) at 700 °C despite the direct correlation between amount of excess lithium and CO₂ uptake by the sorbents.
Table 5.11 CO₂ uptake capacity of waste-derived Li₄SiO₄ sorbents with different amounts of excess lithium at isothermal sorption conditions in diluted CO₂ environment at the end of analysis duration.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Amount of excess lithium (%)</th>
<th>CO₂ uptake at different sorption temperatures (mg CO₂/g sorbent)</th>
</tr>
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<tr>
<td>SS-R-Li₄SiO₄</td>
<td>0</td>
<td>94.22 110.1 47.91</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>51.75  86.39 27.21</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>73.72  102.8  57.23</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>54.55  78.38  47.37</td>
</tr>
<tr>
<td>SS-F-Li₄SiO₄</td>
<td>0</td>
<td>64.33  105.7  43.00</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>78.36  106.3  39.19</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>62.18  88.80  33.73</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>81.13  117.3  53.27</td>
</tr>
<tr>
<td>SS-B-Li₄SiO₄</td>
<td>0</td>
<td>111.5  152.6  34.41</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>82.78  142.5  16.35</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>111.2  162.1  25.90</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>126.1  186.1  28.24</td>
</tr>
</tbody>
</table>

5.3. Regeneration of waste-derived Li₄SiO₄ sorbents

Following the CO₂ uptake analysis, regeneration performance of waste-derived Li₄SiO₄ sorbents in both pure and diluted CO₂ environments are discussed in this section. Regeneration performance analyses were carried out in cyclic isothermal sorption conditions at which the sorbents captured the highest amount of CO₂ i.e. at 700 °C. Regeneration of sorbents at 600 °C was also carried out for comparison purposes. The sorption time was held for 30 minutes in CO₂ environment (pure or diluted) before being regenerated in an inert environment (N₂) for 30 minutes.
The sorption/regeneration cycle was then repeated for 10 times in order to establish preliminary study of the stability of the sorbents in cyclic conditions.

5.3.1. *Regeneration of waste-derived sorbents in pure CO$_2$ environment*

Figure 5.17 shows the multiple cycles regeneration profiles of SS-P-Li$_4$SiO$_4$ sorbents with 0, 5, 10 and 20% excess lithium at a) 600 °C and b) 700 °C. While the addition of excess lithium improved the overall CO$_2$ uptake capacity in a single cycle at 600 °C (Table 5.3), it did not seem to affect the stability of the sorbents in multiple cycles regeneration process at the same temperature (Figure 5.17a). In addition, the amount of CO$_2$ uptake capacity of sorbents did not reach sorption equilibrium. This is expected as the CO$_2$ uptake analysis of the same sorbents also did not attain sorption equilibrium during 120 minutes of analysis duration, as shown in Figure 5.5.

Moreover, it is evident in Figure 5.17a that the amount of CO$_2$ uptake capacity of sorbents progressively increasing despite the decreasing sorption rate with each regeneration cycle. This suggests that the sorbents were continuously capturing more CO$_2$ as the analysis advances until sorption equilibrium is reached. At 700 °C (Figure 5.17b), the CO$_2$ uptake capacity no longer increased with regeneration cycles as it was observed at 600 °C. The regeneration cycles now are observed to be more stabilised after the first two cycles and continued performing in this manner until the end of analysis duration. There is, however, a slight degradation
in the amount of CO\(_2\) uptake (approximately 2 mg CO\(_2\)/g sorbent) by SS-P-Li\(_4\)SiO\(_4\) sorbents between the first and the 10\(^{th}\) regeneration cycle.

![Figure 5.17 Regeneration profiles of SS-P-Li\(_4\)SiO\(_4\) sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium.](image)

Similar to the performance in single cycle at 700 °C, the CO\(_2\) uptake capacity by SS-P-Li\(_4\)SiO\(_4\) sorbents increased with the addition of excess lithium. However, the difference of CO\(_2\) uptake capacity and the amount of excess lithium was not significantly improved, considering the amount of excess lithium that needs to be
added to achieve a small degree of improvement in the amount of CO₂ captured. For example, 20% of excess lithium will only improve approximately 20 mg CO₂/g sorbent throughout the regeneration cycles. From the perspective of potential industrial application, it might not be worth adding an excess amount of lithium if this would not significantly improve the CO₂ uptake capacity performance of the sorbent. Comparing the amount of CO₂ uptake between the regeneration cycles at 600 and 700 °C, it is evident that the latter performed better with cumulative amount of CO₂ captured by SS-P-Li₄SiO₄ sorbents of approximately 850 mg CO₂/g sorbent after 10 cycles. On the other hand, the same sorbents captured about 580 mg CO₂/g sorbent at 600 °C throughout the analysis.

Figure 5.18 shows the regeneration profiles of SS-C-Li₄SiO₄ sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium. In general, there was no sorption equilibrium attained at 600 °C, as can be expected from the CO₂ uptake analysis of the same sorbents at the same sorption temperatures in Figure 5.7. It is also observed in Figure 5.18a the familiar increment of CO₂ uptake capacity of sorbents as the analysis advances. As explained in the previous paragraphs, this suggests that the sorbents were progressively capturing more CO₂ as the analysis progresses until sorption equilibrium is eventually reached.

It is observed that the CO₂ uptake capacity of sorbents decreased as a function of excess lithium. This is expected as similar trend was detected during the CO₂ uptake analysis of the same sorbent (Table 5.4). Sorbents with no excess lithium captured significantly higher amount of CO₂ (up to 170 mg CO₂/g sorbent) than
sorbents with 20% of excess lithium (up to 85 mg CO$_2$/g sorbent) in multiple regeneration cycles. This brings to a deduction that apart from the CO$_2$ uptake capacity of sorbents, the addition of excess lithium seems to have neither a positive nor a negative effect to the performance of CO$_2$ regeneration by SS-C-Li$_4$SiO$_4$ sorbents at 600 °C in pure CO$_2$ environment.

Figure 5.18 Regeneration profiles of SS-C-Li$_4$SiO$_4$ sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium in pure CO$_2$ environment.
The regeneration profiles of SS-C-Li$_4$SiO$_4$ sorbents at 700 °C in Figure 5.18b seemingly exhibit a different trend compared to at 600 °C, where all SS-C-Li$_4$SiO$_4$ sorbents attained sorption equilibrium throughout the analysis. As a result of this, the profiles showed a more stabilised sorption/regeneration cycles compared to at 600 °C. In addition, the CO$_2$ uptake capacity increased as a function of excess lithium, as can be expected from the single cycle analysis shown in Table 5.4.

Figure 5.19 shows the regeneration profiles of SS-B-Li$_4$SiO$_4$ sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium. In general, Figure 5.19 presents similar regeneration profiles to that of SS-C-Li$_4$SiO$_4$ sorbents in Figure 5.18. The effect of excess lithium on CO$_2$ uptake performance of both SS-C-Li$_4$SiO$_4$ and SS-B-Li$_4$SiO$_4$ sorbents are to be expected, as similar trend was also observed in their respective single cycle CO$_2$ uptake performances in Figures 5.7 and 5.10. Also, it is evident that no sorption equilibrium was reached at 600 °C, as shown in Figure 5.18a. This is to be expected from previous observations, where no sorption equilibrium was reached at sorption temperatures lower than 700 °C. Despite showing similar regeneration performances, SS-B-Li$_4$SiO$_4$ sorbents seemed to have higher CO$_2$ uptake capacities than SS-C-Li$_4$SiO$_4$ sorbents. For example, SS-B-Li$_4$SiO$_4$-20 captured cumulatively 2540 mg CO$_2$/g sorbent at 700 °C, while SS-C-Li$_4$SiO$_4$-20 captured about 2300 mg CO$_2$/g sorbent at the same temperature.
5.3.2. Regeneration of waste-derived sorbents in diluted CO\(_2\) environment

SS-C-Li\(_4\)SiO\(_4\) and SS-B-Li\(_4\)SiO\(_4\) sorbents were also studied for their multiple cycles regeneration performance in diluted CO\(_2\) environment. It is worthy to note that apart from the concentration of CO\(_2\) used in the analysis, other experimental
conditions such as regeneration temperatures (600 and 700 °C) and duration of regeneration cycles (30 minutes sorption, 30 minutes regeneration) remain unchanged to that of conditions reported in the previous section, so that meaningful comparisons can be established.

Figures 5.20a and 5.20b represent the regeneration profiles of SS-C-Li$_4$SiO$_4$ at 600 and 700 °C, respectively, with different amounts of excess lithium in diluted CO$_2$ environment. As expected at 600 °C, no sorption equilibrium was attained during the sorption step of the regeneration cycle by the sorbents. As the analysis progresses, the CO$_2$ uptake capacity of sorbents gradually increased, a similar trend that was also observed in pure CO$_2$ environment (Figure 5.18).

The CO$_2$ uptake capacity trend in multiple cycles as a function of excess lithium corresponds to that of CO$_2$ uptake analysis of the same sorbents in diluted CO$_2$ environment in section 5.2.2 (Table 5.10). Sorbents with no excess lithium captured significantly higher amount of CO$_2$ (up to 160 mg CO$_2$/g sorbent) than sorbents with 20% of excess lithium (up to 112 mg CO$_2$/g sorbent) in multiple regeneration cycles.

It is observed that the same sorbents performed differently at 700 °C. Evidently, the overall CO$_2$ uptake capacity of sorbents decreased substantially (Figure 5.20b) compared to the performance of the same sorbents in pure CO$_2$ environment (Figure 5.18b). As discussed in section 5.2.2, the considerable change in CO$_2$ uptake of sorbents in a significantly reduced CO$_2$ partial pressure has changed the
Δ$G$ of the sorption reaction between CO$_2$ and Li$_4$SiO$_4$ particles and thus, decreasing the CO$_2$ uptake of sorbents (Seggiani et al., 2013). For this reason, it is expected that the sorbents performed in a similar trend in multiple regeneration cycles as they did during the CO$_2$ uptake analysis.

Figure 5.20 Regeneration profiles of SS-C-Li$_4$SiO$_4$ sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium in diluted CO$_2$ environment.
Analysing the effect of excess lithium in sorbents, it is observed that the sorbents maintained the familiar decreasing trend of \( \text{CO}_2 \) uptake capacity as a function of excess lithium. However, the downward tendency of \( \text{CO}_2 \) uptake capacity was not as obvious in SS-C-Li_4SiO_4-0 compared to the rest of the SS-C-Li_4SiO_4 sorbents. Additionally, the \( \text{CO}_2 \) uptake capacity of SS-C-Li_4SiO_4-5, SS-C-Li_4SiO_4-10 and SS-C-Li_4SiO_4-20 sorbents evidently captured significantly less \( \text{CO}_2 \) compared to SS-C-Li_4SiO_4 sorbent. This indicates that the excess lithium inhibits the \( \text{CO}_2 \) uptake capacity of sorbents, which was previously discussed in section 5.2.2.

Similar regeneration performance can be observed in Figure 5.21, which shows the regeneration profiles of SS-B-Li_4SiO_4 sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium. It is evident that the overall amount of captured \( \text{CO}_2 \) by SS-B-Li_4SiO_4 sorbents at 700 °C (Figure 5.21b) decreased significantly compared to that at 600 °C (Figure 5.21a), comparable to SS-C-Li_4SiO_4 sorbents regeneration profiles observed in Figure 5.20. It is worthy to note that amount of excess lithium had the opposite effect on \( \text{CO}_2 \) uptake capacities in between both sorbents. This suggests that the dependency of the amount of excess lithium to improve overall \( \text{CO}_2 \) uptake capacities varies with the waste materials used to develop waste-derived Li_4SiO_4 \( \text{CO}_2 \) sorbents.
Figure 5.21 Regeneration profiles of SS-B-Li$_4$SiO$_4$ sorbents at a) 600 °C and b) 700 °C with different amounts of excess lithium in diluted CO$_2$ environment.

5.4. Effect of sorbent preparation method on CO$_2$ uptake capacity

Following the preparation of the pure and waste-derived Li$_4$SiO$_4$ sorbents, a study on the effect of sorbent’s preparation method on the CO$_2$ uptake capacity of the sorbents was carried out. A wet impregnation method, namely, suspended
Impregnation (SI) was implemented on the parent waste material POMBA. POMBA was selected as the waste material to be investigated in this study due to the highest CO₂ uptake capacity showed by SS-B-Li₄SiO₄ in comparison to other waste-derived Li₄SiO₄ sorbents, as reported in section 5.2.1.

It is worthy to note that only 20% excess lithium was added during preparation of the sorbent, as it was found that sorbents with this amount of excess lithium i.e. SS-B-Li₄SiO₄-20 captured the highest amount of CO₂ (257 mg CO₂/g sorbent). The preparation procedures of this method and the subsequent CO₂ capture analysis on the sorbent followed that of previously described in Section 3.2. The resulting sorbent deriving from this preparation method is labelled as SI-B-Li₄SiO₄-20. Furthermore, XRD analysis was carried out on SI-B-Li₄SiO₄-20 to verify the presence of Li₄SiO₄ in the sorbent prepared by this SI method.

Figure 5.22 shows XRD diffractograms of SI-B-Li₄SiO₄-20 resulting from SI preparation method and the previously prepared by solid state (SS) method, SS-B-Li₄SiO₄-20. It is observed that SI-B-Li₄SiO₄-20 exhibited sharp peaks representing Li₄SiO₄ comparable to SS-B-Li₄SiO₄-20 sorbent, denoting a successful attempt in producing a Li₄SiO₄-based sorbent using the procedures described in Section 3.2. Also, there seems to be no significant differences observed between both diffractograms, showing that a different preparation method did not seem to significantly change the mineral phase composition of the sorbent. Reaction products other than Li₄SiO₄ such as LiAlSiO₄ were expectedly detected, since there were significant amounts of aluminosilicates present in the parent waste material.
(Table 4.2). The coexistence of Li$_2$SiO$_3$ in SI-B-Li$_4$SiO$_4$-20 is also expected, as this proved that the reaction between Li$_2$CO$_3$ and the SiO$_2$ in POMBA advanced according to equation 2.2 (Section 2.3.2).

Figure 5.22 XRD diffractograms of a) SI-B-Li$_4$SiO$_4$-20 and b) SS-B-Li$_4$SiO$_4$-20 sorbents.

Figure 5.23 shows the comparison of isothermal CO$_2$ profiles of SI-B-Li$_4$SiO$_4$-20 and SS-B-Li$_4$SiO$_4$-20 sorbents at sorption temperatures 500, 600 and 700 °C. Generally, CO$_2$ uptake capacity of SI-B-Li$_4$SiO$_4$-20 sorbent increased with sorption temperature (Figure 5.23a), although there was not much difference in uptake capacity between 600 and 700 °C towards the end of analysis duration. It was not observed that the CO$_2$ uptake capacity of the sorbent achieved sorption
equilibrium at lower sorption temperatures (500 and 600 °C). However, the CO₂ uptake capacity of the sorbent finally achieved sorption equilibrium at 700 °C. The highest CO₂ uptake capacity during the sorption duration was 197 mg CO₂/g sorbent at 700 °C, while the lowest uptake capacity was 144 mg CO₂/g sorbent at 500 °C.

Similar observations of increasing uptake capacity with sorption temperature were also detected for SS-B-Li₄SiO₄-20 (Figure 5.23b) as well as other waste-derived sorbents, as discussed in section 5.2.1. In addition, the sorption rate of both sorbents did not seem to change much, as indicated by the slope of the sorption isotherms. Kinetic parameters (Table 5.12) showed that there are no significant changes in the values of k₁ and k₂ of SI-B-Li₄SiO₄-20 compared to SS-B-Li₄SiO₄-20, with the exception of k₁ values at 500 °C (5.77 x 10⁻³ and 9.60 x 10⁻³ for SI-B-Li₄SiO₄-20 and SS-B-Li₄SiO₄-20, respectively). These observations indicate that the different in preparation method did not alter the overall trend of uptake capacity with respect to the sorption temperature.

Nevertheless, the overall CO₂ uptake capacity of SI-B-Li₄SiO₄-20 sorbent was lower (up to 197 mg CO₂/g sorbent) than that of SS-B-Li₄SiO₄-20 (up to 257 mg CO₂/g sorbent). This shows that although different preparation method did not drastically alter the overall kinetics performance, it seems to affect the maximum uptake capacity of the sorbents.
Figure 5.23 Isothermal CO₂ profiles of a) SI-B-Li₄SiO₄-20 and b) SS-B-Li₄SiO₄-20 sorbents at 500, 600 and 700 °C.

Table 5.12 Kinetic parameters and R² values comparison between SI-B-Li₄SiO₄-20 and SS-B-Li₄SiO₄-20.

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<thead>
<tr>
<th>Sorbents</th>
<th>Sorption temperature (°C)</th>
<th>k₁ (s⁻¹)</th>
<th>k₂ (s⁻¹)</th>
<th>R²</th>
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<td>SI-B-Li₄SiO₄-20</td>
<td>500</td>
<td>5.77 x 10⁻³</td>
<td>3.25 x 10⁻⁴</td>
<td>0.998</td>
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<tr>
<td></td>
<td>600</td>
<td>1.20 x 10⁻²</td>
<td>4.48 x 10⁻⁴</td>
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<td>700</td>
<td>3.50 x 10⁻²</td>
<td>2.46 x 10⁻³</td>
<td>0.990</td>
</tr>
<tr>
<td>SS-B-Li₄SiO₄-20</td>
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<td>3.31 x 10⁻⁴</td>
<td>0.999</td>
</tr>
<tr>
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<td>1.14 x 10⁻²</td>
<td>4.73 x 10⁻⁴</td>
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<tr>
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<td>700</td>
<td>3.17 x 10⁻²</td>
<td>2.27 x 10⁻³</td>
<td>0.986</td>
</tr>
</tbody>
</table>
5.5. Summary

Chapter 5 discussed the CO$_2$ capture by parent waste materials and their corresponding waste-derived Li$_4$SiO$_4$ sorbents. CO$_2$ capture analyses were conducted at isothermal sorption temperatures of 500, 600 and 700 °C in pure (100 vol%) and diluted (14 vol%) environments. Additionally, waste-derived Li$_4$SiO$_4$ sorbents were also analysed for their CO$_2$ sorption/desorption performances. Parent waste materials (CPFA, RPFA, FBA and POMBA) were not subjected to any pre-treatment method before the analysis to provide ‘raw’ CO$_2$ uptake capacity of waste materials prior to calcination process and also serves as the benchmark values for the progress of subsequent modification of the materials.

5.5.1. CO$_2$ uptake by parent waste materials

In general, it was found that the highest CO$_2$ uptake capacity of parent waste materials was about 4 mg CO$_2$/g sorbent by FBA. The CO$_2$ uptake values by waste materials are significantly lower than that of commercially available liquid solvent e.g. MEA (approximately 176 mg CO$_2$/g sorbent) (Samanta et al., 2012). This proves unsuitability of the waste materials as CO$_2$ sorbents if they were to be used without any pre-treatment. It was also observed that the CO$_2$ uptake profiles did not reach sorption equilibrium during the 120-minute analysis duration for CPFA, while others showed sorption equilibrium at 600 (RPFA and FBA) and 500 °C (POMBA). In addition, CO$_2$ uptake profiles were affected by sorption temperatures, depending on the residence time. Peaking behaviour was observed in all parent
waste materials, indicated by momentary maximum CO₂ uptake capacity before decreasing rapidly.

It was found that peaking behaviour of waste materials was due to the instability of the materials at high sorption temperatures. Additional experiments were carried out under N₂ flow in isothermal conditions 500, 600 and 700 °C confirmed this, as it was apparent that instability of the parent waste materials increased as a function of temperature.

Low CO₂ uptake by parent waste materials could be contributed by several factors, including low concentrations of metal oxides present on the surface of the waste materials. Significantly low concentrations (<10 wt%) of these metal oxides in waste materials was deemed to be key reason for the low CO₂ uptake. Pure metal oxides such as MgO and CaO are known to chemically absorb CO₂ at elevated temperatures of higher than 400 °C (Martavaltzi and Lemonidou, 2008; Hassanzadeh and Abbasian, 2010) producing MgCO₃ and CaCO₃, respectively.

5.5.2. CO₂ uptake by waste-derived Li₄SiO₄ sorbents in pure and diluted CO₂ environments

All pure (SS-P-Li₄SiO₄) and waste-derived (SS-C-Li₄SiO₄, SS-R-Li₄SiO₄, SS-F-Li₄SiO₄ and SS-B-Li₄SiO₄) sorbents presented direct correlations between the CO₂ uptake capacities in pure CO₂ environment and the sorption temperatures throughout the
duration of analyses. All sorbents captured the lowest amount of CO₂ at 500 °C and the highest at 700 °C, with intermediate amount of captured CO₂ at 600 °C.

This observation correlates well with the double shell CO₂ capture mechanism by Li₄SiO₄ proposed in previous studies (Essaki et al., 2005; Duran-Munoz et al., 2013). At low sorption temperature, two layers of shells covered the Li₄SiO₄ particle i.e. Li₂SiO₃ and Li₂CO₃ as CO₂ is chemically sorbed by Li₄SiO₄. Diffusion of Li⁺ and O²⁻-ions from the bulk of Li₄SiO₄ particle is then activated at higher sorption temperature, allowing more CO₂ to be captured by the sorbent. In addition, the direct correlation between CO₂ uptake capacities of waste-derived Li₄SiO₄ sorbents and sorption temperatures is in good agreement with previous studies (Olivares-Marin et al., 2010; Wang et al., 2011).

In addition, all sorbents showed increase in sorption rate as the sorption temperature increased, as indicated by the slope of the CO₂ uptake capacity at the beginning of analysis. This observation is believed to be due to increased CO₂ diffusion activity within the Li₄SiO₄ particles, resulting in faster sorption rate compared to that at lower sorption temperature. Kinetic analysis was performed on SS-B-Li₄SiO₄ sorbents in an attempt to corroborate the data obtained in this study with the double exponential model, as this model was well-established to simulate the CO₂ sorption mechanism described earlier. As shown in Table 5.8, the kinetic parameters obtained following the kinetic analysis verified the diffusion step kinetically limits the overall CO₂ sorption on S-B-Li₄SiO₄ sorbents at sorption temperatures 500, 600 and 700 °C. This is indicated by the significantly larger k₁
values of the sorbents compared to $k_2$ values, which represent the chemisorption and diffusion rate of the process, respectively.

The addition of excess amounts of lithium seems to inhibit CO$_2$ uptake by SS-P-Li$_4$SiO$_4$ and fly ash-derived (SS-C-Li$_4$SiO$_4$ and SS-R-Li$_4$SiO$_4$) sorbents at lower sorption temperature (500 °C for SS-P-Li$_4$SiO$_4$ and 600 °C for SS-C-Li$_4$SiO$_4$ and SS-R-Li$_4$SiO$_4$ sorbents). As suggested by Duran-Munoz et al. (2013), it is assumed that there is insufficient thermal energy provided at this temperature to fully activate the diffusion of CO$_2$ through the bulk of Li$_4$SiO$_4$ particles, and therefore, the addition of excess lithium inhibits the overall sorption process (Duran-Munoz et al., 2013). As the sorption temperature increased to 600 and 700 °C, it is assumed that there is enough thermal energy to completely activate the diffusion process. The subsequent addition of excess amounts of lithium that previously acted as inhibitor now facilitates the sorption process instead, resulting in an increase in CO$_2$ uptake capacities by the sorbents.

Arrhenius plots of SS-B-Li$_4$SiO$_4$ sorbents seemed to support this theory, where the activated energy values associated with the diffusion step ($E_{ad}$) of the reaction increased with the addition of excess amount of lithium (Figures 5.11 to 5.14). This indicates that the diffusion step of the overall CO$_2$ sorption process is being kinetically limited by the addition of excess lithium. Moreover, the activated energy values associated with the chemisorption step ($E_{ac}$) decreased with increasing amount of excess lithium. This suggests that although the diffusion was kinetically limited, the chemisorption step was actually enhanced by the addition of excess lithium.
Comparing the CO₂ uptake capacity of pure and waste-derived Li₄SiO₄ sorbents, SS-P-Li₄SiO₄ sorbents captured significantly less amount of CO₂ (e.g. 24.47 mg CO₂/g sorbent by S-P-Li₄SiO₄-0 and 114.4 mg CO₂/g sorbent by SS-C-Li₄SiO₄-0 at 500 °C) despite pure SiO₂ was used in the preparation of the sorbents. The amorphous phase found in the waste-derived Li₄SiO₄ sorbents is believed to contribute to the enhanced CO₂ uptake performance of the sorbents due to the versatility of amorphous structure in capturing CO₂ molecules. In comparison to the more ordered structure of its crystalline counterpart which is predominantly found in SS-P-Li₄SiO₄ sorbents, the coexistence of amorphous Li₄SiO₄ is thought to have increased the CO₂ sorption capacity of the waste-derived sorbents. Faster diffusion of sorbate into amorphous structure than that in crystalline due to the atomic disorder (Sadoway, 2010) is also believed to increase the rate of CO₂ sorption of the sorbents.

In diluted CO₂ environment, the CO₂ uptake profiles of pure and waste-derived Li₄SiO₄ sorbents did not reach sorption equilibrium at the end of analyses. It is also observed that the amount of CO₂ uptake capacity by sorbents decreased accordingly in diluted (111.5 mg CO₂/g sorbent by SS-B-Li₄SiO₄-0 at 500 °C) CO₂ environment compared to that in pure (128.6 mg CO₂/g sorbent in pure CO₂ environment by SS-B-Li₄SiO₄-0 at 500 °C) one. This observation is in good agreement with a study by Essaki et al. (2005) which reported the CO₂ uptake capacity of pure Li₄SiO₄ pellets decreased significantly (from 27 wt% in 15 vol% CO₂ at 600 °C to 2 wt% in 5 vol% CO₂ at the same sorption temperature) as the partial pressure of CO₂ decreased (Essaki et al., 2005). Analysing the effect of
excess lithium on CO₂ uptake capacities of the sorbents in diluted CO₂ environment, almost no obvious correlations again were observed, although they followed the same trend as in the pure CO₂ environment. In addition, the rate of CO₂ sorption by all Li₄SiO₄ sorbents increased as a function of sorption temperature, also as observed in pure CO₂ environment.

Additionally, there is a distinctive trend of CO₂ uptake profiles in diluted CO₂ environment, where the amount of CO₂ uptake increased with sorption temperature up to 600 °C before decreasing significantly at 700 °C. The decrease in CO₂ uptake capacity is expected due to the substantially low CO₂ partial pressure making it harder for the sorbents to capture CO₂ efficiently. Seggiani et al. (2013) explained this occurrence to be attributed to the Gibbs free energy changes (ΔG) of the sorption reaction between CO₂ and Li₄SiO₄ (Seggiani et al., 2013). As the CO₂ sorption is an exothermic reversible gas-solid reaction with equilibrium constant equivalent to an inverse of CO₂ partial pressure, the lower the CO₂ concentration the lower the equilibrium emission temperature, which is the temperature where CO₂ sorption and regeneration both share the same temperature. Consequently, desorption process was initiated at lower (600 °C) temperature in diluted CO₂ sorption environment compared to the pure (700 °C) one (Seggiani et al., 2013).

5.5.3. Regeneration of waste-derived Li₄SiO₄ sorbents

While the addition of excess lithium improved the overall CO₂ uptake capacity in a single cycle at 600 °C (Table 5.3), it did not seem to affect the stability of the
sorbents in multiple cycles regeneration process at the same sorption temperature. In addition, the amount of CO₂ uptake capacity of sorbents did not reach sorption equilibrium. This is expected as the CO₂ uptake analysis of the same sorbents also did not attain sorption equilibrium during 120 minutes of analysis duration, as shown in Figure 5.5. It was also observed that the amount of CO₂ uptake capacity of sorbents progressively increasing despite the decreasing sorption rate with each regeneration cycle.

5.5.4. Effect of sorbent preparation method on CO₂ uptake capacity

The results showed that the preparation method via suspended impregnation (SI) decreased, albeit small changes, the overall CO₂ uptake capacity of SI-B-Li₄SiO₄-20 sorbent when compared to SS-B-Li₄SiO₄-20 sorbent, which was prepared using a dry impregnation method. The CO₂ uptake capacity decreased from 257 mg CO₂/g sorbent by SS-B-Li₄SiO₄-20 to 197 mg CO₂/g sorbent by SI-B-Li₄SiO₄-20. Although the CO₂ uptake capacity of SI-B-Li₄SiO₄-20 decreased with a wet impregnation method, other behaviour of the sorbent remained the same to that SS-B-Li₄SiO₄-20.
Chapter 6 Conclusions and recommendations for future work

This chapter summarises the results and conclusions derived from the experimental studies (Section 6.1). Suggestions for further work are presented in Section 6.2.

6.1. Conclusions

This study aimed to develop high temperature CO$_2$ sorbents using a selection of solid wastes from power generation plants. The principal results were derived from the preparation and characterisation of sorbents and CO$_2$ capture analyses. This section summarises the conclusions for these experimental studies.

The waste materials used as precursors to be developed into Li$_4$SiO$_4$-based sorbents include two samples of fly ashes (CPFA and RPFA) and two samples of bottom ashes (FBA and POMBA). Amongst these parent waste materials, three samples were coal-derived waste materials (CPFA, RPFA and FBA) while POMBA was a biomass-derived waste material. Different characterisation analyses were carried out on all parent waste materials, including particle size distribution, loss-on-ignition and major oxides composition and mineral phase composition analyses.

The CO$_2$ uptake capacities of parent waste materials were analysed to determine the benchmark capacity of the materials prior to be developed as high temperature
sorbents. The maximum of CO$_2$ sorption capacity of parent waste materials was found to be 4 mg CO$_2$/g sorbent, which was lower than that of a commercially available solvent (176 mg CO$_2$/g sorbent). This proved the unsuitability of the parent waste materials if they were to be used for CO$_2$ capture without any pre-treatment. The generally low sorption capacity of parent waste materials was believed to be contributed by the low contents of metal oxides that are capable of chemically absorbing CO$_2$, such as CaO and MgO.

The data obtained following the characterisation of parent waste materials and their corresponding waste-derived Li$_4$SiO$_4$ sorbents were used to predict the CO$_2$ uptake performance of the sorbents, as summarised in Section 4.3. Particle size of the parent waste materials was predicted to have an advantage over larger ones due to larger surface area that can be provided for the waste-derived Li$_4$SiO$_4$ sorbents for the CO$_2$ sorption to take place. This prediction was not exclusively accurate due to the inconsistent CO$_2$ uptake capacity of sorbents with the particle size of the parent waste materials used. For example, SS-B-Li$_4$SiO$_4$ which derived from parent waste material with the largest particle size distribution, i.e. POMBA, absorbed the highest amount of CO$_2$ at all sorption temperatures.

In addition to particle size, LOI values of the parent waste materials played an important role to anticipate the degree of decomposition caused by volatile matters in the waste materials. Although the LOI values of the parent waste materials did not directly correlate with the CO$_2$ uptake performance of the resulting Li$_4$SiO$_4$ sorbents, they certainly affected the CO$_2$ uptake capacities of
parent waste materials. Peaking behaviour was observed during CO$_2$ capture analysis on parent waste materials, as indicated by the maximum CO$_2$ sorption capacity observed before it decreased rapidly. This behaviour was caused by the instability of the materials at high sorption temperatures, which directly related to the LOI values of the materials.

Furthermore, at least 47 wt% of SiO$_2$ present in the parent waste materials was deemed sufficient to be developed into Li$_4$SiO$_4$-based sorbents. This conclusion was verified by the detection of crystalline and amorphous Li$_4$SiO$_4$ peaks in XRD diffractograms of waste-derived Li$_4$SiO$_4$ sorbents. Additionally, the presence of amorphous mineral phase of Li$_4$SiO$_4$ found in waste-derived Li$_4$SiO$_4$ sorbents was previously predicted to have an advantage over crystalline phase of Li$_4$SiO$_4$ which were predominantly found in pure SS-P-Li$_4$SiO$_4$ sorbents. This prediction seems to be accurate in the context of this study, as the CO$_2$ uptake capacity of waste-derived Li$_4$SiO$_4$ sorbents were higher than those of pure SS-P-Li$_4$SiO$_4$ sorbents. The versatility of amorphous structure in capturing CO$_2$ molecules compared to the more ordered structure of its crystalline counterpart, which is predominantly found in pure Li$_4$SiO$_4$ sorbents, is thought to be the cause of such observations (Sadoway, 2010).

Also, this study experimented for the first time the suitability of a palm oil mill boiler ash (POMBA) as a precursor for Li$_4$SiO$_4$-based high temperature CO$_2$ sorbent. It was found that not only it was suitable to be developed as a high temperature CO$_2$ sorbent, but the sorbents derived from POMBA obtained CO$_2$
sorption capacities higher (up to 257 mg CO\textsubscript{2}/g sorbent) than some of the coal waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents developed in this study. In addition, the CO\textsubscript{2} sorption capacity of biomass-derived SS-B-Li\textsubscript{4}SiO\textsubscript{4} sorbents were comparable not only to that of coal-derived SS-C-Li\textsubscript{4}SiO\textsubscript{4} (up to 263 mg CO\textsubscript{2}/g sorbent), SS-R-Li\textsubscript{4}SiO\textsubscript{4} (216 mg CO\textsubscript{2}/g sorbent) and SS-F-Li\textsubscript{4}SiO\textsubscript{4} (199 mg CO\textsubscript{2}/g sorbent) sorbents that were prepared in this study, but also to waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents from previously published work, namely, fly ash (up to 26 mg CO\textsubscript{2}/g sorbent) (Olivares-Marin et al., 2010) and rice husk ash (up to 324 mg CO\textsubscript{2}/g sorbent) (Wang et al., 2011). The results of CO\textsubscript{2} uptake capacity of waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents proved that the research objectives 1 and 2 (Section 1.3) have been successfully met.

Pure and waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents were mainly prepared using the solid-state (SS) impregnation method. This type of preparation method has been widely applied by previous studies (Essaki et al., 2005; Tang et al., 2009; Wang et al., 2011), but it was primarily adopted from Olivares-Marin et al. (2010). Compared to previous studies on lithium deprivation (Tang et al., 2009), this work investigated the effect of excess amounts of lithium (5, 10 and 20%) on CO\textsubscript{2} sorption performance. Depending on the waste materials used, it was found that excess amounts of lithium affected CO\textsubscript{2} sorption performance. The sorbents that were derived from fly ash samples (CPFA and RPFA) exhibited decreasing trend in CO\textsubscript{2} uptake capacity with increasing amount of excess lithium at lower sorption temperatures (500 and 600 °C), but increasing trend in uptake capacity at higher sorption temperature (700 °C). On the other hand, the bottom ash samples
showed increasing trend in uptake capacity with increasing amount of excess lithium.

It was also found that the CO$_2$ uptake capacities of pure SS-P-Li$_4$SiO$_4$ sorbents were constantly lower than that of waste-derived sorbents. It is believed that the impurities in the starting waste materials, e.g. K$_2$O, contributed to the improvement of CO$_2$ uptake capacities of waste-derived Li$_4$SiO$_4$ sorbents, in particular the SS-B-Li$_4$SiO$_4$ sorbents. This conclusion was derived from the observations of Wang et al. (2013), where the authors found a correlation between the content of impurities in the starting waste materials, such as K$_2$O and Na$_2$O, to be directly related to the enhancement of CO$_2$ uptake capacity of the resulting waste-derived sorbents.

The influence of different sorption temperatures (500, 600 and 700 °C) on CO$_2$ sorption capacity of the sorbents was also investigated in this study. It was found that the CO$_2$ uptake capacities of waste-derived sorbents significantly increased with each increment of sorption temperatures. This observation can be explained using the double shell CO$_2$ sorption mechanism where at low temperature, two layers of shells covered the Li$_4$SiO$_4$ particle i.e. Li$_2$SiO$_3$ and Li$_2$CO$_3$ as CO$_2$ is chemically sorbed by Li$_4$SiO$_4$ (Essaki et al., 2005). Diffusion of Li$^+$ and O$^{2-}$ ions from the bulk of Li$_4$SiO$_4$ particle is then activated at higher sorption temperature, allowing more CO$_2$ to be captured by the sorbent (Duran-Munoz et al., 2013). With the establishment of the correlation between CO$_2$ uptake capacity of waste-derived
Li$_4$SiO$_4$ sorbents and sorption temperatures proved that the research objective 3 (Section 1.3) have been successfully met.

Kinetic analysis was performed on waste-derived Li$_4$SiO$_4$ sorbents with the highest CO$_2$ uptake capacity, i.e. SS-B-Li$_4$SiO$_4$, in an attempt to corroborate the double shell mechanism with the data obtained in this study. The results showed that the CO$_2$ sorption by SS-B-Li$_4$SiO$_4$ sorbents fit well with the double exponential model, and therefore, verified the double shell CO$_2$ sorption mechanism described earlier. The kinetic parameters obtained following the kinetic analysis verified the diffusion step kinetically limits the overall CO$_2$ sorption on SS-B-Li$_4$SiO$_4$ sorbents at sorption temperatures 500, 600 and 700 °C. This is indicated by the significantly larger $k_1$ values compared to that $k_2$, which represent the chemisorption and diffusion rate of the process, respectively. $k_1$ and $k_2$ values obtained in this study were also found to be in good agreement with published studies. Olivares-Marín et al. (2010) reported similar findings, where $k_1$ values were at least 1 magnitude higher than those of $k_2$ for fly ash-derived Li$_4$SiO$_4$ sorbents.

In addition to the dry preparation method, this study also investigated a wet, i.e. suspended impregnation (SI), method to explore the effect of wet and dry preparation methods on CO$_2$ sorption capacity and performance of the sorbents. The SI preparation method was adopted from Chang et al. (Chang et al., 2001). It was found that the wet SI preparation method decreased the CO$_2$ sorption capacity of the sorbent, while maintaining other sorption performances such as
temperature dependency of CO\textsubscript{2} uptake sorption and kinetic behaviour of the sorbents.

CO\textsubscript{2} sorption performance by waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents under diluted CO\textsubscript{2} environment was also studied. It was found that the sorption capacities of sorbents decreased drastically, particularly at sorption temperature 700 °C. This is because of the considerably reduced CO\textsubscript{2} partial pressure making it harder for the sorbents to capture CO\textsubscript{2} efficiently, as also reported in previous studies (Essaki et al., 2005). As the CO\textsubscript{2} sorption is an exothermic reversible gas-solid reaction with equilibrium constant equivalent to an inverse of CO\textsubscript{2} partial pressure, the lower the CO\textsubscript{2} concentration the lower the equilibrium emission temperature, which is the temperature where CO\textsubscript{2} sorption and regeneration both share the same temperature. Consequently, desorption process was initiated at lower (600 °C) temperature in diluted CO\textsubscript{2} sorption environment compared to the pure (700 °C) one (Seggiani et al., 2013). The results obtained following the study of CO\textsubscript{2} sorption by waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents under diluted CO\textsubscript{2} environment confirmed that the research objective 4 (Section 1.3) has been met.

Regeneration study of waste-derived Li\textsubscript{4}SiO\textsubscript{4} sorbents uncovered the addition of excess lithium did not seem to affect the stability of the regeneration cycles of waste-derived sorbents. The inability of the sorbents to achieve sorption equilibrium during regeneration cycles was expected, as the CO\textsubscript{2} uptake analysis of the sorbents selected for regeneration study also did not achieve sorption equilibrium during 120 minutes of single cycle analysis. The results and
discussions presented following the regeneration performance study of waste-derived Li$_4$SiO$_4$ sorbents showed that research objective 5 has been met.

6.2. Recommendations for future work

There are several areas that are worthy of further studies. Firstly, further improvement of CO$_2$ uptake capacities of the sorbents could be done by adding K$_2$CO$_3$ to the waste-derived sorbents. A successful improvement of CO$_2$ uptake capacities by fly ash-derived Li$_4$SiO$_4$ sorbents was reported by a previously published study (Olivares-Marín et al., 2010).

The waste-derived sorbents could also be prepared with sodium as substitution of lithium, due to higher toxicity of the latter. A preliminary study of this preparation method was done by the author, as collaboration with another colleague within the research group. It was discovered that the sodium-based sorbents successfully captured CO$_2$, albeit in smaller amounts compared to that of lithium-based (Sanna et al., 2014). A future work of this would be to further improve the CO$_2$ uptake capacities of the sorbents, as well as to study their regeneration cycles.

Also, the CO$_2$ capture analysis of the waste-derived Li$_4$SiO$_4$ sorbents under CO$_2$ environment with varying sorption temperatures could also be analysed. This is to simulate fluctuating temperature, where it is a normal occurrence in industrial applications.
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Appendix

Figures A.1 to A.3 show the isothermal CO$_2$ uptake profiles of SS-R-Li$_4$SiO$_4$, SS-F-Li$_4$SiO$_4$ and SS-B-Li$_4$SiO$_4$ sorbents in diluted CO$_2$ environment. As previously stated in section 5.2.2, these isotherms exhibit similar trend to that of SS-C-Li$_4$SiO$_4$ sorbents and therefore, are presented here in the Appendix section.
Figure A.1 Isothermal CO$_2$ uptake profiles of a) SS-R-Li$_4$SiO$_4$-0; b) SS-R-Li$_4$SiO$_4$-5; c) SS-R-Li$_4$SiO$_4$-10 and d) SS-R-Li$_4$SiO$_4$-20 in diluted CO$_2$ (14 vol%) environment.
Figure A.2 Isothermal CO$_2$ uptake profiles of a) SS-F-Li$_4$SiO$_4$-0; b) SS-F-Li$_4$SiO$_4$-5; c) SS-F-Li$_4$SiO$_4$-10 and d) SS-F-Li$_4$SiO$_4$-20 in diluted CO$_2$ (14 vol%) environment.
Figure A.3 Isothermal CO$_2$ uptake profiles of a) SS-B-Li$_4$SiO$_4$-$0$; b) SS-B-Li$_4$SiO$_4$-$5$; c) SS-B-Li$_4$SiO$_4$-$10$ and d) SS-B-Li$_4$SiO$_4$-$20$ in diluted CO$_2$ (14 vol%) environment.