Cation-exchanged zeolites-A prepared from South African fly ash feedstock for CO$_2$ adsorption

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Abstract

ABSTRACT

In South Africa coal combustion constitutes up to 90% of the country’s energy need. This coal combustion activity is known to contribute to the amount of about 40% of the total CO$_2$ atmospheric emissions worldwide that are responsible for global warming effects. In addition burning of coal generates a large quantity of fly ash which creates environmental pollution since only a small portion of it is currently used in some applications.

In order, on one hand to mitigate and sequester CO$_2$ and on the other hand to reprocess fly ash and reuse it, this study focuses on developing new technologies with cost-effective and less energy consumption in the domain of CO$_2$ capture and sequestration. CO$_2$ has priority attention for being the largest contributor to global warming. Various techniques have been used for CO$_2$ capture and sequestration, such as aqueous alkylamine absorption or adsorption onto a solid adsorbent such as zeolites.

In this study NaA zeolite adsorbent was hydrothermally synthesised from South African fly ash. This fly ash based NaA zeolite was then used as starting material to prepare LiA, CaA, and MgA zeolite catalysts via ion-exchange for comparative CO$_2$ adsorption capacity. A systematic design of the ion-exchange procedure was undertaken at either 30 °C or 60 °C for a contact time of 1 hr, 4 hrs, and 8 hrs with 1, 2 and 3 consecutive exchanges in each case in order to determine the optimum conditions for loading each cation exchanged. The adsorption of CO$_2$ on the ion-exchanged fly ash based zeolite-A catalysts was carried out at 40 °C similar to the temperature of flue gas since the catalysts obtained in this study were also prepared with a view to their applications in flue gas system. The CO$_2$ desorption temperature ranged between 40-700 °C.

All materials used in this study, starting from fly ash feedstock, were characterized using various techniques to monitor the mineral and structural
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composition, the morphology, surface area and elemental composition and the adsorption capacity. The techniques included mainly Fourier transform infra-red, X-ray diffraction, Scanning electron microscopy, Transmission electron microscopy, Energy dispersive spectroscopy, X-ray fluorescence, Temperature programmed desorption.

The results obtained from both Fourier transform infra-red and the X-ray diffraction spectroscopy for samples exchanged at either 30° C or 60 °C showed lower crystallinity in CaA and MgA zeolite samples. This decrease in crystallinity mainly affected the D4R (0-20° 2θ) and was demonstrated in the study to be inversely proportional to the increase of the atomic radius of cations (Li+ > Mg2+ > Ca2+). In the Fourier transform infra-red, the vibration band at 677 cm⁻¹ attributed to the extra-framework cation, also proportionally increased with the decrease of the atomic radius or size of the cations, and was intense in LiA zeolite samples.

The EDS results at either 30 °C or 60 °C showed that the removal of the host Na⁺ cation was partial and none of the cation exchange conditions applied completely removed the host Na⁺ cation. Among other cations, the ion-exchange using the Ca²⁺ cation showed the highest removal of the host Na⁺ cation. The CO₂-TPD thermogram profiles revealed that CO₂ physisorption was the major interaction observed for all fly ash based ion-exchanged zeolite-A which displayed significant weak strength adsorption sites at low temperature (40-150 °C) but it was found that the Na⁺ cation was the preferred cation for low temperature CO₂ adsorption application. However, at higher temperature (150-700 °C), the highest amount of CO₂ was desorbed from CaA zeolites followed by MgA zeolites, but the former showed dominant strong CO₂ adsorption sites between (400-650 °C) compared to the latter which showed medium strength sites (150-400 °C). These high temperatures CO₂ desorption peaks observed especially for CaA zeolites are ascribed to the formation of carbonate compounds.
Abstract

In summary, the XRD patterns and FT-IR spectra revealed unique structural modifications which were independent of the temperatures, contact time and consecutive exchanges applied during the ion-exchange. These structural features observed for fly ash based zeolite-A after the ion-exchange were found to be essentially influenced by the intrinsic characteristic of Li\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) cations.

The contact time of 4 hr at 30 °C with 3 consecutive exchanges was found to be ideal to exchange Ca\(^{2+}\) cation whereas the increased temperature of 60 °C was favourable for Li\(^+\) and Mg\(^{2+}\) cations. CaA zeolite showed significant CO\(_2\) adsorption but required high temperatures for CO\(_2\) desorption showing potential for long term capture compared to NaA, LiA and MgA zeolite samples which are suited for low temperature swing desorption of CO\(_2\).
DECLARATION

“I declare that “Cation-exchanged zeolites-A prepared from South African fly ash feedstock for CO₂ adsorption” is my own work, that it has not been submitted for any degree or examination in any other university and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references”.

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May 2015

Signed:
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<th>Description</th>
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<tbody>
<tr>
<td>AMD</td>
<td>Acid Mine Drainage</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>BRICS</td>
<td>Brazil Russia India China South Africa</td>
</tr>
<tr>
<td>COPs</td>
<td>Conference of the Parties</td>
</tr>
<tr>
<td>CCPs</td>
<td>Coal Combustion by-Products</td>
</tr>
<tr>
<td>CUBs</td>
<td>Coal Utilization By-products</td>
</tr>
<tr>
<td>CDM</td>
<td>Clean Development Mechanism</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon Capture and Storage</td>
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<tr>
<td>CTL</td>
<td>Coal-To-Liquid</td>
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<tr>
<td>DEA</td>
<td>Diethanolamine</td>
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<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EOE</td>
<td>Enhanced Oil Recovery</td>
</tr>
<tr>
<td>ESP</td>
<td>Electrostatic precipitator</td>
</tr>
<tr>
<td>ESKOM</td>
<td>Electricity supply commission of South Africa</td>
</tr>
<tr>
<td>EAJ</td>
<td>Environmental Agency of Japan</td>
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<tr>
<td>FA</td>
<td>Fly ash</td>
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<tr>
<td>FGD</td>
<td>Flue gas desulphurization gypsum</td>
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<tr>
<td>FED</td>
<td>Field emission gun</td>
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<tr>
<td>FT-IR</td>
<td>Fourier Transformed Infra-Red</td>
</tr>
<tr>
<td>FBC</td>
<td>Fluidized bed combustion</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gases</td>
</tr>
<tr>
<td>HHV</td>
<td>Higher heating value</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>IGCC</td>
<td>Integrated coal gasification combined cycle</td>
</tr>
<tr>
<td>IZA</td>
<td>International Zeolite Association</td>
</tr>
<tr>
<td>IUFRO</td>
<td>International Union of Forestry Research Organization</td>
</tr>
<tr>
<td>JSE</td>
<td>Johannesburg Stock Exchange</td>
</tr>
<tr>
<td>LU</td>
<td>Land use</td>
</tr>
<tr>
<td>LUCF</td>
<td>Land use change and forestry</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss of ignition</td>
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<tr>
<td>MDGs</td>
<td>Millennium Development Goals</td>
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<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<tr>
<td>NEAA</td>
<td>Netherlands Environmental Assessment Agency</td>
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<td>NYSE</td>
<td>New York Stock Exchange</td>
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# List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>OECD</td>
<td>Organization for Economy Co-operation and Development</td>
</tr>
<tr>
<td>PBU</td>
<td>Primary Building Unit</td>
</tr>
<tr>
<td>PSA</td>
<td>Pressure swing adsorption</td>
</tr>
<tr>
<td>PCC</td>
<td>Pulverized coal combustion</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>RBCT</td>
<td>Richard Bay Coal Terminal</td>
</tr>
<tr>
<td>SASOL</td>
<td>Synthetic oil of South Africa</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary Building Unit</td>
</tr>
<tr>
<td>SS</td>
<td>Sodium-silicate</td>
</tr>
<tr>
<td>SA</td>
<td>Sodium-Aluminate</td>
</tr>
<tr>
<td>S/L</td>
<td>Solid to Liquid ratio</td>
</tr>
<tr>
<td>TBU</td>
<td>Tertiary Building Unit</td>
</tr>
<tr>
<td>TSA</td>
<td>Temperature swing adsorption</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethanolamine</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>UNFCCC</td>
<td>United Nation Framework Convention on Climate Change</td>
</tr>
<tr>
<td>UNDP</td>
<td>United Nation Development Program</td>
</tr>
<tr>
<td>VSA</td>
<td>Vacuum swing adsorption</td>
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<tr>
<td>WEO</td>
<td>World Energy Outlook</td>
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<tr>
<td>WCI</td>
<td>World Coal Institute</td>
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<tr>
<td>WCA</td>
<td>World Coal Association</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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CHAPTER ONE

1. INTRODUCTION

This chapter gives a brief background related to this study and also outlines the main focus of this work. The background includes a short overview of coal based energy generation worldwide particularly in the Republic of South Africa and its drawbacks including fly ash generation and CO₂ emissions. CO₂ capture and sequestration management and technologies are briefly presented in this section. The problem statement, aims, objectives and research questions are also outlined later in this chapter followed by a defined scope and delimitation and thesis structure.

1.1 Energy trends

Energy is a fundamental and crucial factor to sustain the development worldwide and also necessary to reduce poverty. Many aspects of development, such as social, economic and environmental issues including access to water, agricultural productivity, health, population levels and education are all affected by energy availability. According to the United Nation Development Programme (UNDP), it is almost impossible to accomplish any of the Millennium Development Goals (MDGs) without major improvement in the quality and quantity of energy services in the world, especially in developing countries. (www.undp.org).

Energy needs worldwide are likely to continue to grow steadily for the next two decades due to the population increase as well as industrialization in the developing countries. The World Energy Outlook (WEO) projects that the world’s energy needs would be more than 50 % higher in 2030 than current demand, with an average annual growth of 1.6 %. Furthermore, more than two-
third of the global energy use will come from the developing countries where economies and population growth are highest (IEA, 2005). Amongst various sources of energy such as nuclear power, hydroelectric power, solar, geothermal, wind etc., fossil fuels remain the mainstay of energy supplies, meeting more than 85 % of the projected increase in primary energy demand. This is, if current world energy production and consumption patterns persist into the 21st century and foreseeable future. Fossil fuels continue to dominate global energy markets because they present competitive advantages such as their availability, low cost and abundance; compared with other alternatives such as those mentioned above (EIA, 2007; Olivier et al., 2011).

Of the 85 % of energy sourced from fossil fuels, coal plays a very important role by fuelling about 43 % of the electricity worldwide. In many countries this figure has been shown to be higher basically because of the lack of alternative sources of energy that can compete with coal combustion as a cheap source of electricity. According to the World Coal Institute (WCI, 2009); South Africa and Poland both generate approximately 94 % of their electricity from coal combustion, in China coal accounts for around 72 % of the total primary energy consumption and about 50 % in United States (USA) (www.worldcoal.org).

Although coal remains the mainstay of current source of electricity generation, its combustion is known to be responsible for generating various by-products (IEA, 2012). These coal by-products are generally referred to as coal combustion products (CCPs) in Europe or coal utilization by-products (CUBs) in USA (Querol et al., 2002). During the coal combustion process, three typical states of CCPs are generally identified, namely solids (fly ash, slag etc.), liquids (brine etc.) and gases (carbon dioxide etc.). CCPs such as fly ash (FA), brine and FGD are known to be possible soil and water pollutants whereas CO₂, SO₂ and NOₓ emissions contribute to atmospheric air pollution (Senapati and Banerjee, 1999; IEA, 2012).
Natural gases occurring in the atmosphere, allow regulation of the temperature of the earth by trapping radiation; this is known as the greenhouse effect. The major greenhouse gases (GHG) include water vapour, carbon dioxide (CO₂), methane (CH₄), nitrous oxide (NOₓ), sulphur oxide (SOₓ) etc. However, anthropogenic activities such as the combustion of fossil fuels generate additional GHG, increasing the effect of these GHG which accumulate in the atmosphere (www.worldcoal.org).

The high concentrations of GHG in the atmosphere enhance the greenhouse effect which results in global warming and climate change. The greenhouse effect has received widespread attention for the past three decades. Among these GHG, CO₂ contributes more than 60 % to the global warming because of its huge amount, 15 % is from CH₄ and the remaining 25 % is shared by CFC, N₂O and O₃ (Lemos de Sousa et al., 2008; Albo et al., 2010). CO₂ concentration in the atmosphere was about 400 ppm during the period of 2011-2012 which is higher than the pre-industrial level of about 300 ppm (Oh, 2010). Through examinations of ocean sediments for seawater pH and calcium, magnesium and carbonate mineralogy, it has been demonstrated that the atmospheric concentration has not approached such a high level over the past 4000 centuries (Fisher et al., 1999).

Global CO₂ emissions have increased by approximately 80 % over the period 1970-2004 with 21-38 Gt/year being released and this figure is projected to increase further to 43 Gt/year by 2030 (Kharaka et al., 2009). These emissions are projected to increase even further over the next 10 decades owing to rises in energy demand associated with a growing global population, economies and industrial development particularly in developing countries (Sumida et al., 2012). Some impacts related to the high concentration of GHG, may be slow to become apparent since stability is an inherent characteristic of the interacting climate, ecological and also socio-economic systems. Although the stabilisation of the atmospheric concentration CO₂ can be achieved, the emissions’ impact upon global warming phenomena and sea level rise would continue for centuries due
to the time scales associated with climate processes and feedbacks. Therefore
some changes in the climate system would be irreversible in the course of human
existence. Because of the long life time of CO\textsubscript{2} in the atmosphere, stabilising
concentrations at any level would require large reductions of global CO\textsubscript{2}
emissions from current levels. The lower the chosen level for stabilisation, the
sooner the decline in global emissions would need to begin, or the deeper the
emission reduction would need to be over time (IEA, 2012). Due to this major
global warming, several resolutions by specific organizations have been made
worldwide in order to mitigate CO\textsubscript{2} emissions and other GHG.

For instance the United Nations Framework Convention on Climate Change
(UNFCCC) has set an overall framework for intergovernmental efforts to address
climate change. Under UNFCCC, countries that are parties meet annually at the
Conference of the Parties (COP). It was at COP3, held in Kyoto in 1997, that
member countries have negotiated the Kyoto Protocol which sets legal targets for
emissions reductions. The Kyoto Protocol entered into force in February 2005,
with 128 countries overall (but only 30 developed countries with emissions
targets) that were Parties to the Protocol, except Australia and the USA which
decided to undertake their own domestic measures to stabilise GHG emissions.
The Kyoto Protocol covers emissions of the six main GHG: CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, HFC,
PFC and SF\textsubscript{6}. Rather than placing a specific target on each of the gases, the overall
emissions targets for all six is combined and translated into CO\textsubscript{2} (IPCC, 2007;
WCI, 2009). The Protocol currently urges about 37 industrialized countries and
the European Union to thoroughly reduce their overall emissions of GHG by at
least 5.2 % below the 1990 level. This is also supported by the Copenhagen
Accord which requests the temperature increase worldwide to be limited to 2 °C
above the pre -industrial level by 2100, since this has been predicted by the IPCC
2007 to increase by the end of the 21st century to a global average of 1.8 to 6.4 °C
(IPCC, 2007 ;Yu et al., 2012).
Brazil, the Russian Federation, India, China and South Africa, the so-called BRICS countries participate in the Kyoto commitments through non-annex I group, except the Russian Federation. In 2010, the BRICS represented almost 33% of global energy utilization and 37% of CO$_2$ emissions from fuel combustion. This scenario is expected to rise further in the next decade if the strong development or economic performance occurring in these five countries continues. China, the Russian Federation and India are three of the four that absolutely emit the most CO$_2$ (IEA, 2012).

South Africa, besides being a member of the BRICS countries, also participates in the Kyoto protocol through the Clean Development Mechanism (CDM) non-annex I. Under the CDM, industrialized countries are committed to invest in projects that reduce emissions in a manner which is real, measurable and over the long term for climate change mitigation. Currently South Africa has only registered about 17 projects compared to other members of the BRICS such as Brazil with 179 projects, India and China, with respectively 547 and 1003 (Randal, 2011).

South Africa relies mainly on fossil fuels as primary energy source which was about 90% in 2010, with coal combustion providing 74% of the country’s energy needs. Although South Africa accounted for 37% of CO$_2$ emissions from fuels combustion across all Africa in 2010, this amount only represented 1% of the total global emissions (IEA, 2012). One of the major climate change mitigation issues facing South Africa is the need to reduce GHG emissions from the power sector, primarily by reducing reliance on coal. Thus South Africa is currently taking steps to expand the utilization of both renewable and nuclear energy and to explore the use of carbon capture and storage (CCS) technologies as well as looking at ways to reduce energy demand on a national scale. Additionally Eskom, which is the public utility, has also targeted to reduce the dependence on conventional coal to about 70% by 2025 as well as reducing GHG emissions in absolute terms by 2050 (EIA, 2012).
1.2 Coal

Coal is an extremely heterogeneous and very complex material. Coal is formed by geological processes and is composed of various organic entities of about 70% by volume (macerals or carbonaceous) and lower amounts of inorganic minerals (Van, 1993). The overall behaviour of a given coal is known to be controlled by its macerals and mineral constituents that impart its physicochemical properties. Although coal is made of macerals and minerals, it is not a uniform mixture of these substances but they occur in distinct associations (Van, 1993). Clay minerals such as illite (60-90% of the total mineral content of coal) and kaolinite, pyrite and marcasite, carbonates such as dolomite, ankerite, calcite, siderite and quartz are the most widespread inorganic constituents that are found in almost all coal rock. Quartz is present in almost all coal making up 1 to 20% of the inorganic share of the total weight of the material. In addition, coal deposits contain various traces elements which range in the parts per million (ppm) concentrations (Gitari, 2006).

1.3 Coal combustion by-products

Fly ash (FA) is a coal combustion by-product (CCP) which is mainly made of spherical glassy particles of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$. FA as CCP and its chemical and physical characteristics are strongly controlled by the coal from which it originated. Furthermore, the boiler temperature, the operating conditions, the post-combustion parameters and also the minerals present in the coal dictate its elemental composition. The design of the boiler is known to play a very important role in the mineralogy and crystallinity of FA (Shao et al., 2012). During the last three decades, extensive research has been carried out on the utilization of FA in various sectors (Senapati and Banerjee, 1999). This utilization of FA is broadly viewed from two angles, mitigating environmental effects and addressing disposal problems (low value and high volume utilization). This
aspect of FA utilization can further be described in different specific areas such as:

- In the manufacturing of cement, materials of construction, road pavements, concrete and geopolymers (Nyale et al., 2013).
- In the neutralization of acid mine drainage, FA is used as neutralizer (Petrik et al., 2005; Gitari, 2006).
- In zeolite synthesis and wastewater treatment as reported by several authors (Molina and Poole 2004; Yaping et al., 2008). This last application of FA is mainly possible due to the significant presence of silica (\(\text{SiO}_2\)) and alumina (\(\text{Al}_2\text{O}_3\)) contained in FA. These oxides are known to constitute the core of the structural framework of zeolite materials (Querol et al., 2001; Somerset et al., 2004).

The use of FA as feedstock in the preparation or synthesis of zeolites is currently one of the main focus areas for fly ash reuse due to various industrial applications related to the properties of zeolite materials. These applications include the use of zeolites in catalysis or as sorbents for the removal of heavy metal ions and inorganic contaminants from wastewater, for gas separation and also as replacements for phosphates in detergents (Walton et al., 2006).

### 1.4 Zeolites

Natural and synthetic zeolites are microporous aluminosilicates based materials that contain pores and channels with molecular dimensions widely exploited in industry. Zeolites occur principally in three dimensional networks containing \([\text{Al}_2\text{O}_3]\) and \([\text{SiO}_2]\) tetrahedra linked to each other by sharing all oxygen atoms (Auerbach et al., 2003). The substitution of silicon (\(\text{Si}^{4+}\)) by aluminium (\(\text{Al}^{3+}\)) creates a negative charge in the framework of the zeolite (Brönsted acid site) which can be compensated by extra-framework charge balancing cations such as \(\text{Na}^+, \text{Ca}^{2+}, \text{K}^+\) or \(\text{Mg}^{2+}\). This results in the formation of ionic sites in the vicinity of
Al$^{3+}$ atoms providing the cation-exchange property of zeolites. The extraframework cations of zeolite can therefore easily be exchanged (Bailey et al., 1999; Kyung-Mi and Young-Min, 2010). The large internal surface area and the presence of active Brönsted acid sites in the pores as well as various pore sizes are characteristics for different zeolites materials, impacting their catalytic activity and selectivity.

Zeolites are also characterized by their high thermal stability, chemical inertness and high mechanical strength (Bayati et al., 2008). Several synthetic methods can be applied in the synthesis of zeolites such as NaP1, NaA, and ZSM-5 from a wide range of coal fly ash sources. For instance the hydrothermal synthesis has been used during this study to achieve the synthesis of zeolites NaA from South African fly ash as reported by Musyoka (2009, 2012). In this study fly ash based NaA zeolite materials made by Musyoka’s procedure have been modified with various alkali and alkaline earth metals and applied for CO$_2$ adsorption and sequestration purposes.

1.5 CO$_2$ capture and sequestration technologies

CO$_2$ capture and storage (CCS) technologies are currently required worldwide for a continuous utilization of fossil fuels, since they aid in reducing CO$_2$ emissions. It is therefore necessary to develop CCS technologies to manage the current global demand for CO$_2$ reduction (Yu et al., 2012). CO$_2$ mitigation and management, generally include two main approaches, biological fixation or geological storage. This last process is further split into open systems (oceans and diverse porous lithologies), mineral carbonation or closed systems (salt cavitations, deep saline aquifers, depleted oil and fields and coal seams) (Lemos de Sousa and Rodriguez, 2008). CO$_2$ fixation by biological fixation comprises integration of photosynthetic functions of microorganisms (microalgae) by formation of new biomass that can serve as animal food source, since it contains high crude protein (Chae et al., 2006).
Geological storage captures gaseous CO$_2$ from the specific sites of emission and injects it as a supercritical fluid into underground formations (active and depleted oil and gas reservoirs, deep unmineable coal seams, saline aquifers etc.). The storage of CO$_2$ in these reservoirs can be achieved through various mechanisms such as stratigraphic or structural trapping (physical isolation), solubility trapping (dissolution in aqueous phase) and/or hydrodynamic trapping. The challenge that faces hydrodynamic trapping is its potential leakage that can occur through imperfect confinement. In saline aquifers, CO$_2$ is converted into various carbonates (calcite, magnesite, dolomite and siderite) which can be stored in aquifers for millions of years (Gunter et al., 2000). However the conversion of CO$_2$ in geological forms for generation of stable minerals is known to be a slow process which can take hundreds to thousands of years due to the slow kinetics involved in carbonate mineral precipitation and silicate mineral dissolution.

The need for materials that can be utilized in CO$_2$ sequestration or storage systems has prompted the study of several classes of materials to date. The development of such materials necessitates a wide range of parameters which are related firstly to the type of CO$_2$ capture undertaken and secondly to specific stationary sources of CO$_2$ (coal-power or gas-fired plants) (Sumida et al., 2012). The most crucial performance parameter of any material for CO$_2$ capture is its selectivity. However the affinity of the material toward CO$_2$ is also essential, particularly when considering the energy penalty of storage. In fact if the interaction is too strong, it leads to a high energy requirement during the desorption process of the captured CO$_2$. In contrast, weak interactions, while lowering the regeneration cost, would probably have low selectivity for CO$_2$ over other components such as CH$_4$ and N$_2$ in a flue gas mixture (D’Alessandro et al., 2010). In addition CO$_2$ capture materials should also exhibit a high stability under condition of capture and regeneration, especially when they have to be deployed in power plants (Sumida et al., 2012). The main existing CO$_2$
sequestration technologies in the context of the above mentioned performance considerations are aqueous alkanolamine solutions or porous solids materials such as zeolites and activated carbons. Aqueous alkanolamine solutions have been extensively used for CO$_2$ capture and still find application to date (Rochelle, 2009). In this process the amine functionalities allow a nucleophilic attack of the carbon atom in the CO$_2$ component to form a C-N bond. This reaction can result, either in the formation of a carbamate or bicarbonate species depending upon the amine (Da Silva and Svendsen, 2007). Monoethanolamine (MEA) is the most well-known alkanolamine used for CO$_2$ capture applications. The operation consists of dissolving MEA in water at a concentration of approximately 20-30% of weight. Depending upon the specific configuration of the scrubbing process, the total working capacity of a 30 wt % MEA solution can fall in the range of 2.1-5.5 wt % (Oyenekan et al., 2007). In some cases MEA is used in mixture with secondary or tertiary alkanolamines such as diethanolamine (DEA) and triethanolamine (TEA) (Da Silva and Svendsen, 2007). However use of alkanolamine solutions as adsorbents for large scale CO$_2$ capture have several significant limitations such as the relative instability toward heating of these solutions, which limits the temperatures available for full regeneration of the solution. The decomposition of the amine also results in a decrease of absorbent performance over time, which diminishes the lifetime of the solutions. The amine solutions are known to be corrosive toward the vessels in which they are contained. This is generally prevented by addition of inhibitors or by limiting the concentration of the alkanolamine species to below 40 wt %. Since a lower concentration results in a larger volume of water that has to be heated for regeneration of the material, concentration limitations becomes a key disadvantage of this technology (Da Silva and Svendsen, 2007). The heat capacity of MEA solutions (20-40 wt % or mol %) is also closer to the heat capacity of pure water (Weiland et al., 1997).
Hence the lower heat capacity of solid porous adsorbents such as zeolites is the key advantage for their utilization in CO$_2$ capture (Cejka and Corma, 2010). Adsorbent materials such as zeolite 13X, which has a relatively high surface area (around 700 m$^2$/g) and micro pore volume (0.25 cm$^3$/g), has been shown to display promising capacities for CO$_2$ at room temperature (about 16.4 wt % at 0.8 bar and 298 K) (Wang and Levan, 2009). A wide range of zeolite structures have been reported up to date that present adsorption performances which are related to their compositional, structural or chemical features (Wang and Levan, 2009). This also has some crucial implications toward the adsorption selectivity, and the regeneration costs associated with the capture process (Palomino et al., 2010). In comparison with CO$_2$ capture and storage employed in alkanolamine solutions, zeolites present more rapid adsorption and a lower energy penalty for the regeneration process (Zhang et al., 2008). Both the low cost and well developed chemical structures of zeolites render these materials attractive for their utilization in CO$_2$ sequestration applications. In addition the presence of charge balancing metal cations within the pores of zeolite is the main feature which enhances the selectivity towards the CO$_2$ component. Highly charged species on the surfaces of zeolites can impart high affinities for CO$_2$ and also owing to it, the propensity for CO$_2$ to be polarised to a higher extent than other species such as N$_2$ or CH$_4$ or H$_2$.

Alkali and alkaline earth metal cation-exchange have also been investigated by several authors for CO$_2$ capture in zeolites and their presence within the pores led to a higher affinity for CO$_2$ (Zhang et al., 2008). Bae et al (2013) evaluated the potential applications of various cation-exchanged zeolites NaA and NaX which were purchased as powders from Sigma-Aldrich for CO$_2$ capture. It was highlighted by these authors that zeolite-A containing calcium (CaA form) exhibited the highest CO$_2$ uptake among other investigated cations and furthermore, its selectivity towards CO$_2$ was higher than towards N$_2$ molecules (in a gas mixture) under conditions relevant to coal-fired power plants (0.15 bar
and 40 °C). In addition, the presence of strong interactions between CO₂ and the CaA zeolite framework indicated the formation of carbonates like complexes as also reported by Martin-Calvo et al., (2014).

1.6 Regeneration of adsorbents

In any CO₂ capture process, the adsorbent has to be regenerated after each adsorption cycle. Therefore pressure swing adsorption (PSA), vacuum swing adsorption (VSA) or temperature swing adsorptions (TSA) are potential techniques for removing adsorbed CO₂ or regenerating the adsorbent (solid adsorbent such as zeolites) (Ranjani et al., 2003). The basic principle of these processes consists of increasing the temperature (TSA) or reducing the pressure (PSA and VSA) in order to regenerate the adsorbent. In the TSA, the saturated adsorbent is heated from ambient pressure to an optimal desorption temperature of the porous materials. As the temperature increases, CO₂ gas molecules are desorbed from the adsorbent surface or pores and the increased gas pressure drives the desorbed gases out the system (adsorbent). In the PSA or VSA systems, the regeneration process is achieved by lowering the pressure after adsorption in order to desorb the captured gas molecules (Berger and Bhown, 2011). It is highlighted that PSA or VSA are physisorption processes with weak interactions between adsorbent and adsorbate whereas TSA is a chemisorption process which involves strong interactions and high energy during regeneration process (Napolitano et al., 2011). In this thesis a TSA process was employed under temperature programmed desorption in order to evaluate both the capacity and interactions between ion-exchanged zeolites-A and CO₂ and the main attention was put on these two aspects rather than the regeneration process.

1.7 Problem statement

Coal combustion is the main source of electricity generation in South Africa. This is expected to remain the case for the next decades due to the lack of alternatives
Various waste products are generated during the combustion of coal such as fly ash and \( \text{CO}_2 \). Fly ash is known as a soil pollutant and \( \text{CO}_2 \) is a major GHG contributor. Therefore, there is a need, on the one hand to recycle fly ash into useful materials such as zeolites and on the other hand, to mitigate \( \text{CO}_2 \) emissions in the atmosphere since this gas constitutes the main GHG (IEA, 2012).

Thus while current \( \text{CO}_2 \) capture technologies are costly for widespread applications in the absence of a large tax on \( \text{CO}_2 \) emissions (Yu et al., 2012); solid adsorbent based systems such as zeolites have demonstrated potential capacities towards reducing the cost and also improving performance compared to existing systems that rely on aqueous amine solutions (Rao & Rubin, 2002). Zeolites (natural and synthetic) are affordable porous materials that are already produced on a large scale for several applications. However their utilization and performance for \( \text{CO}_2 \) adsorption at conditions relevant to power plant stations and flue gas still have not been fully characterized for many zeolites in their pure form. Thus there is a need to develop a cost-effective \( \text{CO}_2 \) capture-zeolite system in order to reduce global \( \text{CO}_2 \) emissions and in particular South African emissions as power plants continue to burn coal.

Muriithi (2012) prepared NaA and NaX zeolites from South African coal fly ash for \( \text{CO}_2 \) adsorption. Her findings demonstrated that physisorption was the most prevalent phenomena observed in both fly ash based zeolites and the main cation in these zeolites was Na\(^+\). In addition, it was concluded that these materials were suitable to be used at low temperatures and/or pressure swing adsorption of \( \text{CO}_2 \) due to the presence of the weak adsorption sites in their framework. Thus zeolite materials containing other cations rather than the host zeolite based-cation (mostly Na\(^+\)) are currently under investigation for improving \( \text{CO}_2 \) adsorption or sequestration and also for tailoring the pore opening or pores sizes of zeolite molecular sieve such as NaA zeolite (increase or decrease of the pore size). Alkali and alkaline earth metals such as K\(^+\), Li\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) have mostly been reported
as guest cations which can be exchanged with the host cation such Na\textsuperscript{+} as mentioned earlier above (Walton et al., 2006). The present study intends to investigate both chemisorption and physisorption phenomena on different zeolite-A based catalysts containing Li\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+} cations prepared from South African fly ash based NaA zeolite for CO\textsubscript{2} adsorption and sequestration.

1.8 Aims, objectives and research questions

After a brief background and a short overview which have been given above concerning CO\textsubscript{2} adsorption and sequestration using zeolite, this present study aims mainly to develop fly ash based zeolite-A adsorbents for CO\textsubscript{2} adsorption and sequestration that could be applied in power station flue gas plants. Thus the crucial achievement of this study will be achieved by answering the developed questions below:

1. What impact do different selected cations have on the structure of fly ash based zeolite? And does the respective cation (Na\textsuperscript{+}, Li\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}) influence this?

2. Can the ion-exchange procedure using different cations be optimized for fly ash based zeolite-A, and what is the optimum cation uptake capacity?

3. To which extent, and under which conditions can the host cation Na\textsuperscript{+} be exchanged with Li\textsuperscript{+}, Ca\textsuperscript{2+} or Mg\textsuperscript{2+} in fly ash based zeolite-A?

4. Is CO\textsubscript{2} adsorption onto fly ash based exchanged zeolite-A, a physisorption or chemisorption process?

5. Which cation (Na\textsuperscript{+}, Li\textsuperscript{+}, Ca\textsuperscript{2+}, and Mg\textsuperscript{2+}) allows the greatest CO\textsubscript{2} capture in terms of physisorption or chemisorption?

1.9 Hypothesis

Answering these above research questions leads to some hypotheses which have been selected according to the literature review examined in this thesis. This includes mainly:
1. Fly ash based NaA zeolite and its exchanged forms can easily be used for CO\(_2\) adsorption and sequestration.

2. The host Na\(^+\) cation in the framework of NaA zeolite can partially be exchanged with mono and divalent ions such as Li\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) etc.

3. Zeolite-A and its ion-exchanged forms with LiA, CaA and MgA can chemisorb and physisorb CO\(_2\).

1.10 Research approach

The ion-exchange technique permits substitution of the host cation contained in the zeolite framework with a guest cation which results in the tailoring of pores and also could increase interactions between the zeolite framework and an adsorbate such as CO\(_2\) during adsorption. In this study fly ash sourced from South African Arnot power station site was characterized prior to synthesis of zeolites-NaA. Thereafter NaA zeolite was ion-exchanged using alkali and alkaline earth metals in order to replace the Na\(^+\) host cation of NaA zeolite obtained after synthesis into monovalent and divalent cationic form. The ion-exchanged zeolites were characterized by physico-chemical analysis using techniques such as XRD, XRF, and FT-IR etc. The XRD and FT-IR characterizations were performed before and after the loading process of monovalent and divalent metals in order to monitor the integrity and structural crystallinity of the framework of the zeolite-A while substituting the extra-framework cation (and removing the host cation, Na\(^+\)). The EDS was carried out for elemental analysis through SEM and TEM techniques. In addition SEM and TEM were used for determination of the morphology of zeolite materials, before and after the ion-exchange process. The catalysts generated through ion-exchange were applied in the CO\(_2\)-TPD adsorption in order to investigate the CO\(_2\) sorptions through temperature swing desorption. This last part of characterization represents the second part of this thesis and consisted of adsorbing CO\(_2\) onto selected ion-exchanged zeolite catalysts, whereas the first phase consisted of finding conditions for an optimum loading capacity of Li\(^+\),
Chapter One

Ca\textsuperscript{2+} and Mg\textsuperscript{2+} cations during the ion-exchange process. The results obtained were compared to those that are found in the literature.

1.11 Scope and delimitation of thesis

This study seeks to address the problem associated with CO\textsubscript{2} sequestration by developing a cost effective fly ash based zeolite adsorbent which could be applied for CO\textsubscript{2} capture and sequestration at power stations. The developed fly ash based zeolite-A adsorbents were investigated in comparison with what is known in the existing literature. The present thesis will only consist of loading cations through the ion-exchange technique. Three metals have been selected in order to achieve the main objectives of this study. These cations include Li\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+}, the fourth metal will be the non-exchanged Na\textsuperscript{+} cation contained as charge balancing cation in association with the framework of the synthesized fly ash NaA zeolite which will be used as control material.

1.12 Thesis structure

Except for the above given introduction which is the first chapter of this thesis, the present work contains five more chapters whose summaries are given here below.

The second chapter of this thesis will give an overview of the literature by highlighting work that has already been done on CO\textsubscript{2} adsorption and sequestration using NaA zeolite adsorbent. The review will essentially cover an overview of energy, coal combustion and associated by-products, fly ash generation and handling, synthesis of NaA zeolite from fly ash, NaA zeolite modification for CO\textsubscript{2} adsorption, CO\textsubscript{2} management and CCS technologies. The achievements and limitations regarding CO\textsubscript{2} adsorption onto NaA zeolite will be highlighted as well. This section will be supported mainly by papers drawn from scientific literature and the thesis elaborated on this topic.
The third chapter will give an experimental research approach of this work, by describing firstly all methods used for fly ash characterization prior to zeolite synthesis. Secondly the synthesis procedure for preparing NaA zeolite and the ion-exchange method chosen for the loading of Li\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) cations onto the zeolite-A will be also presented. Finally the experimental method for CO\(_2\) adsorption and/or desorption and for the instruments used for characterization will be set out. Parameters such as temperature, contact time, adsorption and/or desorption of CO\(_2\) uptake were investigated.

The fourth chapter will present and discuss different results generated, starting from the fly ash to the synthesized NaA zeolite, its various exchanged forms after ion-exchange process and the CO\(_2\) adsorption. This will include the results generated from XRD, FT-IR, HR-SEM, HR-TEM, XRF, EDS and CO\(_2\)-TPD characterizations. Discussion in this part of the thesis will be supported by data existing in the literature in an attempt to draw a comparative base line for deeper understanding of the generated data.

The fifth chapter will give a summary of this work and draw general conclusions. A list of recommendations for future work will be also presented in this chapter.

The sixth chapter presents all the references used to support this study.
2. LITERATURE

2.1 Introduction

The present chapter gives an overview on the utilization of coal for electricity production. This utilization generates a huge amount of solids (e.g. fly ash), liquid (e.g. brine) and gases (e.g. CO$_2$) as by-products during the combustion process. Hence, this section discusses and suggests ways to recycle fly ash by-products into useful material such as zeolites that can be in turn used for sequestration and storage of CO$_2$ which is another potent coal combustion by-product.

Fossil fuels, amongst other sources of energy remain the mainstay of global energy production into the 21st century. However the combustion of coal for energy production (electricity), is responsible for generating tons of fly ash and several emissions such as carbon dioxide (CO$_2$), methane (CH$_4$) etc. CO$_2$ is known to be the main greenhouse gas (GHG) contributing 50 % in itself. The 50 % of its contribution can be shared depending on the source of emissions as 73 % (fossil fuel utilization), 25 % (deforestation) and 2 % (cement industry). The rest of the emissions in addition to the 50 % of CO$_2$ contribution is mainly composed of CH$_4$ with 18 % as GHG and 32 % of other potent GHGs (Lemos de Sousa and Rodriguez, 2008). In 2010 the global CO$_2$ emissions from fuels were shared as follows, about 43 % of CO$_2$ emissions were generated from coal, 36 % from oil and 20 % from gas (EIA, 2012). Anthropogenic CO$_2$ emissions were in the order of 7 Gt/a in the late 1990’s. This amount almost quadrupled in 2007 from the 1990’s with approximately 29 Gt of CO$_2$ that were added to the atmosphere and this has been projected to increase to about 43 Gt by 2030 (Hongqun et al., 2008).
In 1999 USA contributed 23% to the total world’s emissions of CO$_2$ while China contributed 13%. This scenario changed in 2006 when China’s emissions surpassed those of USA by 8% according to Netherlands Environmental Assessment Agency (NEAA). The European Union with fewer emissions occupies the 3$^{rd}$ position followed by Russia, India and Japan respectively. CO$_2$ emissions from fuel combustion in South Africa were about 340 Mt/a, in 2006, making the country the 15$^{th}$ largest emitter of CO$_2$ in the world (Eberhard, 2011). This amount was slightly reduced in 2010 to about 300 Mt CO$_2$. In this amount, Eskom coal-fired power stations accounted for around 225 Mt of CO$_2$ (Eskom, 2011); and Sasol’s coal-to-liquid (CTL) plants about 72.7 Mt of CO$_2$.

Coal combustion represents the main source of energy in South Africa providing about 93% of its crucial energy. This practice remains unfortunately inevitable and uncertain to change for the next decades, due to the lack of alternative sources of electricity production, such as hydroelectric waterfalls rather than the combustion of coal. Though South Africa is a coal dependant nation, the country itself possesses one of the important coal reserves in the world and is classified amongst major coal exporters (www.eskom.co.za).

Coal mines are located in five provinces of South Africa namely the Limpopo, Mpumalanga, Free State, Kwazulu-Natal and Eastern Cape. Most collieries are concentrated around towns, such as Witbank, Ermelo and Secunda. Highveld, Waterberg and Witbank are three main coal fields where 70% of recoverable reserves exist. Coal mining activity occurs through various collieries ranging among the largest in the world and exploiting coal at small and large scale. Five main companies namely Anglo-American, Exxaro, Sasol, BHP Billiton and Xstrata account for about 80% of coal production in South Africa. These companies in association with other coal mining industries exploit South African coal deposits for both local grids (electricity and CTL process) and international grids (exports) (Eberhard, 2011).
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Amongst other coal exporters, South Africa exports about 28% of its coal to Europe and to a large part of Asia making it the sixth coal exporter worldwide behind Colombia and the USA (WCA, 2014). The export of South African coals has currently declined due to the new plan announced in March 2013 via the Department of Mining, which aims to reduce exports and also to protect the country’s natural coal resource which is supposed to serve for domestic use, for both electricity production and fuels (www.dme.gov.za/energy/coal.stm).

The export of South African coals occurs principally through the Richard Bay coal terminal (RBCT). The RBCT is located alongside the Kwazulu Natal north coast of South Africa. It has currently the capacity of over 91 million tonnes per annum. (www.rbct.co.za). Eskom and Sasol are both giant South African companies which rely essentially on coal as raw materials for their respective operations where each one plays a significant role in the country’s daily activities. The electricity company Eskom, is the main power provider in South Africa; this company utilizes its entire deposit of coal in the burning operations for electricity production purpose for both local and international grids. On the other hand Sasol is the second local industrial coal user and the world’s biggest and unique leading producer of synthetic fuels and chemicals from South African low-grade coal and natural gas. This company is listed on the Johannesburg Stock Exchange (JSE) since 1979 and the New York Stock Exchange (NYSE) in 2003 (www.dme.gov.za/energy/coal.stm).

Coal being the main feedstock for both Eskom and Sasol, these companies are subsequently facing some issues related to the remediation of the environmental and atmospheric impacts caused by solid, liquid and gas CCPs generated during their respective operations. Therefore recycling these CCPs has become a major concern in the present century especially the mitigation and the reduction of the atmospheric CO₂ emissions which are known to be a source of GHG.
Thus South Africa among developing countries such as Brazil and China; has acceded to and participates in the Kyoto protocol commitments as an annex 1 through the Clean Development Mechanism (CDM). The CDM allows industrialized countries with emission reduction commitments to meet part of their commitments by investing in projects that reduce emissions in developing countries. The projects need to support sustainable development in the host countries and must lead to emissions reduction that are real, measurable and long term in climate change mitigation such as energy efficiency, cleaner production, fuel switching. Many scenarios of the future suggest that the world coal markets will continue to grow steadily over the course of the 21st century, in the absence of enforceable CO₂ emission limits, even though increased energy efficiency and use of renewable and nuclear energy afford good opportunities for reducing CO₂ emissions. Fossil fuels are abundant and economic making their continued utilization an attractive option (Olivier et al., 2011). Hence various steps have been taken internationally due to this major challenge which is on the one hand the continued utilization of coal and on the other reducing and mitigation of CO₂ emissions. For instance the creation of the United Nations Framework Convention on Climate Change (UNFCCC) and also the ratification of the Kyoto protocol, together bring constraints upon emissions with significant attention paid to industrialized countries, including both developed and emerging economies.

2.2 Coal

2.2.1 Origin of coal

Coal is described as a fossil fuel, a combustible, sedimentary, organic rock, which is composed mainly of carbon, hydrogen and oxygen. It is formed from vegetation that has been consolidated between other rocks and altered by the combination of both the effects of temperature and pressure over millions of years to form coal. The coalification occurs in the absence of oxygen and in the
presence of anaerobic bacteria which results in physical and chemical changes of
the vegetative aspect of the peat into coal. The quality of each coal deposit is
determined by temperature and pressure and by the length of time in formation
(organic maturity). Coal also contains an important share of inorganic matter and
other materials such as oil, gases, waxes and water (about 40% by weight)
(www.worldcoal.org/coal/).

2.2.2 Mineral composition of coal

Coal is a complex and exceptional heterogeneous carbon-based rock in which
about 316 minerals or mineral groups have been identified mostly as accessory or
trace minerals (Vassilev and Vassileva, 2005). The coalification process (beside
the organic share) occurs in association with different types of inorganic minerals
such as aluminosilicates (clay), carbonates (calcite and dolomites), sulphides
(pyrite), chlorides and silica (quartz). The elements such as sulphur can either
occur in the organic or inorganic fraction of the coal. The most abundant
inorganic minerals of coal include: calcite, marcasite, quartz, pyrite, siderite,
gypsum, anhydrite, and clays (Scheetz and Earl, 1998, Querol et al., 1995).

In general the inorganic mineral portion can reach approximately 5-15 % of the
coal composition. However, some South African coals have been found to have
higher values ranging from 25-65 % of the inorganic minerals fraction. These
values reflect a typical range of a low grade coal, because the quantity of ash that
is subsequently generated is much higher compared to a range of 10-15% for
higher grade coal that is found elsewhere (Solem and Mc Carty, 1992; Petrik et al,
2003).

2.2.3 Utilization of coal

Coal has the potential of being used in various ways. This includes mainly its
burning for electricity generation, gasification and liquefaction for heat and CTL-
plants process (WCI, 2009). The following section gives different techniques that
are mostly used in the combustion of coal for both electricity generation and the CTL process.

**2.2.3.1 Pulverized coal combustion**

Pulverized coal combustion (PCC) is the standard method utilized throughout many coal-fired power plants around the world. In PCC process, coal is firstly ground to a fine powder and then ignited in the combustion chamber. The heat resulting from this combustion is used to generate steam which turns large turbines that generate electrical power (Langston et al., 1997). The efficiency of this system is generally expressed in terms of the higher heating value (HHV). In other words, the HHV of the fuel including the latent heat of vaporization of water or moisture formed in the combustion. This efficiency ranges between 33-39 % and 38-42 % for coals such as bituminous depending upon the type of the plant (Nalbandian, 2008). During this operation, a large quantity of wastes known as CCP’s are generated. This includes fly ash, slag, ash and gaseous emissions (sulphur dioxide (SO$_2$), nitrous oxide (NO$_x$), carbon dioxide (CO$_2$) (Lokeshappa and Anil, 2011). Figure 2.1 gives a schematic diagram of a typical PCC.

![Figure 2.1: Typical electricity power plan using PCC technique (WCI, 2009).](image)

Figure 2.1: Typical electricity power plan using PCC technique (WCI, 2009).
2.2.3.2 Fuels and electricity generation

In the integrated coal gasification combined cycle (IGCC), coal is first gasified in order to remove all impurities from the gas before the combustion. IGCC is considered to be interesting since, a significant diminution of gaseous pollutants, such as $\text{SO}_2$ generated in a PCC process can be achieved and also this method is known to be suitable for carbon capture sequestration (CCS) rather than a conventional PCC process. Additionally IGCC has the potential to be used for electricity generation and synthetic fuels (CTL) and/or chemicals production in the same facility (Minchener, 2005). A typical operating IGCC is found in South Africa at Sasol plants, where coal is used for both CTL-plant and electricity generation. A schematic description of IGCC process employed at Sasol is given in Figure 2.2.

Figure 2.2: Typical diagram of an IGCC process used at Sasol-Lurgi gasification process (source: Sasol-Lurgi technology).

Another technique less commonly used is the fluidized-bed-combustion (FBC); in this technique coal is suspended on jets of air during the process. This is actually
to allow the mixing of coal (solid fuel) and the gas to be more efficient, resulting in an efficient heat transfer. One of the advantages of FBC is that the combustion reaction can take place at lower temperatures, which is a very important fact; because it reduces the formation of toxic NOx and also allows a cheap, easy treatment and removal of SO$_2$ during the combustion rather than using stack scrubber technology (Dyk et al., 2006).

2.3 Coal combustion by-products (CCPs)

Prior to the combustion of coal, particularly the PCC process commonly used in power generation such as at Eskom in South Africa, coal needs to be ground to a fine powder. This powdered coal, once ignited produces various wastes known as coal combustion by-products (CCPs).

CCPs result from inorganic minerals and incomplete combustion of organic materials that originally constitute coal (Kalyoncu, 2001) and include principally: wet bottom ash boiler slag, dry bottom ash, fly ash (FA), flue gas desulphurization gypsum (FGD) and cenospheres. The amount of solids CCPs which is left over after the combustion reflects the quantity of mineral matter present in coal. This is also related to the chemical changes that occurred during the combustion process and the nature of the mineral matter (Kalyoncu, 2001). Since one of the objectives of this study is the utilization of South African fly ash as feedstock in the synthesis of NaA zeolite, the section below offers a brief discussion of coal fly ash, especially its applications.

2.4 Fly ash

Fly ash (FA) can be identified as the solid matter resulting from thermally altered inorganic constituents that were initially contained in the core of coal (Scheetz and Earl, 1998). At the first view, FA is a fine-grained, inorganic powder residue, composed essentially of tiny sphere-shaped glassy particles which are related to the mineral composition of coal and the process employed during its combustion.
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(Kutchko and Kim, 2006; Ahmaruzzaman, 2010). FA is abrasive, alkaline and refractory in its nature. The characteristics of FA can vary depending upon the type of coal that has been used in the burning process (the treatment undertaken on coal before combustion and the operating conditions of the boiler) (Eary et al., 1990). FA is carried off in the flue gas as it leaves the combustion chamber and is usually collected from the flue gas by means of electrostatic precipitators, bag houses, or mechanical collection devices such as cyclones.

2.4.1 Mineral composition of fly ash

Three different phases are identified to be contained in fly ash (FA) the crystalline minerals such as quartz, mullite, spinel; non-crystalline alumina-silicates glass and non-burnt carbon constituents; silica (SiO$_2$), alumina (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$) represent the primary components of FA together with additional elements such as carbon, calcium, sulphur and magnesium that are present in the original coal material in various amounts (Wang et al., 2006). The specific gravity of FA has been demonstrated to be in the range of 2-3 g/cm$^3$ approximately, while its specific surface area can vary from about 170-1000 m$^2$/kg and the particle sizes can range generally from 0.5-200 microns (Scheetz and Earle, 1998; Crelling et al., 2010).

2.4.2 Properties of fly ash

Fly ash (FA) is physically a fine grained-powder, its chemical and physical properties as well as the mineral composition are essentially related to the type of coal combusted whilst its composition is strongly related to conditions applied during the combustion process (Bhanarkar et al., 2008). The major elements in the order of decreasing abundance in FA are: Si, Al, Ca, C, Fe, Mg, K, Na, S, Ti, P and Mn; most of these major elements exist in the core (relatively stable) of the FA, probably because they do not volatilize during the combustion process (Lokeshappa and Anil, 2011). In addition the chemical composition of FA can vary from one type of coal to another (Adriano et al., 1980). FA also contains
large quantities of major impurities such as oxides, hydroxides and sulphates of iron and calcium, as well as significant quantities of hazardous leachable trace elements such as arsenic (As), boron (B), cadmium (Cd), chromium (Cr), selenium (Se) and vanadium (V) (Querol et al., 1999). During the burning process of coal, the organic matter is utilised to produce heat and as a result, the concentrations of trace elements are increased relatively to those in the initial coal material (Lokeshappa and Anil, 2011). As a result many trace elements such as As, Se, Cd, Cr, Ni, Sb, Pb, Sn, Zn and B are enriched by factors of 4–10 in FA and the presence of some of these elements has a negative impact on the utilization of FA due to environmental restrictions (Fernandez et al., 1994).

2.4.3 Classification of fly ash

According to the American Society for Testing and Materials (ASTM), coal fly ash can be found into two main classes namely class F or C (ASTM, 1994). This classification is exclusively based on the proportional amounts of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ found in the ashes. Thus, if the sum of these oxides (SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$) is higher than 70 %, the ash is said to belong to Class F, however when this sum is comprised between 50-70 % (or < 70 %) the ash is said to belong to Class C. The Class C type ashes are also characterized by a higher CaO content (20-30 %) while Class F is reported to contain less than 10 % CaO content (ASTM, 1994). According to Somerset et al, (2004) South African ash is found to contain a relatively high concentration of SiO$_2$, Al$_2$O$_3$ and CaO, therefore belongs to Class F. Table 2.1 illustrates the two main classes of ashes with respect to the ASTM standards (1994).
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Table 2.1: ASTM standard classification of coal fly ash (ASTM C204, 1994).

<table>
<thead>
<tr>
<th>Components (%)</th>
<th>Class F</th>
<th>Class C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2+\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$, min</td>
<td>70</td>
<td>50.0</td>
</tr>
<tr>
<td>$\text{SO}_3$, max</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>&lt;10</td>
<td>20</td>
</tr>
<tr>
<td>Moisture content, max</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Loss of Ignition, max</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

2.4.4 Utilization of fly ash

The increasing demand for energy in the world, has led also to the increase of coal utilization in power stations. This practice of burning coal has subsequently generated millions of tonnes of fly ash (FA) as waste products all over the world (Hui et al., 2005). According to Iyer and Scott (2001) less than 25 % of the total annual FA produced worldwide is utilized. The use is mainly as an additive in the cement and concrete as filling material while the rest (about 75 %) is disposed or land filled which is currently a most widely practised technique used in the management of coal FA (Álvarez-Ayuso et al., 2008; Kruger, 1997; Gitari, 2006). However in 1996 over 95 % of the total FA produced was signalled to be used in Belgium, Germany, and Netherlands and about 50 % in the United Kingdom during 1998. On the other hand, in USA and China where huge quantities of FA are currently produced annually, only 32 % and 40 % respectively of their fly ash has been used during the year 1995 (Senapati, 2011).

In Africa and particularly in the Republic of South Africa where a considerable amount is also generated annually about 36 Mt of fly ash were produced in 2011 and from such amount only 5 % of it is generally used with benefit and the rest is disposed in ash dams, landfills or ponds (Mainganye et al., 2013; Petrik et al., 2005). Some characteristics of coal fly ash such as its mineralogy, class and chemical composition play a major role during its utilization in many applications (Wang and Wu, 2006). Therefore the section below describes some common areas where coal fly ash is mostly used worldwide.
2.4.4.1 Fly ash as pozzolan in cement

The high content of oxides such as SiO$_2$ in fly ash (FA) renders it a potential candidate in the cement industry, where it is used as pozzolan in replacement of clinker. In fact, FA which has a high amount of SiO$_2$ and Al$_2$O$_3$ in reactive form complements the hydration chemistry of cement in the presence of moisture (H$_2$O) by chemically reacting with calcium hydroxide (Ca (OH)$_2$) at room temperature to form compounds possessing cementitious properties such as tricalcium silicate (alite, Ca$_3$SiO$_5$), dicalcium silicate (belite, Ca$_2$SiO$_4$), tricalcium aluminate (Ca$_3$Al$_2$O$_6$), and tetracalciumaluminoferite (Ca$_4$Al$_2$Fe$_2$O$_{10}$) (Seshadri et al., 2010). Kruger (1997) reported that South African fly ashes such as those generated at Matla and Lethabo power stations, have some pozzolanic characteristics and these FA are mostly used in concrete and building materials in order to enhance the properties of these materials. It was also reported by Kruger and Krueger (2005) that approximately 50 % of the cement clinker produced in South Africa is made up of coal fly ash.

2.4.4.2 Fly ash as acid mine drainage neutralizer

Acid mine drainage (AMD) is one of the by-products generated during mining processes. It is considered as an environmental threat which causes problems, because of its high heavy metal content low pH as well as its high SO$_4^{2-}$ concentrations. The formation of SO$_4^{2-}$ from the reaction between pyrite (FeS$_2$) with oxygen (O$_2$) and H$_2$O, causes a decrease in the pH of water which results in acidic conditions (in the range of 2-4) (Gitari, 2006). Several studies have shown that fly ash (FA) can be used as AMD pH neutralizer due to its alkaline nature (Gitari et al., 2008; Madzivire et al., 2010). Both the low-cost and the availability of FA render it a potential source of lime (CaO) for treating waste waters (AMD) rather than caustic material (hydrated lime (Ca (OH)$_2$), caustic soda (NaOH), ammonia (NH$_3$), lime (CaO) and also soda ash (Na$_2$CO$_3$) which have been
routinely used in the past in order to raise the pH of AMD in particular and other waste waters (Robb and Robinson, 1995; Petrik et al., 2003, 2005).

2.4.4.3 Synthesis of zeolite from fly ash

Natural zeolites are minerals composed essentially of hydrated aluminium silicates of alkali and alkaline earth metals (Break, 1984). Although these minerals occur naturally in veins and cavities of igneous rocks, synthetic zeolite can also be generated from fly ash (FA) and can find similar applications to natural zeolites (catalyst and catalyst support, removal of ions and heavy metals, cation exchange, waste water treatment) (Somerset et al., 2004; Hussar et al., 2011). This is due mainly to the high percentage of silica (SiO$_2$) and alumina (Al$_2$O$_3$) contained in FA making it a potential feedstock for the synthesis of zeolite and other useful materials such as geopolymers (Querol et al., 2002; Nyale et al., 2013). Various applications of zeolites have currently promoted its synthesis since synthetic zeolites are economically advantageous because coal fly ash is readily available as a raw material and most importantly, fly ash is considered as a low-cost source of SiO$_2$ and Al$_2$O$_3$ during the synthesis (Musyoka, 2009). The applications mentioned above remain non-exhaustive since this material is so far insufficiently utilized as raw material rather than a waste product itself. Thus Wang and Wu (2006) reported some possible ways in which FA can be used as starting material for a wide range of applications. Their investigations concentrated mainly on the properties of fly ash that are related to chemical composition, size range, pozzolanic nature as well as some factors such as abundance (availability). Figure 2.3 presents a summary of the possible applications of FA as raw material (adapted from Wang and Wu, 2006).
Figure 2.3: Possible applications of coal fly ash as raw material based on some properties and factors (adapted from Wang and Wu, 2006).

2.4.5 Fly ash disposal

The disposal and management of fly ash (FA) constitutes a major problem for most coal-fired thermal power plants. FA generated in the thermal power plant needs to be disposed outside the plant location so that it causes least disturbance to the principal plant operation. Therefore two techniques are currently used for the disposal of coal fly ash namely the wet or dry disposal methods which depend upon the type of plants (Lokeshappa and Anil, 2011). For instance, in South Africa both Eskom and Sasol used these techniques of fly ash disposal (Fatoba, 2010). In addition according to the Environmental Agency of Japan (EAJ, 1973) coal fly ash complies with land filling disposal. Although coal fly ash complies with land filling regulations, it is however considered as an ecological nuisance because of its impacts in the environment and its disposal concerns (Petrik et al., 2003; Álvarez-Ayuso et al., 2008).
2.4.6 Environmental health issues of fly ash

Health hazards and also environmental impact from thermal power plants mainly originate from the mobilization of toxic and radioactive elements associated with CCP's (Ilic et al., 2003; Baba and Kaya, 2004). The environmental impact of coal fly ash is mostly associated with its metal content leaching during ash ponding. These metals are considered as pollutants because of their leaching potential which is expected to be significant. FA which contains toxic metals such as lead (Pb), is of large public concern due to the toxicity to animals as well as human beings, especially young children (Manz, 1999). It has been demonstrated that all toxic metals (Ni, Cd, Sb, As, Cr, Pb, etc.) found in FA are generally of toxic aspect in nature. Moreover they cannot be degraded biologically into less harmful products unlike organic wastes (Senapati, 2011). Furthermore, contaminated leachates from ashes can cause a high toxicity problem for the aquatic environments (Roy et al, 1984). Table 2.2 below provides some diseases that are caused due to the presence of toxic metals contained in FA.

Table 2.2: Some diseases caused by the presence of toxic metals in fly ash (Senapati, 2011).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Content (ppm)</th>
<th>Diseases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (Ni)</td>
<td>77.6</td>
<td>Respiratory problem, lung cancer</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>3.4</td>
<td>Anaemia, hepatic disorder</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>4.5</td>
<td>Gastroenteritis</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>43.4</td>
<td>Skin cancer, dermatitis</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>136</td>
<td>Cancer</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>56</td>
<td>Anaemia</td>
</tr>
</tbody>
</table>
2.5 Zeolites

2.5.1 Introduction and structure

Zeolites have received considerable attention only in the last few decades, though being discovered more than 250 years ago (Breck, 1984). The history started in 1756 with the discovery of stilbite by A.F Crönstedt (Swedish mineralogist). Zeolites, when heated release occluded H$_2$O, this behaviour confers their name “zeolites”. This name is an acronym originally from two Greek words “zeo” meaning “to boil”, and “lithos” “stone”. Many zeolites occur naturally as minerals and are extensively mined worldwide and others are synthetically made for both commercial and scientific applications (Querol et al.; 1995, 1997, 2001, 2002). A representative chemical formula of zeolites that is best expressed for the crystallographic unit cell is given in Figure 2.4. This formula can be divided into three, to clearly distinguish the main components. The first component which is the ion exchangeable (extra framework) portion is a crucial component since it allows various applications of zeolites. The second part represents the basic crystal framework which is generally unchangeable and the third part represents molecular water contained in any zeolite structure from their synthesis or natural formation (Breck, 1984).

![Figure 2.4: Zeolite framework structure and its three main components developed from Breck, (1984).](image)

2.5.2 Mineralogical composition

Zeolites are crystalline aluminosilicates that contain pores and channels with molecular dimensions widely utilized in industry as ion exchangers, molecular...
sieves, sorbents and catalysts. These crystalline aluminosilicates occur mainly in three dimensional networks containing \([\text{AlO}_4]^{5-}\) and \([\text{SiO}_4]^4\) tetrahedra linked to each other by sharing all oxygen atoms forming an open anionic framework which is able to adsorb molecules or cations because they also form interconnected cages or voids as part of their structure (Auerbach et al., 2003; Dimitar et al., 2009). Cations are introduced in these cages as extra framework species since they are acting as charge compensating ions in order to preserve the electronic neutrality when tetravalent silicon atoms (Si^{4+}) are substituted by the trivalent form of aluminium atoms (Al^{3+}). This results in the formation of ionic sites in the surrounding area of aluminium atoms and the extra framework cation of the zeolite structure can therefore be easily exchanged (Dimitar et al., 2009). Figure 2.5 gives an illustration of NaA zeolite with an open framework showing two sites available (negative charge) where cations can be accommodated (Kyung and Young, 2010).

![Diagram of NaA zeolite](image)

Figure 2.5: The open framework of NaA zeolite containing channels and interconnected voids which can be occupied by cations such as Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) etc. (Kyung and Young, 2010).

### 2.5.3 Classification of zeolites

Pore sizes are one of the ways among others that can be used to distinguish different zeolite materials. The pore sizes generally range between 3-10 Å in
diameter which gives zeolites the unique ability of acting as molecular sieves in the presence of molecules and ions that are below these pore sizes by excluding bigger molecules or ions and vice-versa (Vivek et al., 2011; Byrappa and Yoshimura, 2001). Considering the objectives listed above, the main focus of this study will be on the pore sizes modification of fly ash NaA zeolite prior to CO₂ adsorption. Figure 2.6 gives different size ranges of the pores of some zeolite frameworks. As can be seen, zeolite LTA is the structure that possesses the smallest pores size opening of about 0-4 Å whereas zeolite CLO has the largest pores (~13 Å). This aspect is essential, especially in the sieving applications of zeolites.

Figure 2.6: Different type of zeolite frameworks according to their pores size dimensions (adapted from Byrappa and Yoshimura, 2001).

During the past two decades approximately 40 natural zeolites have been identified and the most well-known are: Analcime, Chabazite, Clinoptilolite,
Erionite, Ferrierite, Heulandite, Laumontite, Mordenite and Phillipsite (Wang et al., 2008). On the other hand, over 150 synthetic zeolites have been synthesized during the past few years and the most common types synthetically obtained are: zeolite A, FAU (X and Y) and ZMS-5 (Mosca, 2006; Musyoka, 2009). Because of their unique properties both, natural and synthetic zeolites find commercial applications such as adsorption, ion-exchange, molecular sieving and catalytic properties (Vivek et al., 2011). The structure commission and the IUPAC nomenclature of the International Zeolite Association (IZA) identify each framework of a particular zeolite with a three-letter code; this is known as mnemonic code. Table 2.3 lists some zeolites with their three-letter codes according to their Si/Al ratios.

Table 2.3: The nomenclature of different types of zeolites based on the Si/Al ratio (IZA).

<table>
<thead>
<tr>
<th>Si/Al ≤ 2</th>
<th>2 &lt; Si/Al &lt; 5</th>
<th>Si/Al ≥ 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low silica</td>
<td>Intermediate silica</td>
<td>High silica</td>
</tr>
<tr>
<td>FAU, NaX</td>
<td>CHA, chabazite</td>
<td>BEA, zeolite β</td>
</tr>
<tr>
<td>LTA, zeolite-A</td>
<td>FAU, faujasite ,NaY</td>
<td>FER, ferrierite</td>
</tr>
<tr>
<td>SOD, sodalite</td>
<td>LTL, linde Type L</td>
<td>ZSM-5</td>
</tr>
</tbody>
</table>

2.5.4 Structural composition of zeolites

The zeolite framework is fundamentally built of two types of building units known as primary building units (PBUs) and secondary building units (SBUs). The PBUs is known as the simpler building which can lead to any form of zeolite (Baerlocker et al., 2007). In PBU the tetrahedron (TO$_4$), four oxygen ions surround a central ion or cation of either Si$^{4+}$ or Al$^{3+}$ as shown in Figure 2.7. In the secondary building units (SBUs), different combinations of the same PBUs may
give rise to numerous distinctive polyhedral structures formed from aggregation of smaller ring units (4R, 6R, R=ring) (Baerlocker et al., 2007; Dimitar et al., 2009).

![Diagram of a tetrahedron unit](image)

Figure 2.7: The tetrahedron unit called TO$_4$ (T=Si$^{4+}$ or Al$^{3+}$) (Dimitar et al., 2009).

A wide range of polyhedra could be also formed due to the interconnection of the building units resulting in tertiary building units (TBUs) such as D4R, D6R (D=double). In turn, these TBUs can connect to form the extended frameworks of various specific zeolite crystal structures. It is highlighted that individual structures of zeolites can contain a single basic unit or many of them (Dimitar et al., 2009). Figure 2.8 illustrates the development of different zeolite structures LTA, SOD, FAU where the PBUs TO$_4$ tetrahedron are connected through their corners of shared oxygen atoms to form a wide range of small SBUs such as a 4R, 6R etc (Byrappa and Yoshimura, 2001). The corners of the polyhedron represent Si$^{4+}$ or Al$^{3+}$ atoms while the connecting lines represent the shared oxygen atoms.
Zeolites are mineral materials possessing exceptional properties that depend mainly upon their crystalline structures as well as the type of inner cavities such as pores, their sizes and also their shapes. These properties are mostly desirable for several applications which include environmental protection and some operations such as cation exchange capacity, adsorption and acid stability (Querol et., 1997). Zeolites are thermally stable over a large range of temperatures. The decomposition temperature for instance of low-silica zeolites is about 700 °C, while siliceous zeolites such as silicalites can be stable up to 1300 °C. Low-silica zeolites are generally unstable in acid, whereas high-silica zeolites are stable in acids, though unstable in basic solution. Low-silica zeolites tend to have also different types of structures with 4 MR, 6 MR, and 8 MR whereas more
siliceous zeolites contain 5 MR (Dimitar et al., 2009). Low-silica zeolites are hydrophilic, while high-silica zeolites are hydrophobic. Zeolites are also characterized by their unique property of having an internal surface which is highly accessible and constitutes more than 98% of the total surface area. Surface areas are typically of the order of 300-700 m$^2$/g. Table 2.4 gives some general physical and chemical properties of zeolites while Table 2.5 illustrates physical properties of three common zeolite types (Byrappa and Yoshimura, 2001).

Table 2.4: Physico-chemical properties of zeolites and related molecular sieves (Byrappa and Yoshimura, 2001).

<table>
<thead>
<tr>
<th>Properties</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size</td>
<td>~4-13 Å</td>
</tr>
<tr>
<td>Pore shape</td>
<td>Circular, Elliptical</td>
</tr>
<tr>
<td>Dimensionality of pore</td>
<td>1-D, 2-D, 3-D</td>
</tr>
<tr>
<td>Pore configuration</td>
<td>Channels, Cages</td>
</tr>
<tr>
<td>Surface properties</td>
<td>Hydrophilic, Hydrophobic</td>
</tr>
<tr>
<td>Void volume</td>
<td>Less than 50%</td>
</tr>
<tr>
<td>Framework oxide composition</td>
<td>Si, Al etc</td>
</tr>
</tbody>
</table>
Table 2.5: Physical properties of three types of common zeolites (Byrappa and Yoshimura, 2001)

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Isotypes</th>
<th>Si/Al ratio</th>
<th>Pore window</th>
<th>Pores/channels</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA</td>
<td>Zeolite A</td>
<td>~1</td>
<td>8-ring: 0.41 nm</td>
<td>3-D spherical 1.14 nm cavities</td>
</tr>
<tr>
<td></td>
<td>Linde type A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FAU</td>
<td>Zeolite X</td>
<td>1-1.5</td>
<td>12-ring :0.74 nm</td>
<td>3D spherical 1.18 nm cavities</td>
</tr>
<tr>
<td></td>
<td>Zeolite Y</td>
<td>1.5-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFI</td>
<td>ZSM-5</td>
<td>12-30</td>
<td>10-ring :0.60 nm</td>
<td>3D straight 0.60 nm channels</td>
</tr>
</tbody>
</table>

2.5.6 Ion exchange capacity of zeolite

Zeolites show remarkable ion-exchange capacity. This means that they are capable of reversibly desorbing adsorbed phases that are dispersed throughout voids of the crystal without displacing any of the atoms (Si$^{4+}$ and Al$^{3+}$) that make up the permanent crystal structure or framework (Breck, 1984). The substitution of Si$^{4+}$ by Al$^{3+}$ atom in the framework of zeolite, introduces a net negative charge. Thus charge balancing cations are then needed in order to preserve the neutrality of the framework. The presence of cations does not only allow zeolite crystals to be used as ion-exchange materials, however it also creates a Bronsted acidic site since protons are acting as counter ions. The cation exchange in a zeolitic material can take place based on parameters such as the concentration of the cation; the nature of the cation species; the type of the anion species associated with cations and the nature of solvent (Nagy et al., 1998; Weitkamp and Puppe, 1999).
2.6 Carbon dioxide

2.6.1 Origin

Carbon dioxide (CO₂) has been originally discovered by Joseph Black in 1756 where he published his results under the title “Experiments upon Magnesia alba, Quick lime, and some other Alkaline substances” (Marini, 2007). During his studies on “magnesia alba” (4MgCO₃·Mg(OH)₂·4H₂O), Black discovered that an unknown gas was released during the heating process of 4MgCO₃·Mg(OH)₂·4H₂O. He named the product of heating reaction as “magnesia calcinata” (MgO). The gas released during this reaction was called “fixed air “(CO₂) by Black because it was fixed (contained in 4MgCO₃·Mg(OH)₂·4H₂O) in solid form of magnesia. Thus Black is the first person to achieve the production and sequestration of CO₂ (Marini, 2007).

2.6.2 Chemical and Physical properties of CO₂

CO₂ is a chemical compound formed from the combination of two atoms, carbon and oxygen; the two elements are chemically found in the ratio of one to two respectively. At standard temperatures and pressures CO₂ is a gas and its melting point when in the solid state is -78 °C. Above 5.2 bars, CO₂ can be found in liquid form and its triple point is -56.6 °C. Gaseous CO₂ is not particularly reactive; due to the strong covalent bonds between carbon atom and the two atoms of oxygen. It is relatively stable and does not readily break down into simpler compounds. Generally the reactions between the CO₂ molecule and others substances are achieved at either high temperature or pressure mainly by the influence of a catalyst (Topham, 1986). CO₂ gas is colourless, odourless, non-flammable, and heavier than air and has a slight sour taste (acidic) and its molecular size is about 3.4 Å, thus slightly smaller compared to oxygen (O₂) and nitrogen (N₂) molecules of gas, which are respectively 3.5 Å and 3.6 Å. Under high pressure, the density of CO₂ gas can be enhanced approaching or even
Chapter Two

exceeding the density of liquid water. This behaviour of CO$_2$ is an important aspect especially for current CO$_2$ storage technologies (Hongqun et al., 2008).

Of all the constituents of the air, CO$_2$ represents the smallest percentage of about 0.05%, far behind N$_2$ (79%) and O$_2$ (20%). CO$_2$ is the fourth most abundant gas found in the atmosphere and is uniformly distributed over the surface of the earth with a concentration of about 385 ppm (Marquis and Tans, 2008). However the anthropogenic activities such as the combustion of fossil fuels and other carbon containing materials are currently considered to be the main causes of CO$_2$ emissions besides the natural process sources such as the volcanic activity (IPCC, 2003, 2007).

2.6.3 Utilization of CO$_2$

The utilization of CO$_2$ can be summarized in three main pathways which include (Halmann, 1998; Aresta, 2010):

- CO$_2$ as a storage medium for renewable energy,
- CO$_2$ as a feedstock for chemicals,
- CO$_2$ as a solvent or working fluid.

Figure 2.9 below summaries different ways for the utilization of CO$_2$ where it can be applied as raw material for various purposes. CO$_2$ conversion by solar energy into biomass for multiple renewable fuels is currently widely supported by industry and governments worldwide as a means to secure future energy supplies and also to decrease the net CO$_2$ emissions in the atmospheric environment (EIA, 2010).
2.6.4 Impacts of increased CO$_2$ emissions

An increase of greenhouse gases (GHG) in the atmosphere is known to be responsible for the global warming (climate change). The global warming is caused by a build-up of these gases in the atmosphere which are accumulated during anthropogenic activities. In other word, the global warming is the absorption of infrared radiation by atmospheric gases such as CO$_2$ (Mitchell et al., 1989). These GHGs absorb solar radiation that would otherwise be reflected back into space. Thus a high concentration of these GHG, especially CO$_2$, inside the earth’s atmosphere means that more heat is trapped in the neighbourhood of the surface of the earth resulting in a gradual warming or variation of the temperature which is the first and foremost impact of global warming. According to the IPCC (2007), by the year 2100 the atmosphere may contain a CO$_2$ concentration up to 570 ppm translating to an increase of global temperature in the possible range of about 1.1-6.4 °C and an increase in mean sea level of 38 m (Hongqun Yang et al., 2008). Other consequences of the global warming due to
CO₂ increase could also be numerous without intervention (Parry et al., 2007). This includes:

- The direct result of global warming will be further melting of glaciers and snow cover which will result in the availability of water being reduced especially in places where snow-capped mountains are sources of water.

- An increase of atmospheric CO₂ concentrations is known also to cause a rise in ocean acidity. Recent suggestions project that by 2100, the pH of the ocean is likely to fall to about 7.8 which will dramatically impact aquatic life and organisms (IPCC, 2007).

- Effects of global warming will be coupled with an increasing number of weather extremes. Some areas prone to droughts and floods will likely be experiencing an escalation in such drastic events. In addition, there will be development of stronger hurricanes, wildfires and other serious natural calamities which have already started at this present time (IPCC, 2007).

- According to the International Union of Forest Research Organizations (IUFRO) under the report title “Adaptation of Forest and People to Climate Change-A Global Assessment”; forests have been increasingly affected by the climate change. Therefore a high concentration of CO₂ can further induce forest mortality and forests will release higher CO₂ quantities resulting in even warmer temperatures.

- Some mass extinction of many species from the ecosystem in particular those with low capacity to adapt (for example marine life) is predicted. Global warming due to climate change could lead to the presence of some dead zones in the ocean, for instance the depletion of oxygen in the world’s oceans. The IPCC report on “Climate Change Impacts, Adaptation and Vulnerability” suggests 20-30 % of these species are likely to be at high risk of irreversible extinction (IPCC, 2007).
According to IPCC (2007), about 250 million people in Africa will also be exposed to the lack of water due to global warming for the next decades (IPCC, 2007).

2.6.5 Global CO\textsubscript{2} emission trends

Although CO\textsubscript{2} is naturally present in the atmosphere, its concentration has been gradually increasing and, since the industrial revolution the concentration of CO\textsubscript{2} has increased by almost 40 % (Luthi et al., 2008). Global CO\textsubscript{2} emissions in 2010 originated mainly from electricity and heat generation and transport which accounted for about 41 % whereas transport produced 22 % (EIA, 2012). Two-thirds of CO\textsubscript{2} emissions worldwide for 2010 were generated from ten countries (China, USA, Indian, Russian Federation, Japan, Germany, Korea, Canada, Islamic Republic of Iran and the United Kingdom). China and the United States were major contributors with a combined amount of about 12.6 Gt CO\textsubscript{2} emissions in the year 2010, which represents a share of 42 % (24 % and 18 % CO\textsubscript{2} emissions, respectively for China and USA) of the world CO\textsubscript{2} emissions. Over 7 billion tonnes of CO\textsubscript{2} were generated in China in 2010. China is the largest emitter of the BRICS countries, accounting for 24 % of the global emissions. China overtook the USA’s emissions in 2007 as the world’s largest annual emitter of energy-related CO\textsubscript{2} even though in cumulative and per capita terms, the USA remains far larger. It is projected that emissions in China could be more than the 2010 levels, reaching about 40 % by 2035 (IEA, 2012).

CO\textsubscript{2} emissions in India almost tripled from 1990 to 2010 with global average emissions of over 5 %; an annual increase of 3.5 % is expected in India during the period of 2010-2035. Of all BRICS members countries, India had the lowest CO\textsubscript{2} emissions per capita in 2010 (1.4 t CO\textsubscript{2}) which represented one-third of the global average. The Russian Federation is the only country of the BRICS which has seen CO\textsubscript{2} emissions dropping to about 27 % between 1990 and 2010; however its CO\textsubscript{2} emissions grew in 1990 by 2 % and in 2000 by 3 % and 4 % in 2010 due to the
Russian Federation’s strong economic recovery that was stimulated by the increase of energy prices around the world. In 2010 the electricity and heat generation sector represented about 53% of the Russian CO\textsubscript{2} emissions compared to 41% of the global average. The Russian Federation had the highest CO\textsubscript{2} emissions per capita (11.2 t CO\textsubscript{2}) in 2010 compared to all BRICS countries making it slightly above the average of the OECD countries (10.1 tCO\textsubscript{2}) (IEA, 2012). The transport sector was reported to be the second largest source of emissions and represented approximately 25% of the total global CO\textsubscript{2} emissions in 2010. It is highlighted that three-quarters of the emissions from transport were road related. The demand worldwide for transport appears unlikely to decrease in the foreseeable future; according to WEO (2012) it has been projected that transport fuel demand will grow by almost 40% by 2035. In order to limit emissions from this sector, several measures have been taken globally, such as the implementation of policies to encourage and/or require improved vehicles efficiency as the USA and European Union have already done. These policies encourage a move from cars to public transportation in order to lower emissions. The use of trains and buses provide an advanced solution whereas a total zero emission can be achieved by cycling and walking which are the most environmental sustainable alternatives. However, according to Cairns and Newson (2006), transportation by means of aviation is known to be as the most damaging since other GHG emissions such as N\textsubscript{2}O additionally to CO\textsubscript{2} are directly ejected into the upper atmosphere during fuel combustion causing more impacts.

Electricity power generation constitutes the main source of emissions in South Africa and coal is abundantly the main fuel available which makes up over 92% of fuel used in electricity production. The balance is from nuclear power generation, accounting for about 5% and hydroelectric power (1%) and others. The 2000 report of the Department of Environmental Affairs and Tourism (DEAT) showed that the total emissions in South Africa, with land use, land-use
change and forestry (LULUCF) excluded, were about 300915 Gt CO$_2$ (DEAT, 2010). About 70% of this amount was principally associated with energy supply and consumption, with smaller contributions of 12% from industrial processes, 12% from transport and the rest of the amount attributed to minor source of emission such as agriculture and waste treatment (Table 2.6).

Although in South Africa, CO$_2$ emissions per capita remained fairly constant over the last 21 years, South Africa is currently facing one of the major climate change mitigation issues, which is the need for reducing GHG emissions at stationary sources such as the power stations mainly by reducing reliance on coal. Eskom, which is the South African public utility, has targeted the reduction of dependence on conventional coal to about 70% by 2025 and also aims to reduce GHG emissions in absolute terms by 2050 (EIA, 2012). South Africa accounted for 37% of CO$_2$ emissions from fuel combustion across all Africa in 2010, but this amount represented only 1% at global level. About 70% of Africa CO$_2$ emissions originated from the energy sector (EIA, 2012). Thus South Africa may justify and argue about its carbon emissions (GHG) due to the fact that it still an emerging economy and needs to promote its economic growth in order to create employment and reduces poverty; it is also obliged to manage the reality related to its nationwide carbon emissions and global regulations (Eberhard, 2011). Table 2.6 provides a breakdown of energy sector emissions from South African CO$_2$ emissions in 2000 (DEAT, 2010).
Table 2.6: 2000 South African energy sectorial inventory of CO\textsubscript{2} emissions per industry (Gt/a) (DEAT, 2010)

<table>
<thead>
<tr>
<th>Energy</th>
<th>CO\textsubscript{2} amounts (Gt/a)</th>
<th>CO\textsubscript{2} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy industries</td>
<td>212226</td>
<td>70.48</td>
</tr>
<tr>
<td>Manufacturing</td>
<td>38879</td>
<td>12.91</td>
</tr>
<tr>
<td>Transport</td>
<td>38655</td>
<td>12.83</td>
</tr>
<tr>
<td>Commercial/institutional</td>
<td>1902</td>
<td>0.63</td>
</tr>
<tr>
<td>Residential</td>
<td>5547</td>
<td>1.84</td>
</tr>
<tr>
<td>Agriculture/Forestry/Fishing</td>
<td>3706</td>
<td>1.23</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>300915</strong></td>
<td><strong>99.92</strong></td>
</tr>
</tbody>
</table>

As can be seen, energy supply is the largest emissions sector in South Africa and was responsible for about 70\% of CO\textsubscript{2} emissions in 2000. This amount originated from energy industries mainly electricity generation from fuel combustion and the rest originated from manufacturing, transport and other sequestrable and non-sequestrable sources (DEAT, 2010).

2.7 CO\textsubscript{2} separation technologies

Among all the industries emitting CO\textsubscript{2} worldwide, fossil-fuelled power plants generate the largest amount of CO\textsubscript{2} emissions (main stationary point sources of CO\textsubscript{2} emissions) and account for about 30-40\% of the total (Petron et al., 2008). Therefore there is a need for CO\textsubscript{2} to be separated and captured from point sources such as flue gases. Three main techniques are currently employed in order to better improve the capture of CO\textsubscript{2}. This includes: Post-combustion capture for traditional coal-fired power plants; Pre-combustion capture (gasification process) or reforming and Oxy-fuel-combustion (Figueroa et al., 2008). In addition to these three above mentioned processes, chemical-looping combustion (CLC) is an emerging technology which can significantly reduce the separating procedures of CO\textsubscript{2} from gas stream (Hongqun Yang et al., 2008; Sumida et al., 2012).
2.7.1 Post-combustion capture

The post-combustion capture process consists of removing CO₂ from the flue gas that is generated after the combustion of fuel in the air. This is mostly a CO₂/N₂ gas separation owing to the high concentration of N₂ contained in the air which is used for combustion (Figure 2.10). Post-combustion capture technology has been the most utilized to date since its operation system can be readily retrofitted to an existing power plants system. The scrubbing method using mono-ethanol amine (MEA) solution is one of the most well-known techniques used for CO₂ separation from flue gas (Jassim et al.; 2006; Lee et al.; 2008). The equipment sizes (very large due to the flue gas volume) and the low concentration (10-15 %) of CO₂ contained in the flue gas constitute the major disadvantages of the post-combustion capture technique. Additionally, particular measures need to be considered in order to reduce contamination of MEA by impurities such as SOₓ and NOₓ in the flue gas (Engelbrecht et al., 2004).

Figure 2.10: Schematic of post-combustion technology for CO₂ capture and separation (adapted from Sumida et al., 2012).
2.7.2 Pre-combustion capture

In the pre-combustion CO\textsubscript{2} capture process as shown in Figure 2.11, the fuel is decarbonated (pre-gasified with oxygen and steam under high temperature and pressure) prior to combustion. This results in zero CO\textsubscript{2} production during the combustion step. The synthesis gas known as “syngas” produced (mixture of H\textsubscript{2}, CO, CO\textsubscript{2} and H\textsubscript{2}O) is then run through the water gas shift reaction to produce H\textsubscript{2} and CO\textsubscript{2} at high pressure (5-40 bar) and slightly elevated temperature (40 °C). These operational conditions depend with the production plants (Sircar et al., 2000). Pre-combustion CO\textsubscript{2} capture, which also refers to the separation of CO\textsubscript{2} from H\textsubscript{2} within syngas, can be performed in order to obtain pure H\textsubscript{2} that can subsequently be used for coal combustion in power plants for electricity generation. In the pre-combustion technology, the Benfield process can be used for the removal of CO\textsubscript{2}. The Benfield process is described as a reversible chemical reaction and consists mainly of absorbing CO\textsubscript{2} in hot potassium carbonate solution as shown in reaction 2-1.

$$K_2CO_3 + CO_2 + H_2O \rightarrow 2KHCO_3$$

(2-1)

Through the Benfield process, about 30 Mt/a of CO\textsubscript{2} with 90-98 % purity concentrations, are produced at Sasol (Sasolburg and Secunda) (Figueroa et al., 2008). Thus at this high concentration of CO\textsubscript{2} gas, the mixture only needs to be dehydrated and compressed before transportation and injection of CO\textsubscript{2} into geological formations. The use of solid adsorbents in pressure swing adsorption (PSA) based processes, is currently under investigation for more efficient applications. In PSA the high pressure gas mixture is transported through a packed bed of porous adsorbent incorporated into the PSA system and the CO\textsubscript{2} is selectively adsorbed along with other flue gas impurities such as CO from the syngas mixture (Agarwal et al., 2010). In comparison to other technologies, pre-combustion capture offers more advantages, in the way that the gases are
generated at high pressure and the partial pressure of CO$_2$ is also higher compared to post-combustion capture technique.

![Figure 2.11: Schematic of pre-combustion (gasification) CO$_2$ capture process at high pressure, with CO$_2$/H$_2$ separation (adapted from Sumida et al., 2012).](image)

2.7.3 Oxy-fuel combustion

Oxy-fuel combustion refers to the ignition of pulverized coal in an almost pure oxygen environment. Currently this represents a relatively new method for the mitigation of CO$_2$ emissions compared with post-combustion and pre-combustion CO$_2$ capture. The significant advantage of this process is the fact that the flue gas is entirely made of CO$_2$ which considerably simplifies the capture step. Additionally the process employed in this system could be readily retrofitted in the existing power plants. The disadvantage of this process is that an air separation plants is required in order to generate O$_2$. This separation is currently carried out on a scale of over 100 Mt/a but the large energy requirement for this process creates an urgent need for alternative separation methods (Greenwood et al., 2002). A representation of oxy-fuel technology is shown in Figure 2.12 below.
Figure 2.12: Schematic of the oxy-fuel combustion CO\textsubscript{2} capture process at low pressure, O\textsubscript{2}/N\textsubscript{2} separation (adapted from Sumida et al., 2012).

2.8 Characteristic of materials for CO\textsubscript{2} capture

The need for materials that can be used for CO\textsubscript{2} capture has prompted the study of various classes of materials. The development of such materials required the consideration of various performance parameters which have to be tuned depending on the type of CO\textsubscript{2} capture employed and conditions relevant to the plants. Thus investigating and optimizing such parameters, should allow lowering the energy penalty and cost of CO\textsubscript{2} capture enabling extensive implementation of such materials. Amongst others, the selectivity toward CO\textsubscript{2} is the most crucial performance parameter for any CO\textsubscript{2} capture material. A high selectivity is indispensable, such that the CO\textsubscript{2} component of the flue gas is completely removed for subsequent sequestration (Sumida et al., 2012). However the affinity of the material toward CO\textsubscript{2} is also a major consideration for optimizing the energy penalty during the capture process. In fact, if the interaction is too strong, this leads to a high energy requirement for desorption of the captured CO\textsubscript{2}, but weak interactions while also lowering the regeneration cost, will consequently afford lower selectivity of CO\textsubscript{2} over other gases such N\textsubscript{2} in the flue gas mixture. In addition to the above mentioned performances features, a CO\textsubscript{2} capture material should also exhibit a high stability under the conditions such as those relevant to a power plant station for both capture and regeneration.
(adsorption and desorption). Finally, owing to the large amounts of CO$_2$ that need to be captured, the material should also take up CO$_2$ at a high density such that the volume of the material can be minimized (Sumida et al., 2012). In the context of the performances highlighted above some CO$_2$ capture technologies, such as aqueous alkanolamine solutions and porous solids materials are presented in the section 2.9 below.

2.9 CO$_2$ capture and sequestration technologies

Coal combustion for electricity generation is the main stationary source of current anthropogenic CO$_2$ emissions (EIA, 2012) and; post-combustion is the most common technique used in the world (Sumida et al., 2012). Although the post-combustion is commonly used for coal combustion, the composition of the flue gas resulted from this technique differs depending on the type of the coal and the process in which coal is used (electricity or fuels) (Granite et al., 2002). For instance at Eskom power plants in South Africa, the overall composition of the flue gas is essentially made of CO$_2$ as reported by John Keir, (2013) and shown in Table 2.7.

Table 2.7: A typical flue gas composition generated from Eskom power plants in South Africa (John Keir, 2013).

<table>
<thead>
<tr>
<th>Main flue gas</th>
<th>Concentrations (by volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>13 %</td>
</tr>
<tr>
<td></td>
<td>5-8 %</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>6 %</td>
</tr>
<tr>
<td></td>
<td>± 800 ppm</td>
</tr>
<tr>
<td>SO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>± 600 ppm</td>
</tr>
<tr>
<td>NO$_x$ (98 % NO + 2 % NO$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&lt; 100 ppm</td>
</tr>
</tbody>
</table>
CO₂ capture and sequestration via systems such as the post-combustion process remains immature so far despite the existence of various CO₂ capture technologies such as absorption and adsorption (Little et al., 1991, Rochelle, 2009). The former consists of assimilating molecules such as CO₂ throughout a bulk of a solid or liquid whereas the latter technique accumulates molecules at the surface of the adsorbent such as zeolites (Harlick and Tezel, 2004; Chang et al., 2009). These techniques will be described shortly in detail in the following paragraphs.

2.9.1 Absorption

2.9.1.1 Chemical absorption

Among other technologies, the chemical absorption using aqueous alkanolamine solutions has been suggested as the most applicable technology for CO₂ before 2030 (Rochelle, 2009). The chemical absorption process typically consists of an absorber and a stripper in which the absorbent is thermally regenerated after the absorption operation (Bishnoi and Rochelle, 2000). In this technology, the flue gas containing CO₂ enters a packed bed absorber from the bottom and contacts counter currently with a CO₂ lean absorbent. After the absorption, the CO₂ rich absorbent flows into a stripper for thermal regeneration, this is followed by a pumping back of CO₂ lean absorbent to the absorber for cyclic use. Thereafter the CO₂ that is released from the stripper is compressed for the subsequent transportation and sequestration. The temperatures and pressure in the absorber and stripper are generally in the range of 40-60 °C, 120-140 °C respectively and about 1.0 bar pressure during this operation. The minimum energy that is hypothetically required for recovery of CO₂ from flue gas is 0.396 GJ/tonne when working at high pressures (150 bar CO₂ compression). However in a practical operation 0.72 GJ/tonne CO₂ can be possibly achieved (Rochelle, 2009).
The most widely used absorbents in chemical absorption technology for CO$_2$ capture are alkanolamine solutions (Yu et al., 2012). The structures of these absorbents include primary, secondary and tertiary amines containing at least one OH and amine group such as monoethanolamine (MEA), diethanolamine (DEA) and N-methyldiethanolamine (MDEA). The reactivity of these absorbents follows the order: primary, secondary and tertiary amine (reactions constants at 25°C with CO$_2$ are 7,000; 1,200; and 3.5 m$^3$kmol s$^{-1}$, for MEA, DEA and MDEA respectively) (Bishnoi and Rochelle, 2000). The loading capacity for ternary amine is known to be higher (1.0 mole of CO$_2$ per amine) compared to those of primary and secondary (CO$_2$ loading capacity lying between 0.5–1.0 mole per amine) as can be seen in the reactions below:

\[
RR'NH + CO_2 \leftrightarrow RR'NH\cdot COO^- \text{ (zwitterions)} \quad (2-2)
\]
\[
RR'NH + COO^- + RR'NH \leftrightarrow RR'NCOO^- \text{ (Carbamate)} + RR'NH^+ \quad (2-3)
\]

The overall reaction is given as follow:

\[
2RR'NH + CO_2 \leftrightarrow RR'NCOO^- + RR'NH_2^+ \quad (2-4)
\]
\[
RR'NCOO^- + H_2O \leftrightarrow RR'NH + HCO_3^- \quad (2-5)
\]

CO$_2$ reaction with primary and secondary amine form zwitterions firstly and then a carbamate (equations 2-2 and 2-3) while the reaction of the ternary amine with CO$_2$ forms only a bicarbonate and not a carbamate (Xiao et al., 2000). A mixture of amines has been proposed in order to enhance CO$_2$ capture efficiency and also to reduce regeneration cost (Liao and Li, 2002).

2.9.1.2 Physical absorption

The physical absorption is mainly based on Henry’s Law where CO$_2$ is absorbed at high pressure and low temperature, and is desorbed at reduced pressure and increased temperature. Several industrial operations such as natural gas,
synthesis gas and hydrogen production with high concentrations of CO$_2$, have widely used this technology (Olajire, 2010). Current commercial processes employing physical absorption and their respective absorbents include: Selexol process (dimethylether or propylene glycol), Rectisol process (methanol), Purisol process (N-methylpyrrolidone), Morphysorb process (morpholine) and Fluor process (propylene carbonate). The removal of both CO$_2$ and H$_2$S under low temperature and high pressure operations (the absorbent is regenerated by decreasing pressure or stripping) can be achieved using the Selexol process (Olajire, 2010). The Selexol process is known as a low vapour pressure, low toxicity and less corrosive solvent. The Rectisol process is a suitable technique when dealing with the exhausted gas containing sulphur and is a less corrosive solvent and more stable absorbent. The Purisol process is a low energy consumption operation whereas Morphysorb process is still a relatively new process and its operational cost is about 30-40 % lower than in the Selexol process (Gielen, 2003). The most and common drawbacks of the chemical absorption technology that limit its sustained applications mainly include:

- High equipment corrosion rate (degradation of amine, which is the main absorbent, by SO$_2$, NO$_2$ and O$_2$ present in the flue gas).
- High energy consumption for regeneration of absorbents and a large absorber volume required (Haszeldine, 2009).

Thus, considering these drawbacks with liquid phase absorbents, the solid adsorption technology has currently been suggested to overcome the inherent problems met in the chemical absorption (Yu et al., 2012). One of the objectives of this study being to investigate fly ash based zeolites-A for CO$_2$ adsorption, the section below will briefly discuss the solid phase adsorption processes with emphasis on zeolite adsorbents.
Chapter Two

2.9.2 Adsorption

Some aspects of the absorption techniques such as those mentioned earlier in section 2.9 are the main disadvantages and so far limit their utilization. Therefore solid adsorption may be the future and the greener alternative to achieve CO$_2$ capture goals (Sumida et al., 2012). Despite the limited rate of adsorption during the diffusion step of CO$_2$ in the inside of the pore of solid adsorbents such as zeolites; their capacity is about three times higher than the aqueous amine absorption (Khatri et al., 2005). According to Sayari et al., (2011), the development of a new solid material for CO$_2$ capture by the adsorption process should at least satisfy the following criteria:

- Low cost raw material
- Low heat of adsorption
- Fast kinetics
- High CO$_2$ adsorption capacity
- High CO$_2$ selectivity
- Thermal, chemical and mechanical stabilities under extensive cycling operations.

2.9.2.1 Carbon

Carbonaceous adsorbents such as activated carbon have been widely used for CO$_2$ capture (Saha and Deng, 2010). The utilization of activated carbon is principally related to their availability, affordable cost, high thermal stability and low sensitivity to moisture (Plaza et al., 2010). However their application has been shown to be limited for some operations especially when dealing with high pressure gases (Yu et al., 2012). Current studies on carbonaceous materials focus on the improvement of CO$_2$ adsorption capacity and also on the selectivity of these materials mainly through two aspects; the first consists of improving the surface area and pore structure (Cinke et al., 2003; Su et al., 2009) while the
second consists to increase the alkalinity by chemical modification of the surface of the carbon materials (Hsu et al., 2010; Ghosh et al., 2008).

2.9.2.2 Metal organic frameworks

The high surface area, the controllable pore structures and the tuneable pore surface properties which can simply be changed either by metallic clusters or organic ligands have attracted significant interest in current research worldwide for metal organic frameworks (MOFs) (Wang et al., 2008, Millward and Yaghi, 2005). Despite the fact that MOFs have been demonstrated to be promising adsorbents for CO\textsubscript{2} capture at experimental level, more studies however are needed for their practicability for various applications especially at high temperature. This is because MOFs are known to be unstable at higher temperatures (Banerjee et al., 2008; Britt et al., 2009).

2.9.2.3 NaA Zeolite

Materials such as NaA zeolite have been widely reported to be useful for CO\textsubscript{2} separation and sequestration. The adsorption efficiencies of these zeolites are largely imparted by their pore size, charge density and chemical composition of the cation in their porous structures (Wang et al., 2011). NaA zeolite has a Si/Al ratio of 1 and contains Bronsted acid sites (Dedecek et al., 2012). A pseudo cell of NaA zeolite contains 12 Na cations. These Na cations are mainly distributed at three different locations known as sites in the pseudo cell. Among others site I which is the centre of the 6MR, contains 8 Na cations whereas site II (8 MR aperture directly obstructing the entrance) and site III (near the 4 MR inside the large cavity) respectively contain 3 and 1 Na\textsuperscript{+}. It is important to highlight that the unit cell of zeolite-A itself is formed when 8 pseudo cell connect together (see Figure 2.13). The Na cations can be exchanged by other cations, but the cation location varies mainly upon the nature of the cation such as its size and charge (Breck, 1984).
Figure 2.13: A pseudo cell of the framework structure of zeolite A with extra framework cation positions (sites) labelled with Roman numerals (Breck, 1984).

Current investigations on zeolite-A essentially focus on two main fields; firstly on processes altering its composition especially the Si/Al ratio in order to generate zeolites with highly crystalline structure, high surface area and three dimensional pore structures and secondly on the modification of the extra-framework cation generally Na\(^{+}\) using mostly alkali and alkaline earth metals in order to enhance some characteristics such as the affinity, capacity and selectivity for adsorption processes such as CO\(_2\) adsorption (Wang et al., 2011). The adsorptive properties of the extra framework cations depend upon their distribution over the available sites; therefore it is critical to know the position of cation at a particular zeolite site (see Figure 2.13 above). The second field which deals with the modification of the extra-framework cation is generally achieved through either the wet-impregnation or ion-exchange procedure (Breck, 1984). This latter is well known and the most employed method in the case of zeolites; and will be used in this study to exchange Na cations of fly ash based NaA zeolite with alkali and alkaline earth metals.

The ion-exchange in zeolite substitutes the host cation (generally Na\(^{+}\)) with a guest cation such as K\(^{+}\), Li\(^{+}\), Mg\(^{2+}\), and Ca\(^{2+}\) etc. However the mechanism of this process is not straightforward and is fundamentally hard to understand (Breck, 1984). Thus, some authors such as Jeffory et al., (2011) have developed a simple
principle of the ion-exchange by considering two univalent cations (A\textsuperscript{+} and B\textsuperscript{+}) based on simulation approaches. This is shown in the equation below which indicates the ion-exchange in zeolite.

\[(A^+)_\text{zeo} + (B^+)_\text{sol} \rightleftharpoons (A^+)_\text{sol} + (B^+)_\text{zeol} \quad (2-6)\]

In this equation: “zeo” and “sol” respectively represent the ions in the zeolite or in the aqueous solution. Moreover the preference of one cation over the other can be understood using the isotherms (see Figure 2.14) of the ion-exchange as reported by Jeffory et al., (2011).

![Figure 2.14: Cation exchange isotherms (adapted from Jeffory et al., 2011).](image)

In Figure 2.14 above: (X\textsuperscript{B})\text{zeo} and (X\textsuperscript{B})\text{sol} respectively represent the mole fractions of the ingoing cation in the zeolite phase and the ingoing cation in the aqueous solution. Thus isotherm (1) means that both cations A and B are equally preferred; (2) means that the ingoing cation (i.e. B) is preferred and finally (3) means that the outgoing cation (i.e. A) is preferred. In this study, the ion-exchange procedure will be used to exchange the Li\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+} cations with the host Na\textsuperscript{+} contained in a synthesised fly ash based NaA zeolite prior to the CO\textsubscript{2} adsorption study. This will be done to evaluate the intrinsic characteristic of
each cation based on their periodic and group trends such as atomic radius (Figure 2.15) taking into account that this aspect imparts on one hand, the tailoring of the structural framework of zeolite-A (i.e. pore opening); and on the other hand the CO$_2$ adsorption capacity (Bae et al., 2013).

![Figure 2.15: Cation trends in the group and period (adapted from Jensen and William, 2010).](image)

Except for some few limits found in zeolites, such as a low selectivity in gas mixtures when they are applied in flue gases; these materials are known to have the potential of adsorbing molecules with or without permanent dipole moment and also possess other interactions related to selectivity not common to other adsorbents (Nagy et al., 1998). The adsorption profiles of zeolites can be obtained through either temperature programmed desorption (TPD) or Brunauer-Emmett-Teller (BET) method. The adsorption capacity of zeolites is basically enabled by the presence of the large void volume which represents almost 50% of the zeolite volume and where the adsorption process mainly occurs (Weitkamp and Puppe, 1999). Some aspects and features that influence the adsorption of CO$_2$ onto zeolites adsorbents were also reported by Bonenfant and co-workers (2008), and are summarized as follows:
• The strong adsorption of acidic molecules such as CO\(_2\) originates from various electron densities of the framework oxygen which is known as the basic properties of zeolites. The basic strength of these electron densities sites are largely affected by the type of cations. This generally decreases with the electronegativity of the exchangeable cations. For instance the basic strength of zeolites containing Group 1 elements increases as follow: Li\(^+\) < Na\(^+\) < K\(^+\) < Rb\(^+\) < Cs\(^+\).

• The polarizing power of the exchangeable cations, their distribution, size and number altogether influence the local electric field and the polarization of the gas adsorption by zeolites. The polarizing power of the cation is generally inversely proportional to their ionic radius. The interaction between cation and CO\(_2\) component (cation-quadrupole interaction determined through heat of adsorption) is the most essential CO\(_2\) adsorption mechanism in zeolite materials.

• The adsorption capacity and selectivity in polar molecules such as CO\(_2\) are also strongly affected by the Si/Al ratio. The adsorption capacity increases when the Si/Al ratio is decreasing. This property is fundamental and important especially for molecules such as CO\(_2\) possessing high quadrupole moment.

• The capacity and rate of CO\(_2\) adsorption is also influenced by the pore size of the zeolites. The adsorption capacity decreases with the presence of water, by decreasing the strength and heterogeneity of the electric field therefore leading to the formation of bicarbonates through a hydroxyl group formation. In general, the adsorption of molecules such as CO\(_2\) increases with the increase of the pressure but decreases when increasing the temperature (Bonenfant et al., 2008).

Bae et al. (2013) purchased NaA and NaX zeolites as powders from Sigma-Aldrich. These zeolites were treated through ion-exchange technique to generate aluminosilicates zeolites which contained divalent extra-framework cations.
namely Ca\textsuperscript{2+} and Mg\textsuperscript{2+} cations. The ion-exchange was performed using 1:20 solid-liquid ratio at 60 °C for about 15 hrs. The materials were tested for their potential application in post-combustion CO\textsubscript{2} capture. Thereafter CO\textsubscript{2} adsorption was performed on the prepared adsorbents at conditions relevant to a flue gas (0.15 bar and 40 °C) and at 25 °C and 55 °C to generate isotherms. Among other exchanged zeolites (CaX, MgA, MgX) from both NaA and NaX, CaA was found to exhibit exceptional performance characteristics for the capture of CO\textsubscript{2} and demonstrated a highly selective CO\textsubscript{2} uptake of about 5.63 mmol cm\textsuperscript{-3} (or 3.72 mmolg\textsuperscript{-1}) of CO\textsubscript{2} adsorbed. These authors also indicated through the neutron power diffraction experiments that the performance shown by CaA mainly originated from its strong binding interactions with CO\textsubscript{2} molecules at two sites, namely within the 8MR and between two extra-framework cations located in the neighbourhood of the 6MR.

Kyung-Mi and Young-Min (2010) synthesised NaA and NaP1 zeolites through alkaline fusion (NaOH) and hydrothermal treatment using Boryeong (Korean) power plant coal fly ash. The synthesized zeolite materials NaA and NaP1 were then modified with alkali and alkaline earth metals (K\textsuperscript{+}, Li\textsuperscript{+}, Ca\textsuperscript{2+} and Mg\textsuperscript{2+}) through the ion-exchange method. The ion-exchange process involved the dispersion of dry zeolite power of either NaA or NaP1 in 1 M of a salt solution in a ratio of 1:10. This suspension was maintained at about 70 °C for 24 hrs. Thereafter the ion-exchanged zeolites A and P1 forms obtained were applied for the adsorption of a low-level CO\textsubscript{2} (3000 ppm of concentration) at adsorption pressure between 0.2-1.0 atm and at room temperature. These authors found that calcium ion-exchanged samples showed the highest CO\textsubscript{2} adsorption owing to their electrostatic behaviour and acid-base interactions with CO\textsubscript{2} components. The adsorption capacity of CO\textsubscript{2} on the zeolites based samples for either zeolite-P1 or zeolite-A exchanged followed this order: Ca\textsuperscript{2+} > Mg\textsuperscript{2+} > Li\textsuperscript{+} > Na\textsuperscript{+} > K\textsuperscript{+}.

As can be noticed from the review literature, the parameter conditions of the ion-exchange namely the solid to liquid ratio (S/L), temperature, contact time and
the number of exchanges appear to vary from one study to another as illustrated in Table 2.8. This aspect will be explored in this study since one of the objectives seeks to find the optimum conditions of the ion-exchange procedure.

Table 2.8: Some variance in the reported ion-exchange conditions

<table>
<thead>
<tr>
<th>S/L</th>
<th>Temperature</th>
<th>Time</th>
<th>No. of exchanges</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:50</td>
<td>ambient and 90 °C</td>
<td>30 min-days</td>
<td>-</td>
<td>Luhrs et al., (2012)</td>
</tr>
<tr>
<td>1:10</td>
<td>25 °C</td>
<td>3 hrs</td>
<td>9 times</td>
<td>Ackley et al., (1991)</td>
</tr>
<tr>
<td>1:100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Watanabe et al., (2004)</td>
</tr>
</tbody>
</table>

2.10 Other CO₂ sequestration technologies

The most feasible scenario where huge amounts of CO₂ can be stored, is one in which the CO₂ removed from flue gas of power plants as stated in section 2.7, is compressed, injected into an underground containment environment that can facilitate its sequestration without leakage to limit the impact on the surrounding environment. The storage of CO₂ using such geological formations are considered as the most suitable for long term CO₂ storage. Such sites generally include: depleted oil and natural gas wells, shale, coal and saline formations (Benson and Surles, 2006). Saline or brine containing aquifers are known to provide an environment where CO₂ could undergo interaction with minerals such as salts to form carbonates. Several CCS demonstrations and projects are currently in the planning, implementation and operation stages in the world. For example in Kaniov, Poland, about 760 tonnes of CO₂ considered as small scale storage were injected during the 2004-2005 period (Aydin et al., 2010). The largest
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project regarding such storage is the Erdos project in Inner Mongolia, China, where about 3.6 Mt/a of CO₂ is being captured from a CTL fuel plant. This amount is principally used in the enhanced oil recovery (EOR) process. The sequestration of CO₂ in ocean water at depths of about 1000-3000 m is also another option in which CO₂ is suggested to be stored (CO₂ is in the liquid form). It has been demonstrated that up to 1 trillion tonnes of CO₂ could be stored (Metz et al., 2006), and much of CO₂ could be stored on the ocean floor in the form of solid gas hydrates (Klara and Srivastava, 2002).

2.11 Characterization techniques

This section gives a brief overview on the background and principles of selected techniques used in this study for characterization of different materials. This mainly includes, the XRD, FT-IR, SEM, TEM, EDS, XRF and CO₂-TPD.

2.11.1 Powder X-ray Diffraction

X-rays Diffraction (XRD) was discovered in 1895 by William Rontgen and later through others researchers, it was shown that X-rays have the potential to diffract on a crystal such as zeolites if they pass through. X-ray diffraction is a very high energy electromagnetic technique, in which radiations have wavelengths reaching $10^{-10}$ m. These radiations are generated when a metal is bombarded with high energy electrons; as a result, these electrons decelerate and generate a continuous range of wavelengths which are known as Bremsstrahlung radiations. These radiations can collide in sequence by expelling electrons from inner shells as well as electrons of higher energy, which drop into the vacancy and subsequently emit the excess of energy as X-rays (Pecharsky and Zavali, 2005). XRD analysis can be understood by assuming that the lattice planes in a crystal are a mirror. Thus considering the reflection of two parallel rays of the same wavelength by two adjacent planes of the crystal lattice; the reflected rays from the crystal lattice planes will differ in the path length by a distance. The
angle resulting from the incident beam with the crystal lattice plane, away from the normal is known as the glancing angle. Figure 2.16 shows the schematic representation of the glancing angle and then path length difference of the XRD technique. In order to observe a constructive interference, the path length difference should be an integer of the wavelengths. Thus, a reflection would be observed if the glancing angle satisfies the Bragg’s law given as follow (Pecharsky and Zavali, 2005):

\[ n\lambda = 2dsin(\theta) \]  \hspace{1cm} (2-7)  

Where:

- \( n \): is the order of diffraction, and is an integer (\( n=1, 2, \) etc.)
- \( \lambda \): is the wavelength of the X-ray, and moving electrons, protons and neutrons.
- \( d \): is the spacing between the planes in the atomic lattice
- \( \theta \): is the glancing angle or the angle between the incident ray and the scattering planes

Figure 2.16: A schematic representation of the glancing angle and the path length difference in the XRD instrument operating system (Pecharsky and Zavali, 2005).
XRD is an extensively used technique for determining the structure and thus identify mineral phases such as zeolites, or their crystallinity as well as phase purity (Kokotailo et al., 1995). The book known as “Collection of Simulated XRD Powder Patterns of Zeolites” provides information about the space groups and unit cell parameters of zeolites (Treacy and Higgens, 1996, 2001). It is noted that the position and the relative intensities of the powder pattern acts as a fingerprint identifying a particular type of the zeolite. Therefore each type of zeolite has its own specific powder diffraction pattern. Figure 2.17 shows the typical powder diffraction pattern for zeolite-A.

![Figure 2.17: Simulated XRD patterns of zeolite-A (Treacey and Higgins, 2001).](image)

2.11.2 Chemical bonding through Fourier transformed infra-red spectroscopy

Fourier Transform Infra-Red spectroscopy (FT-IR) is one of the characterization techniques widely used in the identification and structural analysis of both organic and inorganic materials. This technique deals with the absorption of electromagnetic radiation in the infra-red region of an electromagnetic spectrum which explores changes based on the vibrational energy levels of the molecule.
The concept of FT-IR is basically illustrated when by analogy one can consider the chemical bond between atoms as a spring or a harmonic oscillator. The only difference in this analogy between chemical bond and spring is that for chemical bonds, the bond between atoms can eventually break when strongly stretched. Table 2.9 shows typical FT-IR vibration bands and their classes based on clinoptilolite zeolite assignments (Breck, 1984) while Figure 2.18 illustrates some of these vibrations in NaA and CaA zeolites (De Pena et al., 2013).

Table 2.9: Typical FT-IR vibration bands based on the assignments from clinoptilolite zeolite (Breck, 1984).

<table>
<thead>
<tr>
<th>Class</th>
<th>Vibrations (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Tetrahedra</td>
<td>Asymmetric stretch (O-T-O) 1250-950</td>
</tr>
<tr>
<td></td>
<td>Symmetric stretch 750-650</td>
</tr>
<tr>
<td></td>
<td>T-O Double Ring 500-420</td>
</tr>
<tr>
<td>External Linkages</td>
<td>T-O Double Ring 650-500</td>
</tr>
<tr>
<td></td>
<td>Pore opening 420-300</td>
</tr>
<tr>
<td></td>
<td>Symmetric stretch 750-820</td>
</tr>
<tr>
<td></td>
<td>Asymmetric stretch 1150-1050</td>
</tr>
<tr>
<td>Additional</td>
<td>H₂O (H-O stretch) 3400 and 1500</td>
</tr>
</tbody>
</table>

Figure 2.18: Typical FT-IR spectra and vibrations of NaA and CaA zeolites (De Pena et al., 2013).
2.11.3 Electron microscopy for morphology

In electron microscopy a beam of electrons is used to create images of the specimen. Electron microscope methods are capable of much higher magnification and have a greater resolution power than light microscopes. Electron microscopes are very useful for identification and analysis of characteristics such as particle size, morphology, pore structure, and also the presence of different phases in a given solid material (Goldstein et al., 2003).

High resolution transmission electron microscopy (HR-TEM) makes use of high voltage electron beam which is emitted by the cathode and formed with the help of magnetic lenses. The electron beam which is transmitted through the specimen carries the information about the structure of the specimen. The spatial variation in the image is magnified with a series of magnetic lenses before it hits the detector. The images produced by this type of electron microscopy are two dimensional images.

High-resolution scanning electron microscopy (HR-SEM) generates images by using and detecting the secondary electrons, emitted from the surface due to the excitation by the primary electron beam. SEM consists of an electron beam which is scanned across the surface of the sample and then detected by the detector. In contrast with TEM, SEM provides three dimensional images giving information regarding the topological and morphological details of the samples (Goldstein et al., 2003). Figure 2.19 shows a typical SEM image (A) and TEM image (B) obtained from zeolite-A crystal analysis.
Figure 2.19: Typical SEM (A) and TEM (B) micrographs obtained from zeolite-A crystal (Hashemian et al., 2013).

The preparation of the sample in SEM includes its drying at about 100 °C in an oven followed by the coating with carbon in order to make it conductive to electricity if the specimen did not have that characteristic. SEM technique as mentioned above is capable of analysing the external structure in the range of objects which comprise biological specimens, ceramic, metals, rocks and other specimens which can be detected via light microscopy. The carbon coating consists generally of a physical vapour deposition process in which plasma is produced by ionizing at low pressure in an inert gas environment such as argon with carbon or noble metal such as gold, silver, platinum, and palladium. Thus the heavier the metal the greater the secondary electron yields will be and this is important because it makes imaging very much easier (Goldstein et al., 2003).

2.11.4 Elemental composition using X-Ray fluorescence spectroscopy

The X-ray Fluorescence Spectroscopy (XRF) technique allows the identification of the elemental composition. XRF operates through radiation of the sample under high energy X-rays. The radiations cause electrons from different atoms in the sample to be expelled. Thereafter an electron from upper orbital drops down to the lower hole, and a certain quantity of energy is released and results in the
generation of radiation commonly known as X-rays fluorescence. The XRF technique can be utilized for both quantitative and qualitative elemental characterization since its radiations are capable of emitting atoms (Bekkum et al., 1991).

2.11.5 Temperature programmed desorption

The temperature-programmed desorption (TPD) technique is used when determining the kinetic and thermodynamic parameters of desorption processes or the decomposition reactions. The TPD technique basically involves principles of physisorption and chemisorption as well as heat of adsorption. In the TPD tests, the adsorbent such as a zeolite is generally saturated by an adsorbate such as CO$_2$ molecules then heated at constant rate to allow physically and chemically adsorbed molecules to be desorbed (Serrano et al., 2007). This technique is currently one of the methods used to measure both the acidity and the basicity of zeolites in the presence of either acidic (e.g., CO$_2$) or basic (NH$_3$) adsorbate (Schroeder and Gottfried, 2002). A typical TPD experiment generally operates in sequence of four steps which include:

**Step 1: Preparation of the adsorbent**

The sample has to be preheated for the removal of adsorbed water and other volatiles molecules. For instance the zeolite sample is heated in helium flow atmosphere to about 400 °C. A heating rate of about 5-10 °C/min is required and depends upon the sample analyzed.

**Step 2: Adsorption process**

After the pre-treatment process, the sample equilibrates at a specific temperature of adsorption. Then the furnace switches automatically or/and manually from the inert gas (e.g.: He) used for purge to the one containing the adsorbate gas (e.g.: CO$_2$).
Step 3: Desorption of the adsorbate

Once the adsorbent reaches saturation the furnace purge has to be switched back to an inert atmosphere in order to remove the amount of extra adsorbate gas which was not adsorbed.

Step 4: Temperature programmed desorption

After desorption of the physisorbed molecules (adsorbate) is complete, the temperature is increased in order to remove the remaining adsorbate molecules. In general a heating rate of 10 °C/min to a maximum temperature of 600 °C is used. For materials such as acidic zeolites, at least two regions of weight loss are observed during this process. At lower temperature desorption, the initial mass loss is attributed to the desorption process from weakly acid or basic sites and the mass loss at higher temperature can be attributed to desorption from strongly acidic or basic sites (Pereira and Gorte, 1992).

2.12 Summary of the literature

The literature review has provided important and interesting information about coal and coal combustion by products such as CO₂ emissions and fly ash which are of major concern in terms of environmental pollution. Various ways are undertaken to manage CO₂ and fly ash in the world and particularly in South Africa which is a coal energy reliant country. Therefore there is a need to prepare materials such as fly ash based zeolite adsorbents which could be applied in power stations for CO₂ sequestration and storage. This is important, on one hand to reduce emissions and on the other to recycle fly ash into useful material. Both the availability and the low cost of fly ash feedstock as source of Si and Al instead of high grade chemicals for the synthesis of zeolite-A has laid the foundation of this study which aims to modify the fly ash based NaA zeolite through ion-exchange. The modified fly ash based zeolite-A will be tested for CO₂ adsorption. This will consist to identify whether CO₂ adsorption onto these
Chapter Two

materials is a chemisorption or physisorption process. According to Breck, (1984) the ion-exchange in zeolite is hard to understand and not a straightforward process. Thus, one of the objectives of this study is also to determine whether optimizing the parameters applied in the ion-exchange process could improve the capacity of zeolite for CO$_2$ adsorption or whether the CO$_2$ adsorption capacity is mainly a function of the type of cation instead of applied parameters during the ion-exchange procedure (contact time, temperature and multiple exchanges).

In chapter three below, all the materials and experimental techniques used in this thesis are laid out in detail.
3. EXPERIMENTAL

3.1 Introduction

The present chapter gives a detailed description of materials and chemicals used in the study. The experimental procedures, equipment set ups and characterization techniques used in the present study are also detailed and a schematic design is given in this chapter. The skeleton diagram that was followed in this research in order to achieve the objectives suggested in section 1.8 starting from South African coal fly ash feedstock to the CO$_2$ adsorption study is shown in Figure 3.1.

3.2 Feedstock

Coal fly ash that was used in the present thesis was selected based on investigations previously conducted at the University of the Western Cape (Musyoka, 2012). Therefore fly ash from Arnot power plants located in the province of Mpumalanga in South Africa was used as feedstock in the synthesis of zeolite NaA in this study. The fly ash samples were collected from the hoppers below the electrostatic precipitators (ESPs) then mixed for homogeneity. Afterwards the samples were stored in sealed containers and placed in a dark environment away from variable temperature to preserve their compositional integrity prior to the synthesis of zeolite NaA. This last treatment was basically accomplished knowing that upon atmospheric exposure, some mineral assemblies present in fly ash that initially formed during coal combustion process at high temperatures, can be altered by atmospheric contact over time and may show significant changes in the overall mineral composition of the initial fly ash (Sonqishe, 2008).
South African coal fly ash

Hydrothermal Synthesis of zeolite NaA

Characterization through XRD, XRF, FTIR, SEM, TEM

Fly ash based zeolite NaA

Ion-exchange at 30°C For 1 hr, 4 hrs and 8 hrs with Li⁺, Ca²⁺, Mg²⁺ (1, 2 and 3 exchanges)

Ion-exchanged Li, Ca, Mg based zeolites-A

Characterization through XRD, FTIR, SEM, TEM, EDS, ICP

CO₂ adsorption Study through TPD

Ion-exchange at 60°C For 1 hr, 4 hrs and 8 hrs with Li⁺, Ca²⁺, Mg²⁺ (1, 2 and 3 exchanges)

Ion-exchanged Li, Ca, Mg based zeolites-
Figure 3.1: A schematic diagram of the experimental approach for each step followed to accomplish the goal of the study, starting from fly ash characterization to CO\textsubscript{2} adsorption study.

### 3.3 Reagents

Table 3.1 gives all chemical reagents that have been used during this study, starting with the synthesis of coal fly ash NaA zeolite and other experiments.

Table 3.1: Reagents used for experiments in this study

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Suppliers</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrite</td>
<td>Kimix</td>
<td>99.00</td>
</tr>
<tr>
<td>Boric acid</td>
<td>Kimix</td>
<td>61.40</td>
</tr>
<tr>
<td>Calcium chloride dehydrate</td>
<td>Merck</td>
<td>99.00</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>Kimix</td>
<td>Min 55.00</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Kimix</td>
<td>Min 65.00</td>
</tr>
<tr>
<td>Lithium chloride anhydride</td>
<td>Merck</td>
<td>99.00</td>
</tr>
<tr>
<td>Magnesium chloride hexahydrate</td>
<td>Merck</td>
<td>99.10</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Merck</td>
<td>99.80</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>Riedel-de Haën</td>
<td>Min 54.00</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>Kimix</td>
<td>99.00</td>
</tr>
</tbody>
</table>

### 3.4 Gases

**Carbon dioxide (CO\textsubscript{2})**

The CO\textsubscript{2} used was of instrument grade (99.9999 % purity) and was used for adsorption experiments which were carried out through temperature
programmed desorption. CO₂ was supplied by Afrox and the properties are presented in Table 3.2 below:

Table 3.2: Some properties of carbon dioxide used

<table>
<thead>
<tr>
<th>Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical temperature</td>
<td>31 °C</td>
</tr>
<tr>
<td>Density (20 °C)</td>
<td>1.977 kg/m³</td>
</tr>
<tr>
<td>Flammability</td>
<td>Non-combustible</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>44.011 g/mol</td>
</tr>
<tr>
<td>Specific volume (20 °C)</td>
<td>5471 m³/kg</td>
</tr>
</tbody>
</table>

**Helium (He)**

Helium was of technical grade (99% purity) and was used as carrier gas during the adsorption experiments. The gas was obtained from Afrox and its properties are presented in Table 3.3 below:

Table 3.3: Some properties of helium used

<table>
<thead>
<tr>
<th>Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point (20 °C)</td>
<td>-268.9 °C</td>
</tr>
<tr>
<td>Density (20 °C)</td>
<td>0.166 kg/m³</td>
</tr>
<tr>
<td>Flammability</td>
<td>Non-combustible</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>4.003 g/mol</td>
</tr>
<tr>
<td>Specific volume (20 °C)</td>
<td>6.024 m³/kg</td>
</tr>
</tbody>
</table>

### 3.5 Equipment

Figure 3.2 below shows some of the instruments that were used in this study. The stirrer (A) and the oven (B) were mainly used during the synthesis process while the water baths (C) and the Micromeritics AutoChem II 2920 (D) set-ups were
respectively used during the ion-exchange process and CO$_2$ adsorption through TPD.

![Figure 3.2: Some instruments used in this study, starting from coal fly ash treatments (A: stirrer), the hydrothermal synthesis process of fly ash based zeolites NaA in PP bottles 350 mL (B: hot air Oven EcoTherm, Labotech), the ion-exchange process (C: Water bath) and CO$_2$-TPD (D: AutoChem II 2920).]

**3.6 Synthesis of fly ash NaA zeolite**

South African Arnot fly ash feedstock was mixed with sodium hydroxide (NaOH (99 % purity either pellets or pearls/beads) in the ratio of 1:1.2 respectively (100 g
NaOH/ 120 g Fly ash). In order to accomplish a perfect homogeneity of both fly ash and NaOH, the mixture was thoroughly shaken and ground for about 5 min. Thereafter, approximately 100 g of the resultant mixture was placed into a 125 mL porcelain container and then fused at a temperature of 550 °C in a furnace for 1.5 hours.

The collected fused sample was then crushed prior to stirring process in the presence of deionised water (see Figure 3.2: A above). The crushed ash was mixed with deionised water in a solid to liquid ratio of 2:10. This means in each case 20 g of the fused sample was weighed and added to 100 mL of deionised water. The obtained liquid mixture was stirred at room temperature for 2 hrs at about 600 rpm. After the stirring operation, the liquid mixture was filtered using a 125 mm filter paper. The solid residue recovered by filtration was considered as a waste while the filtrate was used for synthesis (clear solution). Hence 50 mL of the filtrate (clear solution of yellowish aspect as shown in Figure 3.4: A) collected after filtration was added to 20 mL of sodium aluminate (NaAlO\(_2\)) which was prepared as shortly described in section 3.7. The mixture of the measured 50 mL of the filtrate and 20 mL of NaAlO\(_2\) was transferred into 250 mL polypropylene (PP) bottles (see Figure 3.4: A below) and then placed in an oven at a temperature of 100 °C for 3 hrs for hydrothermal crystallization (synthesis) of NaA zeolite, and finally the PP bottle containing the mixture (see Figure 3.4: B below) was allowed to cool down for about 30 minutes and then filtered using 125 mm filter paper. The collected solid sample (zeolite) was thoroughly washed until reaching pH of 9-10 which was determined using MARTINI pH instruments (Mi) 150. Once the washing was done the collected solid product sample was placed onto an evaporating dish and dried overnight at 100 °C in a hot air oven. Figure 3.3 summarises the experimental procedure of the hydrothermal synthesis of fly ash based NaA zeolite followed in this study whereas Figure 3.4 shows the extracted solution (A) before the hydrothermal synthesis and after synthesis (B).
Figure 3.3: Flow chart illustrating the experimental procedure for hydrothermal synthesis of fly ash based NaA zeolite.
3.7 Preparation of sodium aluminate

38.4 g of sodium aluminate (NaAlO$_2$, 54 % purity) was weighed (in a 250 mL beaker) and mixed with 19.2 g of sodium hydroxide (NaOH, 99 % purity). Approximately 200 mL of deionised water was poured into a 500 mL flask. Thereafter the solid mixture of NaAlO$_2$ and NaOH was transferred into the 500 mL volumetric flask; a magnetic bar was also placed inside the flask prior to stirring process. The volumetric flask was finally placed on a magnetic plate and the mixture was stirred for about 30-45 minutes at 300 rpm. Once the total dissolution of the solid was achieved, the flask was removed from the magnetic plate and was topped up to the mark with deionised water and kept in cool conditions.

3.8 Ion-exchange experiment

The cations used in this study were selected as discussed in section 2.9.2.3 of chapter two. Hence 0.1 g of the synthesised zeolite NaA sample was dispersed in 10 mL of aqueous 1 M salt solutions of either CaCl$_2$.2H$_2$O or MgCl$_2$.6H$_2$O or LiCl
in a solid to liquid (S/L) ratio of 0.1:10. In each case the mixture was subjected to an ion-exchange process at either 30 °C or 60 °C for 1 hr or 4 hrs or 8 hrs as set out in Table 3.4 below. After each ion-exchange procedure the solid sample was gravimetrically collected through centrifugation and the ion-exchange procedure was repeated twice or three times with a fresh salt solution depending on each case. In each case the final product after the ion-exchange was washed 5 times with 40 mL of deionised water and dried at 80 °C in a hot air oven. The degree of ion exchange achieved was estimated by EDS for elemental analysis. Table 3.4 gives the experimental set-up conditions that were used during the systematic ion-exchange experiment and the sample numbering codes.

Table 3.4: Experimental set-up conditions employed during systematic ion-exchange process.

<table>
<thead>
<tr>
<th>Run (x3)</th>
<th>Cations</th>
<th>Contact time (Hrs)</th>
<th>No of contacts</th>
<th>Temperature (°C)</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li⁺, Ca²⁺, or Mg²⁺</td>
<td>1</td>
<td>1, 2, 3</td>
<td>30, 60</td>
<td>Mxyz</td>
</tr>
<tr>
<td>2</td>
<td>Li⁺, Ca²⁺, or Mg²⁺</td>
<td>4</td>
<td>1, 2, 3</td>
<td>30, 60</td>
<td>Mxyz</td>
</tr>
<tr>
<td>3</td>
<td>Li⁺, Ca²⁺, or Mg²⁺</td>
<td>8</td>
<td>1, 2, 3</td>
<td>30, 60</td>
<td>Mxyz</td>
</tr>
</tbody>
</table>

Note: For sample code Mxyz: M represents the cation exchanged (Li⁺, Ca²⁺ or Mg²⁺) whereas x, y and z are respectively the contact time, number of exchanges and temperature (in the case of the temperature: 30 °C=3 and 60 °C=6). For instance Li123, in this thesis, means: LiA zeolite obtained at 1 hr after 2 consecutive exchanges at 30 °C.
3.9 Preparation of salt solutions

All salt solutions that have been used during the ion-exchange procedure were chloride based due to their high solubility in water compared to other salts. The preparation of each single solution containing either a divalent or monovalent earth metal was achieved based on the following empirical equation 3-1:

\[ M = \frac{m(g)}{M_w \times V(L)} \]  

(3-1)

Where:

- \( M \): The concentration of the solution (moles)
- \( m \): The mass of the sample weighed (grams)
- \( M_w \): The molecular weight of each salt (g/moles)
- \( V \): The volume of the solution measured (litre)

The \( M_w \) of each respective salt compound was calculated based upon their respective empirical formula of \( \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \) (99 % purity), \( \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \) (99 % purity) and \( \text{LiCl} \) (99 %). The volumetric flask used was 500 mL and the concentration of 1M was used for each salt. After the calculation of the mass of each compound, the calculated amount was weighed; thereafter it was transferred into a volumetric flask through a funnel. Afterwards approximately 300 mL of ultrapure water was added into the volumetric flask, the resulting mixture was shaken until achieving total dissolution of the solid salt and then the volume of water in the flask was topped up to the 500 mL mark and kept in cool conditions.
Chapter Three

3.10 Characterization techniques

3.10.1 Fourier Transformed Infra-Red spectroscopy

Fourier Transformed Infra-Red (FT-IR) required minimal sample preparation and only a small amount of sample. Prior to FT-IR analysis, a background was first run on the instrument. Thereafter a small amount of each zeolite sample was placed on the crystal of an attenuated total reflectance (ATR) where a certain Gauge force was applied. The set-up parameters are laid out in Table 3.5 below.

Table 3.5: FT-IR set-ups main parameters

<table>
<thead>
<tr>
<th>Instrument Model</th>
<th>PerkinElmer UATR Two</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauge force</td>
<td>140</td>
</tr>
<tr>
<td>Number of scans</td>
<td>5</td>
</tr>
<tr>
<td>Resolution</td>
<td>4 cm⁻¹</td>
</tr>
<tr>
<td>Scan range</td>
<td>4000-400 cm⁻¹</td>
</tr>
</tbody>
</table>

3.10.2 X-ray Diffraction analysis

X-ray Diffraction (XRD) for qualitative analysis of fly ash feedstock and zeolites-A samples was carried out on a wide angle instrument. The set-up parameters of the instrument are given in Table 3.6.

3.10.2.1 Sample preparation

The XRD technique presents little sample preparation prior to analysis. In this study the fly ash feedstock and its based zeolite samples in ground powder form were thoroughly packed onto the sample holder using a spatula. Thereafter the
surface of the powdered sample was rendered smooth or flat, and the sample holder was placed in the X-ray diffractometer for analysis.

### 3.10.2.2 Instrument set-up conditions

The XRD instrument set-up parameters that were used during mineral analysis experiment are tabulated as followed:

Table 3.6: XRD set-up parameters during mineral analysis of fly ash based zeolites.

<table>
<thead>
<tr>
<th>Instrument Model</th>
<th>PW3830 X-ray generator(PANalytical)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radiation</strong></td>
<td>Cu-Kα</td>
</tr>
<tr>
<td><strong>Wavelength</strong></td>
<td>λ =1.54056</td>
</tr>
<tr>
<td><strong>Generator current</strong></td>
<td>25 mA</td>
</tr>
<tr>
<td><strong>Voltage</strong></td>
<td>40 kV</td>
</tr>
<tr>
<td><strong>Scan type</strong></td>
<td>Continuous</td>
</tr>
<tr>
<td><strong>First angle</strong></td>
<td>3.015</td>
</tr>
<tr>
<td><strong>Scan range</strong></td>
<td>60°</td>
</tr>
<tr>
<td><strong>Step-width</strong></td>
<td>0.03°</td>
</tr>
<tr>
<td><strong>Time per step</strong></td>
<td>0.50</td>
</tr>
</tbody>
</table>

### 3.10.3 Scanning electron microscopy analysis

The scanning electron microscopy (SEM) analysis of fly ash feedstock and zeolite products was carried out on ZEISS AURIGA for morphological imaging.

#### 3.10.3.1 Sample preparation

Zeolite samples were prepared prior to SEM analysis by sprinkling a small amount of powder onto an aluminium stub covered with double-sided sticky carbon discs. The samples were coated using carbon evaporated by either electric
arc method or by metal heating method using an EmiTech K950X coater. After the pre-treatment process, the samples were then imaged. A similar sample pre-treatment was also used on the same instrument for electron dispersive x-ray spectroscopy (EDS) coupled to HR-SEM. The EDS analysis was employed for elemental analyses. The EDS data were collected from six spot analyses on the zeolite specimen in duplicate and average values were used to evaluate the percentage of exchange for each cation exchanged in this study. The instrumental conditions of HR-SEM-EDS coupled are presented in Table 3.7.

Table 3.7: HR-SEM instrumental set-up conditions

<table>
<thead>
<tr>
<th>Instrument Model</th>
<th>ZEISS AURIGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accelerating voltage</td>
<td>5.00 kV</td>
</tr>
<tr>
<td>Magnification</td>
<td>5.00-100 kX</td>
</tr>
<tr>
<td>Signal A</td>
<td>inLens</td>
</tr>
<tr>
<td>Resolution</td>
<td>High</td>
</tr>
<tr>
<td>Imaging particle size</td>
<td>1 µm-200 nm</td>
</tr>
<tr>
<td>Working distance (WD)</td>
<td>3.5-6.5 mm</td>
</tr>
<tr>
<td>Exposure time</td>
<td>2-5 minutes</td>
</tr>
</tbody>
</table>

3.10.4 Transmission electron microscopy

The transmission electron microscopy (TEM) analysis of fly ash feedstock and zeolite products was performed using TecnaiG²F20 X-Twin MAT instrument for surface mapping and crystallinity.

3.10.4.1 Sample preparation

Prior to TEM imaging analysis, the sample was firstly subjected to specific treatment. A small amount of powdered zeolite sample was diluted in 5 mL of
methanol, the resulting mixture was thoroughly shaken for about 10 seconds and then the sample container was treated under ultrasonic mixing for about 5 minutes. Thereafter one drop of the suspension was deposited on a copper grid and let dry under STP conditions. Table 3.8 gives the main parameters used during TEM analysis.

Table 3.8: TEM experimental set-up conditions

<table>
<thead>
<tr>
<th>Instrument Model</th>
<th>TecnaiG²F20 X-Twin MAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>48 µA</td>
</tr>
<tr>
<td>Operating voltage</td>
<td>200 kV</td>
</tr>
<tr>
<td>Illumination angle</td>
<td>15°</td>
</tr>
</tbody>
</table>

3.10.5 Temperature programmed desorption

The temperature programmed desorption of CO₂ (CO₂-TPD) profiles were carried out using AutoChem II 2920 (Micromeritics) for the parent NaA zeolite and the most exchanged zeolites for each cation investigated (see PART C of Chapter four).

3.10.5.1 Sample preparation and instrument set-ups

100 mg of zeolite powder was weighed. The sample was placed in a clean U-tube sample holder. Thereafter the U-tube containing the zeolite sample was placed in the furnace, for both pre-treatment and adsorption process. Prior to CO₂-TPD adsorption, zeolite was degassed in Helium at 300 °C (ramping rate 10 °C/min and He flow rate 20 mL/min). After the degassing period the sample was allowed to cool down to 40 °C under a flow of dry He and then CO₂-TPD adsorption experiments were commenced at a holding temperature of 40 °C in helium (He flow rate of 20 mL/min and 10 mL/min for CO₂).
Instrument grade CO$_2$ (99.999 \%) was allowed to pass over the sample for 2 hrs (chosen saturation time) at 40 °C to achieve the CO$_2$ adsorption process onto fly ash based zeolite-A. After CO$_2$ saturation, dry He carrier gas was allowed to flow once more through the sample cell in order to flush out the excess CO$_2$ for a period of 2 hrs. Following the flush out, the thermal conductivity detector (TCD) was turned ON; it was allowed to stabilize and then zeroed. Finally CO$_2$ desorption was performed under helium flow at 20 mL/min. At the same time the sample was heated at a temperature of 5 °C/min from 40 °C to 700 °C. The desorbed amounts of CO$_2$ were detected using a TCD signal through a PC to determine the relative amount of CO$_2$ desorbed at each desorption temperature.

3.10.6 X-ray fluorescence spectroscopy

The X-ray fluorescence spectroscopy (XRF) was used in this study mainly to determine the elemental composition of Arnot feedstock ash before the synthesis. 9 g of fly ash was mixed with approximately 1 g of the binder (wax). The resulting mixture was thoroughly ground and placed in a mould, thereafter it was pelletized under high pressure. The Loss of ignition (LOI) was carried out in a furnace (conditions). Table 3.9 gives the set-ups conditions of the XRF instrument.

Table 3.9: XRF instrument set-up conditions

<table>
<thead>
<tr>
<th>Instrument Model</th>
<th>Philips PW 1480</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal analysers (x 5)</td>
<td>LIF 200, LIF 220, GE, PE, PX</td>
</tr>
<tr>
<td>Current</td>
<td>50 mA</td>
</tr>
<tr>
<td>Voltage</td>
<td>40 kV</td>
</tr>
<tr>
<td>Spectrometer tube</td>
<td>Chromium</td>
</tr>
</tbody>
</table>
CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Introduction

The present chapter discusses the results obtained from various techniques used to characterize the materials, starting from the feedstock fly ash from Arnot coal power plant in South Africa to the synthesised NaA zeolite and its ion-exchanged LiA, CaA and MgA forms. The main characterization techniques used included: the X-ray fluorescence spectroscopy (XRF) for elemental composition, X-ray diffraction (XRD) analysis for identification of mineral phases. The XRD analysis was supported with FT-IR analysis for the same purpose by also monitoring the structural modification of all materials prepared in this study, especially after the ion-exchange process with Li$^+$, Ca$^{2+}$ and Mg$^{2+}$ cations. Temperature programmed desorption (TPD) was used for CO$_2$ adsorption onto fly ash based zeolites. In addition to the mentioned techniques; high-resolution transmission electron microscopy (HR-TEM) for surface mapping and crystallinity, and high-resolution scanning electron microscopy (HR-SEM) was used for morphological structure determination. The energy dispersive spectroscopy (EDS) was used for semi-quantitative compositional analysis. This chapter is divided in three parts; part A deals with the results obtained from the synthesis whereas parts B and C respectively discussed the results obtained after the ion-exchange and the CO$_2$ adsorption.
PART A: SYNTHESIS

4.2 Fly ash NaA zeolite

This section reports the characteristics of the feedstock fly ash and NaA zeolite products prepared as set out in section 3.6 of Chapter three.

4.2.1 Elemental composition through X-ray fluorescence spectroscopy

The elemental composition of oxides contained in fly ash feedstock prior to the synthesis of zeolite is crucial. Therefore X-ray fluorescence spectroscopy (XRF) analysis was carried out and the set-up parameters of the analysis were described in section 3.9.6. Table 4.1 presents the results of a triplicate average elemental analysis of the major oxides found in South African Arnot fly ash which was used as feedstock for synthesis of NaA zeolite.

Table 4.1: XRF of major elements analysis of South African Arnot fly ash (n=3).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Mass (%)</th>
<th>Std deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>50.92</td>
<td>0.17</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>27.46</td>
<td>0.14</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>5.69</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>5.31</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>1.63</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>1.53</td>
<td>0.01</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>0.51</td>
<td>0.01</td>
</tr>
<tr>
<td>P(_2)O(_3)</td>
<td>0.34</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr(_2)O(_3)</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>0.19</td>
<td>0.01</td>
</tr>
<tr>
<td>LOI</td>
<td>6.85</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>100.56</td>
<td>0.01</td>
</tr>
<tr>
<td>SiO(_2)/Al(_2)O(_3)</td>
<td>1.85</td>
<td>0.01</td>
</tr>
</tbody>
</table>
The summation technique of the major oxides namely: SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ as recommended by the ASTM (1994) permits the classification of fly ash as class F or C as was mentioned in section 2.4.3. As can be seen in Table 4.1 the sum of SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ was found to be over the value of 70 % in weight. This indicated that the Arnot fly ash was “class F” ash. Similar elemental composition of these oxides in Arnot fly ash was also reported by Musyoka (2009). In addition, Gitari et al., (2006) also reported that such composition reflects class F ash generated from the combustion of bituminous coal in South Africa. The SiO$_2$/Al$_2$O$_3$ ratio of Arnot fly ash was 1.85. This ratio was found to be suitable and crucial for the synthesis of low silica fly ash NaA zeolite in terms of the Si/Al ratio which determines the structural configuration of the tetraedra in the framework of the zeolite material (Querol et al., 2002). The other oxides such as CaO and MgO in fly ash are also of importance since their respective cations play the role of competing cations during the process of zeolite synthesis when fly ash is the feedstock (Musyoka, 2012). The Loss-Of-Ignition (LOI) is an important parameter in the synthesis of fly ash based zeolite because it can determine the quality of the zeolite produced and was found to be 6.85 % weight in Arnot fly ash. This indicated a fairly high proportion of unburnt carbon which remained in the ash.

4.2.2 Morphology of fly ash

The morphological structure study of the fly ash feedstock and the fly ash NaA zeolite were achieved using high resolution scanning electron microscopy (HR-SEM) and high resolution transmission electron microscopy (HR-TEM). These techniques respectively permitted determination of the external and internal structural morphologies (shape, pores etc.) The operating conditions and procedure for both instruments were described in sections 3.9.3 and 3.9.4 of Chapter three.
4.2.2.1 Scanning electron microscopy

Figure 4.1 shows comparative HR-SEM micrograph images of fly ash as received (A) and the fused ash (B) at 550 °C before the synthesis of NaA zeolite.

Figure 4.1: Comparative SEM micrograph images of fly ash as received (A) and fused ash (B) at 550 °C before the synthesis of NaA zeolite.

The SEM micrographs of fly ash (FA) as received and those for the fused ash (NaOH+FA) at 550°C are shown in Figure 4.1 above. The observation of these micrographs revealed that the fly ash as received (A) was more spherically shaped with smooth surfaces compared to the agglomerated fused ash (B). Such morphological changes are as a result of alkaline dissolution of fly ash as produced through fusion (Jin et al., 1999). This dissolution of fly ash resulted in a new mineral phase in the fused materials as will be shown by XRD in section 4.2.3. Figure 4.2 below gives the HR-SEM images and particles sizes of fly ash NaA zeolite prepared from the fused FA after an additional hydrothermal step as set out in section 3.5.
The SEM micrographs of fly ash NaA zeolite (A) and their relative particles size (B) are shown in Figure 4.2. As can be noticed the micrographs revealed crystalline chamfered cube particles which ranged between 1-2 µm of sizes. These chamfered cube shapes were also reported by Musyoka et al., 2012 and were attributed to the typical morphology of zeolite-A. Similar morphologies and shapes of the zeolite-A were also reported in the literature by several authors such as Kyung and Young, (2010).

4.2.2.2 Transmission electron microscopy

The high resolution transmission microscopy (HR-TEM) was used to assess the atomic structure and porous arrangement of fly ash NaA zeolite obtained after the synthesis. Figure 4.3 shows the HR-TEM images of regular Angstrom pore channels of crystals from fly ash NaA zeolite.
Figure 4.3: TEM images of crystals of fly ash NaA zeolite, showing the regular Angstrom scale pore channels at 5 nm (A) and 2 nm (B).

As can be seen from Figure 4.3 (B) measured at 5 nm, the HR-TEM analysis of the surface of a crystal of the synthesised NaA zeolite revealed the regular arrangement of atoms on which the crystal is built. This is demonstrated by the appearance of the regular crystal lattice array of a zeolite crystalline material which is entirely made up of angstrom sized unit cells. These ordered and aligned lattices characterise an ordered crystalline porous material (Davis, 2002). Additionally the HR-TEM analysis revealed that the regular pores and pore walls of the synthesized NaA zeolite were spaced regularly between 0.2-0.85 nm (Figure 4.3: A).

4.2.3 Mineral phases study through X-ray diffraction spectroscopy

Comparative X-ray diffraction patterns of the feedstock ash, fused ash and the synthesised NaA zeolite are shown in Figure 4.4. The operating conditions of the instrument and the procedure were briefly described in section 3.9.2. The analysis was performed by wide angle XRD in the region between 2θ peaks 5- 60° which is the common range for zeolite mineral phase identifications. Figure 4.4
shows a wide angle XRD comparison of major mineral contained in fly ash (FA), fused fly ash (FFA) and fly ash based zeolite (NaA).

Figure 4.4: Wide angle XRD comparison of fly ash (FA), fused fly ash (FFA) and fly ash based zeolite (NaA) and their major respective mineral phases contained. A: zeolite; M: Mullite; Q: Quartz; H: Hematite; SS: Sodium-Silicate and SA: Sodium-Aluminate.

The X-ray diffraction patterns of fly ash (FA) used in the synthesis of NaA zeolite shows a small amount of hematite (H) and indicated that mullite (M) and quartz (Q) were the main phases contained in the fly ash. These phases are believed to act as resistant phases of aluminosilicates which are difficult to convert to the zeolitic phase (Kyung and Young, 2010). Hence the fusion step was required prior to the synthesis, to transform the fly ash into silicoalumino phase as indicated in the diffractogram: (FFA). Ryu et al., (2006) also reported that without a fusion step mineral phases such as mullite and quartz can potentially remain in the synthesized zeolite. As can be noticed both mullite and quartz phases were decomposed completely during thermal alkaline fusion. The main mineral
phases observed after alkaline fusion were composed principally of sodium-aluminate (SA) and sodium-silicate (SS) as indicated in Figure 4.4: (FFA). Lastly SA and SS mineral phases were in turn hydrothermally converted to NaA zeolite (A) and the typical peaks which indicate a crystalline zeolite-A phase appear as shown in the diffractogram of the product NaA. It was also noted that no fly ash mineral phases remained in the zeolite product, which was pure zeolite-A.

4.2.4 Summary of the synthesis

The XRD patterns and the micrograph images from the HR-SEM and HR-TEM analysis showed that NaA zeolite was successfully synthesised from the South African Arnot fly ash. The synthesis process of NaA zeolite was not optimized since it was not the goal of the present study. However this study only focused on the modification of fly ash NaA zeolite with the Li$^+$, Ca$^{2+}$ and Mg$^{2+}$ cations to obtain respectively LiA, CaA and MgA zeolites forms for CO$_2$ adsorption as will be shortly discussed in parts B and C.

PART B: ION-EXCHANGE

The part B of this chapter presents and discusses the results obtained from characterization of the zeolite-A samples that were exchanged at either 30 °C or 60 °C.

4.3 Ion-exchanged zeolite-A

The NaA zeolite synthesised from fly ash as discussed in part A of this chapter was also modified with Li$^+$, Ca$^{2+}$ and Mg$^{2+}$ cations in order to generate LiA, CaA and MgA zeolites. The procedure of the ion-exchange was described in section 3.7 of Chapter three and the main parameters varied during the ion-exchange included the temperature, contact time, number of exchanges and cation type. This section mainly includes data obtained from XRD, FT-IR and SEM-EDS analysis.
4.3.1 Mineral phases study through X-ray diffraction spectroscopy

The X-ray diffraction of the fly ash NaA zeolite before and after the ion-exchange at either 30 °C or at 60 °C with Li\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) cations respectively was performed as described in section 3.9.2. These XRD patterns are discussed in this section in terms of the effects of the parameters varied during the ion-exchange. The crystallinity of the zeolite materials which was expressed in terms of the variation of either the peak height or peak area was investigated using seven major peaks located at 2\(\theta\) values 7.2°, 10.2°, 12.5°, 16.1°, 21.6°, 23.8°, and 30.1° using the technique described in section 7.2 of the appendices.

4.3.1.1 LiA zeolites exchanged at either 30 °C or 60 °C

The X-ray diffraction patterns of LiA zeolites obtained after the ion-exchange either at 30 °C or 60 °C are shown in Figures 4.5 and 4.6 respectively.

- Effects of temperature, contact time and exchanges

As can be seen in Figures 4.5 and 4.6, the structural framework of zeolite A was retained after the ion-exchange with Li cation at either 30 °C or 60 °C. Moreover, it was found that the observed peak intensities (low or high) of the LiA zeolites were dependent upon the temperature rather than the contact time or the multiple exchanges. This aspect was mainly observed in LiA zeolites exchanged at 60 °C which tended to show intense peaks compared to those prepared at 30 °C including the parent fly ash NaA zeolite to some extent. Furthermore, the increase in peak position was observed for some reflexions and may imply that the ion-exchange might have increased the diffraction angle due to the smaller atomic radius of the guest Li cation relative to the size of the host Na in the extra-framework of zeolite. In addition to the temperature, the other parameters varied during the ion-exchange such as the contact time and the exchanges appeared not to have significantly affected the framework structure of the parent NaA zeolite. In fact the LiA zeolites did not demonstrate noticeable trends related to
the increase or decrease of the contact time during the ion-exchange. The contact time used of 1 hr (A), 4 hrs (B) and 8 hrs (C) for various exchanges showed nearly similar trends after the ion-exchange at either 30 °C or 60 °C. This implies that the contact time during the ion-exchange did not have an impact on the structure that could be discerned by XRD. However the peaks located at 20 values 33° and 44° (see parent NaA) which were shifted to high 20 values as shown with the (*) in all LiA zeolites for either 30 °C or 60 °C tended to vary with the number of exchanges and may correspond to higher Na/Al ratios (low removal of the host Na+ cation) as will be discussed in section 4.3.3 of the EDS results (Figure 4.25). Besides the effects of the contact times and exchanges, the other structural changes observed in LiA zeolites such as the peak shifting or peak intensities were related to the inherent characteristic of Li+ cation as will be shortly discussed below.

- **Effects of the Li+ cation**

As can be seen in Figures 4.5 and 4.6, the XRD patterns of all the LiA zeolites exchanged at either 30 °C or 60 °C revealed a peak shifting between 20 values 20° and 60°. This peak shifting was independent of the temperature or contact time and might be due to the smaller Li+ cation charge compensating the Al3+ which is part of the lattice framework. Moreover the Li atom is approximately three times smaller than the host Na+ atom though both atoms provide similar charge compensation via their monovalent charge. Therefore the substitution of Na atom by Li atom in the parent NaA zeolite might have decreased the interatomic distances (interstitial spaces) in both the framework and the extra-framework cation region of the ion-exchanged LiA zeolites causing the shifting observed in peak positions in the region of 20 peak values 20-60°. This peak shifting was considerable in LiA zeolites compared to other zeolites investigated in this study and might explain the FT-IR vibration at 1115 cm⁻¹ which was significantly enhanced in the case of LiA zeolites as discussed in section 4.3.2.1. Additionally the XRD peak at 20 values 20.46° may be related to the diffraction occurring in
the extra-framework region. In fact, it was noticed that the decrease or increase in intensity of this peak in all LiA zeolites corresponded to the decrease or increase in intensity of the band located at 667 cm$^{-1}$ attributed to the vibration of Al-O-M in the FT-IR spectra of LiA zeolites discussed in section 4.3.2.1.
Figure 4.5: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 30 °C with Li⁺ for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Li113, Li413, Li813), twice (Li123, Li423, Li823) and thrice (Li133, Li433, Li833).
Figure 4.6: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 60 °C with Li$^+$ for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Li116, Li416, Li816), twice (Li126, Li426, Li826) and thrice (Li136, Li436, Li836).
4.3.1.2 CaA zeolites exchanged at either 30 °C or 60 °C

The XRD patterns of NaA zeolite before and after the ion-exchange at either 30 °C or 60 °C with Ca\(^{2+}\) cation (CaA zeolites) are shown in Figures 4.7 and 4.8 respectively.

- Effects of the temperature, contact time and exchanges

The XRD patterns of CaA zeolites in contrast with those of LiA zeolites discussed in section 4.3.1.1 did not show much variation in terms of the increase or decrease of the peak intensities which nearly remained similar after the ion-exchange at either 30 °C or 60 °C. This means that the temperatures used during the ion-exchange was not the main factor imparting the structural framework changes observed in CaA zeolites such as the variation of peak intensities. In addition to the temperature, the other parameters used during the ion-exchange such as the contact time and exchanges did not show a regular trend related to the structural changes observed in CaA zeolites. This may imply that the framework structure of fly ash zeolite-A could have remained stable at contact time of 1 hr, 4 hrs and 8 hrs. However the intensities of the peak at 20 values 14.6°, as indicated in Figures 4.7 and 4.8 with the (*) appeared to increase with the increase of the exchanges during the ion-exchange. This increase may relate to the % uptake of Ca\(^{2+}\)-cation discussed in section 4.3.3.2 of the EDS results. This effect might agree with Lührs et al., (2012) who also reported on the variation in intensity of this peak depending on the concentration of the cation during the ion-exchange. In addition to the peak appeared at 20 values 14.6°, the peaks located at 20 values 33° (*) appeared also to decrease with the increase of the number of exchanges for either 30 °C or 60 °C and may correspond to higher removal of the host Na\(^{+}\) cation found in CaA zeolites. Besides the effects of the temperatures, the contact time and exchanges, another important parameter which may impart the framework structural changes was the cation which effect is discussed below.
Effects of the Ca\textsuperscript{2+} cation

The XRD patterns of CaA zeolites did not show any peak shifting compared to the LiA zeolites as demonstrated through the matching of peaks located at 2\(\theta\) values 7.18°, 10.2°, 12.46°, 16.1°, 21.6°, 23.8°, 27.11°, 34.1° and 52.1°. A significant decrease in peak intensities was observed in all the CaA zeolites compared to the parent fly ash NaA zeolite as well as the LiA zeolites. This decrease was attributed to high electron density of Ca atom relative to those of the zeolite framework atoms (Al, Si and O) and the compensating Na atom (Bronić et al., 2006). The peak observed at 2\(\theta\) values 20.46° in the parent NaA zeolite as indicated with the (*) totally disappeared in all CaA zeolites exchanged at either 30°C or 60°C. This indicated that some structural changes occurred in the crystal of zeolite A due to Ca\textsuperscript{2+} cation (Lührs et al., 2012). Moreover the peak at 2\(\theta\) values 20.46° may correspond to the new vibration band observed at 870 cm\(^{-1}\) and the bending at 980 cm\(^{-1}\) as discussed in section 4.3.2.2 of the FT-IR spectra of Ca\textsuperscript{2+} which occurred in the framework structure region of the zeolite A. The XRD peaks that arose at 2\(\theta\) values 14.5° and 17.6° as indicated with the (*) in Figures 4.7 and 4.8 were both attributed to zeolite-A phases according to Treacy and Higgins, (2001). However these two peaks only appeared after the ion-exchange with Ca\textsuperscript{2+} cation and were not present in the background fly ash NaA zeolite and in the LiA zeolite samples. Thus, the heightening of these peaks might be impacted by the interactions from the divalent charge compensating of Ca\textsuperscript{2+} cation in the framework of zeolite-A and also the position of Ca\textsuperscript{2+} cations in zeolite A as was mentioned in section 2.9.2.3 of chapter two (see Figure 2.13).
Figure 4.7: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 30 °C with Ca\(^{2+}\) for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Ca\(^{113}\), Ca\(^{413}\), Ca\(^{813}\)), twice (Ca\(^{123}\), Ca\(^{423}\), Ca\(^{823}\)) and thrice (Ca\(^{133}\), Ca\(^{433}\), Ca\(^{833}\)).
Figure 4.8: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 60 °C with Ca$^{2+}$ for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Ca$_{116}$, Ca$_{416}$, Ca$_{816}$), twice (Ca$_{126}$, Ca$_{426}$, Ca$_{826}$) and thrice (Ca$_{136}$, Ca$_{436}$, Ca$_{836}$).
4.3.1.3 MgA zeolites exchanged at either 30 °C or 60 °C

The X-ray diffraction patterns of the fly ash NaA zeolite before and after the ion-exchange at either 30 °C or 60 °C with the Mg$^{2+}$ cation are shown in Figure 4.9 and 4.10 respectively.

- Effects of the temperature, contact time and exchanges

The XRD patterns of MgA zeolites showed similar trends after the ion-exchange at either 30 °C or 60 °C. This implies that the temperatures may not be the main factor responsible for the structural changes observed such as the decrease in peak intensities observed between 2θ values 5° and 20° in particular at 2θ peaks 10.2° and 16.1°. Thus, the structural stability of the fly ash zeolite A could be retained despite the variation of temperatures used during the ion-exchange. In addition to the effect of the temperature, the XRD patterns of the MgA zeolites revealed that the variation of the contact time during the ion-exchange did not affect the structural framework of zeolite A. In fact the variation of the contact time at 1 hr (A), 4 hrs and 8 hrs was found to be independent of the decrease in peak intensities and structural changes observed after the ion-exchange at either 30 °C or 60 °C. In contrast to the contact time, the number of exchanges used during the ion-exchange appeared to impart greater intensity to some peaks such as those located at 2θ peaks 10.2° and 16.1° in the MgA zeolites. The peaks located at 2θ values 33° (*) for either 30 °C or 60 °C showed almost similar scenario observed in LiA zeolites in terms of its variation in intensity and tended to vary with the number of exchanges and, may correspond to weak removal of Na$^+$ cation as was observed in the Na/Al ratios of LiA and MgA zeolites (Figure 4.25 of the EDS results).

- Effects of the Mg$^{2+}$ cation

The cationic effect was also important to consider after discussing the temperature, contact time and exchanges. The XRD patterns of MgA zeolites did
not show any peak shifting for either 30 °C or 60 °C. This was demonstrated through the matching of the peaks at 2θ values 21.6°, 23.8°, 27.11°, 34.1° and 44.1°. However, a significant decrease in peak intensities at 2θ values 10.2° and 16.1° characterized all the MgA zeolites exchanged at either 30 °C or 60 °C. This decrease might be due to the presence of Mg²⁺ cation which preferably locate in the 6 MR of zeolite A and may cause a decrease in the scattering angle. The XRD peaks appeared at 2θ values 14.5° and 17.6° as indicated with the (*) in all MgA zeolites were attributed to zeolite-A phases according to Treacey and Higgins, (2001). However the increased intensity observed at these positions in the MgA zeolites compared to the parent fly ash NaA zeolite was also ascribed to the intrinsic characteristic of the Mg²⁺ cation such as the atomic radius and charge compensation. The XRD patterns of the MgA zeolites also show that the intensity of the peak at 2θ values 20.4° might correspond to the variation observed in the band located at 667 cm⁻¹ which was assigned to the extra-framework cation of zeolite A as discussed in section 4.3.2.3 of the FT-IR spectra.
Figure 4.9: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 30 °C with Mg$^{2+}$ for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Mg113, Mg413, Mg813), twice (Mg123, Mg423, Mg823) and thrice (Mg133, Mg433, Mg833).
Figure 4.10: XRD patterns of synthesised NaA zeolite before and after ion-exchange at 60 °C with Mg$^{2+}$ for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolite was exchanged once (Mg116, Mg416, Mg816), twice (Mg126, Mg426, Mg826) and thrice (Mg136, Mg436, Mg836).
4.3.1.4 Summary of the XRD analysis of LiA, CaA and MgA zeolites

The XRD patterns of LiA, CaA and MgA zeolites revealed that the framework structure of zeolite-A was retained after the ion-exchange. No new peaks were observed for LiA zeolite samples; however some minor peaks assigned to zeolite-A mineral phases not observed in the background NaA zeolite were identified in the region between 2θ values 5-20° for CaA and MgA zeolites after the ion-exchange at either 30 °C or 60 °C. Furthermore the changes observed in the XRD patterns of LiA, CaA or MgA zeolites such as the increase or decrease in peak intensities were essentially related to the respective inherent characteristics of the charge balancing cation. The peak intensities of these zeolites proportionally decreased with the increase of the atomic radius of the cations exchanged at either 30 °C or 60 °C and; among other zeolites, CaA zeolites depicted the lowest peak intensities followed by MgA zeolites while LiA zeolites showed the highest peak intensities which were generally higher than the parent fly ash NaA zeolite as shown in Figure 4.11. The low peak intensities observed in MgA and CaA zeolites is believed to be caused by the higher electron densities of the Ca$^{2+}$ and Mg$^{2+}$ cations relatively to the electron densities of the zeolite framework cations (Al, Si and O) and the compensating cation (Na) (Bronić et al., 2006).
4.3.2 Bonding and stretching study through Fourier transformed infrared spectroscopy

The FT-IR analysis of zeolite-A obtained before and after the ion-exchange at either 30 °C or 60 °C of the fly ash NaA zeolite with Li\(^+\), Ca\(^{2+}\) or Mg\(^{2+}\) cations was performed as described in section 3.9.1. The FT-IR spectra presented in these sections were discussed in terms of the parameters such as the temperature varied during the ion-exchange.

4.3.2.1 LiA zeolites exchanged at either 30 °C or 60 °C

The FT-IR spectra of the fly ash NaA zeolite before and after the ion-exchange with Li\(^+\) cation at either 30 °C or 60 °C are shown in Figures 4.12 and 4.13.
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- Effects of the temperature, contact time and exchanges

The FT-IR spectra of LiA zeolites revealed similar trends after the ion-exchange at either 30 °C or 60 °C despite the variation in band intensities observed in the LiA zeolites relative to the parent NaA zeolite. This clearly indicated that the temperatures may not be responsible for the increase or decrease in band intensities observed in LiA zeolites. Besides the temperature used during the ion-exchange of Li$^+$ cation, the variation of the contact time appeared to have no effect on the structural framework of zeolite A. This is because, at all the contact times used (1 hr, 4 hrs and 8 hrs) similar structural changes were observed in LiA zeolites as the contact time varied. However the number of exchanges (1, 2 and 3) employed during the ion exchange in an attempt to increase the loading % of Li$^+$ cation, appeared to affect the vibrations at 462 cm$^{-1}$ and 548 cm$^{-1}$ in the framework of LiA zeolites. In fact, the vibration band at 548 cm$^{-1}$ appeared to broaden and lose its original shape gaining a shoulder as the number of exchanges increased while the band at 462 cm$^{-1}$ exhibited constancy in terms of the shapes though the intensity slightly increased as well. These vibrations are attributed to the D4R and T-O bending in the framework of zeolite-A (Flanigen and Khatami, 1971; Yuiro et al., 2004 and Hashemian et al., 2013) and can indicate the degree of the crystallinity when considering the variation of their band intensities (Rayalu et al., 2005).

- Effects of the Li$^+$ cation

Apart from the parameters discussed in the above paragraph such as the exchanges which impacted on the bands at 462 cm$^{-1}$ and 548 cm$^{-1}$, the FT-IR spectra of LiA zeolites as can be seen in Figures 4.12 and 4.13 also revealed that some vibration bands related to the inherent characteristic of the Li$^+$ cation. These vibration bands were mainly those located at 667 cm$^{-1}$, 980 cm$^{-1}$ and 1115 cm$^{-1}$. The vibration at 667 cm$^{-1}$ is assigned to the symmetric stretching of the Al-O-M where M represents the exchangeable cation (Kugbe et al., 2009). Thus, this band
considerably increased and shifted to higher values in all the LiA zeolites compared to the parent NaA zeolite at either 30 °C or 60 °C. The guest Li⁺ cation is three times smaller than Na⁺ cation (host cation), though both cations are monovalent and possess approximately similar electronegativity trends. Therefore the difference in atomic mass and importantly the atomic radius of Li⁺ cation may be the main factor that impacted on the intensity and position of this band. This may be in good agreement with the finding of Mozgawa et al., (2009). Moreover the variation in intensity of the band at 667 cm⁻¹ related to the new vibration band that arose at 1115 cm⁻¹ which might be assigned to asymmetric stretching of the O-T-O due to the interaction of the Li⁺ cation and the framework of zeolite-A. The intensity of the bands at 667 cm⁻¹ and 1115 cm⁻¹ tended to relate to the diffraction peak located at 2θ value 20.46° discussed in section 4.3.1.1 of the XRD results of LiA zeolites in terms of the changes that occurred in the crystal. Finally, besides the vibrations at 667 cm⁻¹ and 1115 cm⁻¹, the effects of the Li⁺ cation was also observed at the vibration located at 980 cm⁻¹ which is characteristic of a zeolitic material (Yujiro et al., 2004). This vibration band altered into a narrow shaped and shoulder ed band in all the LiA zeolites exchanged at either 30 °C or 60 °C compared to the background NaA zeolite after the ion-exchange with Li⁺ cation.
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Figure 4.12: IR spectra of fly ash NaA zeolite before and after ion-exchange at 30 °C with Li\(^+\) cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Li113, Li413, Li813), twice (Li123, Li423, Li823) and thrice (Li133, Li433, Li833).
Figure 4.13: IR spectra of fly ash NaA zeolite before and after ion-exchange at 60 °C with Li⁺ cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Li116, Li416, Li816), twice (Li126, Li426, Li826) and thrice (Li136, Li436, Li836...
4.3.2.2 CaA zeolites exchanged at either 30 °C or 60 °C

The FT-IR spectra of fly ash NaA zeolite before and after the ion-exchange at either 30 °C or 60 °C with the Ca\(^{2+}\) cation are shown in Figures 4.14 and 4.15 respectively.

- Effects of the temperature, time and exchanges

As can be seen in Figures 4.14 and 4.15, the CaA zeolites revealed similar structural changes (band shapes) at either 30 °C and 60 °C for all contact time employed during the ion-exchanges. The major changes that occurred after the ion-exchange were located at four vibration bands namely 462 cm\(^{-1}\), 548 cm\(^{-1}\), 667 cm\(^{-1}\) and 980 cm\(^{-1}\). The vibration bands located at 548 cm\(^{-1}\) and 462 cm\(^{-1}\) as discussed in section 4.3.2.2 are attributed to the vibrations occurring in the D4R and Si-O-T bending (Mozgawa et al., 2005). According to Rayalu et al., (2005) the difference in intensity of these bands can indicate the degree of crystallinity of the zeolite materials. This means that the increase or decrease in intensity of these bands will be proportional to higher or lower crystallinity of the zeolite respectively. Thus these vibration bands decreased in all the CaA zeolites compared to the parent fly ash NaA zeolite. The decrease was mainly observed for the vibration at 462 cm\(^{-1}\) which significantly decreased in intensity and tended to decrease with the increase of the exchanges. This decrease may be due to the % uptake of Ca\(^{2+}\) cation as the number of exchanges increased. The vibration band at 462 cm\(^{-1}\) tended to correspond to the diffraction peak located at 2θ values 14.5° discussed in section 4.3.1.2 of the XRD results of CaA zeolite-A. While the band at 462 cm\(^{-1}\) tended to decrease in intensity with the increase of the exchanges, the band at 548 cm\(^{-1}\) tended to shift to lower frequencies in CaA zeolites. The vibration bands at 667 cm\(^{-1}\), 870 cm\(^{-1}\) and 980 cm\(^{-1}\) as also discussed in the FT-IR spectra of the LiA zeolite samples were related to the inherent characteristic of the Ca\(^{2+}\) cation and are shortly discussed below.
Effect of the Ca\textsuperscript{2+} cation

Apart from the temperature, contact time and the exchanges discussed above, the FT-IR spectra of CaA zeolites revealed that the cation type also imparted the structural changes observed. This aspect was mainly observed at vibration bands located at 667 cm\textsuperscript{-1} which are attributed to the Al-O-M stretching vibrations as discussed in section 4.3.2.1 (Kugbe et al., 2009). Compared to the parent NaA zeolite, this band significantly decreased in intensity for all the CaA zeolites exchanged at either 30 °C or 60 °C. This decrease in intensity might be as a result of the difference in the atomic radius between the guest Ca\textsuperscript{2+} cation and the host Na\textsuperscript{+} cation. This result may be in a good agreement with Mozgawa et al., (2009) who reported that the atomic radius and the charge of the extra-framework cation are the main factors that can induce changes in both the location and intensity of the FT-IR vibration bands of zeolite material after the ion-exchange. The decrease observed in this vibration appeared to be related to the diffraction peak located at 2\theta values 20.46° discussed in section 4.3.1.2 of the XRD results of CaA zeolites. Furthermore the band located at 980 cm\textsuperscript{-1} attributed to the asymmetric stretching of T-O-T (T=Si or Al) (Yujiro et al., 2004), depicted a double band in all the CaA zeolites instead of a narrowed shape observed in the background NaA zeolite. This double shaped band was found to be characteristic of CaA zeolites and might be due to the interactions between Ca\textsuperscript{2+} cation and the framework of zeolite A. A similar double shape of this band for CaA zeolites was also reported by De Pena and Rondon, (2013). Finally the new vibration band that arose at 870 cm\textsuperscript{-1} was assigned to symmetric stretching of the O-T-O which appeared to be enhanced by the stretching that occurred at 980 cm\textsuperscript{-1}. 
Figure 4.14: IR spectra of NaA zeolite before and after ion-exchange at 30 °C with Ca$^{2+}$ cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Ca113, Ca413, Ca813), twice (Ca123, Ca423, Ca823) and thrice (Ca133, Ca433, Ca833).
Figure 4.15: IR spectra of NaA zeolite before and after ion-exchange at 60 °C with Ca$^{2+}$ cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Ca116, Ca416, Ca816), twice (Ca126, Ca426, Ca826) and thrice (Ca136, Ca436, Ca836).
4.3.2.3  MgA zeolites exchanged at either 30 °C or 60 °C

The FT-IR spectra of the fly ash NaA zeolite before and after the ion-exchange at either 30 °C or 60 °C with Mg$^{2+}$ cation are shown in Figures 4.16 and 4.17. These results are discussed in this section in terms of the effects of the temperature, contact time, exchanges and cation.

- **Effects of the temperature, time and exchange**

The changes observed in the intensities of the vibration bands for MgA zeolites occurred mainly at 462 cm$^{-1}$ which decreased while those located at 548 cm$^{-1}$ and 667 cm$^{-1}$ slightly increased. Moreover, the band at 548 cm$^{-1}$ slightly shifted to lower region of frequencies at both 30 °C and 60 °C (see Figures 4.15 and 4.16). The vibration bands at 462 cm$^{-1}$ and 548 cm$^{-1}$ as discussed in sections 4.3.2.1 and 4.3.2.2 were assigned to D4R and particularly to Si-O and Al-O bending in the structural framework of zeolite-A (Yujiro et al., 2004; Hashemian et al., 2013). These bands can also indicate the degree of the crystallinity by considering the variation in intensity. This means that the low or high crystallinity corresponds to the lower or higher intensity of the bands (Rayalu et al., 2005). Hence the vibration band at 462 cm$^{-1}$ slightly decreased while the band at 548 cm$^{-1}$ increased at all contact times for either 30 °C or 60 °C. The decrease of the band at 462 cm$^{-1}$ in the MgA zeolites compared to the CaA zeolites showed a similar trend for this band. This behaviour displayed by MgA and CaA zeolites might be due to the density of the charge compensation in the case of both Ca$^{2+}$ and Mg$^{2+}$ divalent cations compared to the monovalent Na$^+$ and Li$^+$ cations which generally showed an intense band at this position. Moreover, the intensity of the band at 462 cm$^{-1}$ was temperature independent but appeared to decrease with the increase of the exchanges (1, 2 and 3). The decrease observed at this band may be caused by the % loading of the Mg$^{2+}$ cation which increased as the exchanges increased as discussed in section 4.3.3.3.
Chapter Four

- **Effect of the Mg\(^{2+}\) cation**

Besides the bands at 462 cm\(^{-1}\) and 548 cm\(^{-1}\) discussed above, the other bands such as those at 667 cm\(^{-1}\) and 980 cm\(^{-1}\) appeared to be altering with the inherent characteristic of the Mg\(^{2+}\) cation as also discussed in sections 4.3.2.1 and 4.3.2.2 respectively for LiA and CaA zeolites. For instance, the vibration bands at 667 cm\(^{-1}\) slightly broadened and increased in intensity in all the MgA zeolites exchanged at either 30 °C or 60 °C compared to the background NaA zeolite. In fact Na and Mg atoms have approximately equivalent atomic mass but differ in terms of the atomic radius and the charge. The former cation is a monovalent whereas the latter is a divalent cation. Thus the high charge and big atomic radius of the Mg\(^{2+}\) cation as also reported by Mozgawa et al., (2009), could be the main factors that might initiate the increase stretching of the bands located at 667 cm\(^{-1}\) causing a broader band. Moreover the vibration band located at 980 cm\(^{-1}\) attributed to asymmetric stretching of T-O-T also slightly broadened in the MgA zeolites compared to the parent NaA zeolite. The FT-IR spectra compared to the XRD patterns of the MgA zeolites revealed that the intensity of this band varied with the diffraction peak located at 2θ values 14.6° discussed in section 4.3.1.3 of the XRD patterns.
Figure 4.16: IR spectra of fly ash NaA zeolite before and after ion-exchange at 30 °C with Mg$^{2+}$ cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Mg113, Mg413, Mg813), twice (Mg123, Mg423, Mg823) and thrice (Mg133, Mg433, Mg833).
Figure 4.17: IR graphs of fly ash NaA zeolite before and after ion-exchange at 60 °C with Mg\(^{2+}\) cation for 1 hr (A), 4 hrs (B) and 8 hrs (C). For each setup the parent NaA zeolites were exchanged once (Mg116, Mg416, Mg816), twice (Mg126, Mg426, Mg826) and thrice (Mg136, Mg436, Mg836).
4.3.2.4 Summary of the FT-IR analysis of LiA, CaA and MgA zeolites

In addition to the XRD patterns, the FT-IR spectra of the LiA, CaA and MgA zeolites confirmed that the framework structure of zeolite-A was retained, except minor changes observed in the framework region of zeolite-A for some samples. The FT-IR results of LiA, CaA and MgA zeolites obtained after the ion-exchange at either 30 °C or 60 °C showed that the inherent characteristic of each cation was the main driving force responsible for the structural changes observed in the FT-IR spectra. These structural changes were mainly induced by the charge, the atomic radius or the mass of the guest cations relative to the framework cations (Al, Si and O) and the compensating charge cation (Na) and occurred in the D4R and S6R bands of zeolite-A. Furthermore, the structural changes in terms of the variation of the band intensities mainly affected the bands at 462 cm\(^{-1}\), 548 cm\(^{-1}\), 667 cm\(^{-1}\) and 980 cm\(^{-1}\). The band located at 548 cm\(^{-1}\) tended to shift to lower frequencies for fly ash based zeolites exchanged with divalent cations. Among other bands, the intensity of the band at 667 cm\(^{-1}\) related to the atomic radius and inversely increased with the decrease of the atomic radius of the cations investigated in study and followed this increasing order in each zeolites: LiA > MgA ≈ NaA > CaA whereas the atomic radius increases in the opposite direction (Li\(^+\) < Mg\(^{2+}\) < Na\(^+\) < Ca\(^{2+}\)). The new vibration at 1115 cm\(^{-1}\) observed in the LiA zeolite samples was attributed to the internal asymmetric stretching of the aluminosilicates framework of zeolite-A. Finally the variation in band intensities (increase or decrease) as mentioned in the XRD results was also confirmed with the FT-IR spectra in the region 400-600 cm\(^{-1}\).
4.3.3 Semi-quantitative composition study through energy dispersive spectroscopy

The energy dispersive spectroscopy (EDS) for elemental composition of the synthesised NaA zeolite before and after the ion-exchange at either 30 °C or 60 °C with Li\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) cations respectively for LiA, CaA and MgA zeolites was determined as described in section 3.9.3 of chapter three. It is essential to highlight here that the EDS is a semi-quantitative technique, rather than quantitative such as ICP which provides both qualitative and quantitative elemental composition. Therefore this aspect will be taken into account in terms of the correlation while discussing these results. The EDS results presented in these sections were obtained from an average of six spots analysed on each specimen of zeolite material, and ratios are presented because of inherent inaccuracy of the EDS. The ratios were calculated as described in section 7.1 of the appendices.

4.3.3.1 LiA zeolites

i. LiA zeolites exchanged at 30 °C

The EDS results of fly ash NaA zeolite and LiA zeolites obtained after the ion-exchange at 30 °C are given in Table 7.1 of the appendices. These EDS results are presented and discussed in Figure 4.18 in terms of atomic weight (%) ratios of elements based on the Al\(^{3+}\) atom which carries the acid site for the charge compensating in the zeolite-A.
Figure 4.18: EDS results of atomic weight (%) ratios of Na, Li, Si and Al before and after the ion-exchange procedure of the fly ash NaA zeolite with Li⁺ cation at 30 °C.

The calculated values of the Al/Na, Al/Li and Si/Al ratios are shown in Figure 18. These results demonstrated that Li atom could not displace the Na atom in the least exchanged zeolites (L113, L413 and L813). Additionally the exchange of Li with Na appeared to be dependent upon both the contact time and the number of exchanges employed during the ion-exchange. The Na/Al ratios slightly decreased with the increase in Li/Al ratios. The lower values of about 0.2:1 for Na/Al reached in the most exchanged zeolites (L133, L433 and L833) indicated a higher removal of the Na atom after three consecutive exchanges. However an average value of about 0.55:1 Li/Al ratio was found in the zeolites exchanged twice (L123, L423 and L823) and 0.66:1 in those exchanged thrice (L133, L433 and L833). These values of Li/Al ratios, based on the Na/Al ratio of 0.972 calculated in the parent NaA zeolite indicated that about 56.58 % or 67.90 % of Li atom may be exchanged at 30 °C after two or three consecutive exchanges respectively. In addition to the Na/Al and Li/Al ratios, the Si/Al ratio had a consistent average
of 0.97:1 which was near the value found in the parent NaA zeolites indicating that the LiA zeolites retained the framework structure after the ion-exchange at 30 °C. In order to increase the % loading of the Li\(^{+}\) cation, the ion-exchange was performed at 60 °C and the EDS results of the LiA zeolites obtained are presented and discussed in the following section.

ii. **LiA zeolites exchanged at 60 °C**

The EDS results of the LiA zeolites obtained after the ion-exchange at 60 °C with Li\(^{+}\) cation are given in Table 7.2 in the appendices. These results are presented in Figure 4.19 in terms of the atomic weight (\%) ratios of elements based on Al\(^{3+}\) atom which carries the acid site for charge compensating in the zeolite.

![Figure 4.19: EDS results of atomic weight (%) ratios of Na, Li, Si and Al before and after the ion-exchange procedure of the fly ash NaA zeolite with Li\(^{+}\) cation at 60 °C.](image)

The ratios from the EDS results of the LiA zeolites obtained after the ion-exchange at 60 °C are given in Figure 4.19. These results showed that the Na/Al
decreased proportionally with the increase of exchanges (1, 2 and 3). Moreover, the decrease in Na/Al ratios was also inversely proportional to the increase of Li/Al ratios as also found in the LiA zeolites exchanged at 30 °C. This means that the guest Li atom tended to displace the host Na atom in the zeolite as the exchanges increase. Thus, the highest removal of Na atom was reached in the most exchanged samples (Li136, Li436 and Li836) with an average value of Na/Al ratio 0.178 approximately similar to the value of 0.2 obtained in the most exchanged zeolites at 30 °C (Li133, Li433 and Li833). This indicated that the increase in temperature during the ion-exchange did not result in higher removal of Na atom as expected and the value of 0.2:1 for Na/Al seemed to be the limit in LiA zeolites. However, the Li/Al ratios compared to those obtained at 30 °C, revealed a significant increase indicating a high amount of Li$^+$ cation exchanged. The Li/Al ratios reached the values over 1 compared to values of 0.55:1 and 0.66:1 calculated in the LiA zeolites exchanged at 30°C. In addition the contact time of 4 hrs was found to be suitable to exchange Li$^+$ cation at 60 °C rather than the short period time of 1 hr or the longer time of 8 hrs. Finally the EDS results also showed a slight decrease in Si/Al ratios in all the LiA zeolites exchanged at 60 °C compared to those exchanged at 30 °C and the parent NaA zeolite. This decrease for LiA zeolites exchanged at 60 °C may be attributed to some structural alteration.

4.3.3.1.1 Summary of the EDS results obtained from LiA zeolites

The EDS results obtained from LiA zeolites exchanged at either 30 °C or 60 °C have revealed that the removal of the host Na atom during the ion-exchange with Li$^+$ cation was independent of the contact times (1 hr, 4 hrs, 8 hrs) but mostly depended upon the number of exchanges (1, 2, 3) employed. This removal was found to be effective at 3 consecutive exchanges for either 30 °C or 60 °C. The loading of the Li$^+$ cation also depended upon the temperature and not the contact times. The highest loading % of the Li$^+$ cation was found at 60 °C and was demonstrated by higher Li/Al ratios of over 1 compared to those reached for LiA
zeolites exchanged at 30 °C. However the higher temperature of 60 °C tends to
decrease the Si/Al ratios after the ion-exchange as a result of changes that may
have occurred in the framework structure of zeolite.

4.3.3.2 CaA zeolites

i. CaA zeolites exchanged at 30 °C

The EDS results obtained from CaA zeolites after the ion-exchange at 30 °C with
Ca$^{2+}$ cation are given in Table 7.3 of the appendices. These results are shown and
discussed in Figure 4.20 in terms of the atomic weight (%) ratios of elements
based on the Al atom which carries the acid site for charge compensating in the
zeolite-A.

Figure 4.20 shows the atomic % ratios of Na, Li, Si and Al before and after the
ion-exchange procedure of fly ash NaA zeolite with Ca$^{2+}$ cation at 30 °C.

<table>
<thead>
<tr>
<th></th>
<th>NaA</th>
<th>Ca113</th>
<th>Ca123</th>
<th>Ca133</th>
<th>Ca413</th>
<th>Ca423</th>
<th>Ca433</th>
<th>Ca813</th>
<th>Ca823</th>
<th>Ca833</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na/Al</td>
<td>0.972</td>
<td>0.136</td>
<td>0.066</td>
<td>0.024</td>
<td>0.135</td>
<td>0.044</td>
<td>0.033</td>
<td>0.184</td>
<td>0.055</td>
<td>0.026</td>
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<tr>
<td>Ca/Al</td>
<td>0</td>
<td>0.588</td>
<td>0.615</td>
<td>0.563</td>
<td>0.754</td>
<td>0.641</td>
<td>0.593</td>
<td>0.539</td>
<td>0.602</td>
<td>0.63</td>
</tr>
<tr>
<td>Si/Al</td>
<td>0.979</td>
<td>0.967</td>
<td>0.965</td>
<td>0.96</td>
<td>0.948</td>
<td>0.973</td>
<td>0.96</td>
<td>0.969</td>
<td>0.94</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Figure 4.20: EDS results of the atomic weight (%) ratios of Na, Ca, Si and Al
before and after the ion-exchange procedure of fly ash NaA zeolite with Ca$^{2+}$
cation at 30 °C.
As can be seen in Figure 4.20, the calculated values of the Na/Al, Ca/Al and Si/Al ratios for CaA zeolites indicated that the Na/Al ratio significantly decreased. This decrease was proportional to the increase of the exchanges (1, 2 and 3) and was independent of the contact time (1 hr, 4 hrs and 8 hrs) employed during the ion-exchange. The highest removal of Na atom occurred after three consecutive exchanges (see samples: Ca133, Ca433, and Ca833) where an average value about 0.027:1 was found for Na/Al ratios. This value represented about 2.8 % weight of the Na atom that remained after 3 consecutive exchanges for each contact time. Although the Na/Al ratio decreased with the increase of the exchanges; the reverse trend which would have indicated high loading of the Ca\(^{2+}\) cation was not observed regarding the Ca/Al ratios because of the divalent nature of this cation.

Thus, considering the average values of the Ca/Al ratios as per exchange for all the contact times combined (1 hr, 4 hrs and 8 hrs); approximately 0.6:1 of the Ca/Al ratio was found. In fact 1 Ca atom can substitute 2 Na atoms previously occupied at 2 acid sites of 2 Al atoms in terms of the charge compensation resulting in a Ca/Al ratio of 1:2 in the zeolite. Thus, the Ca/Al ratio of about 0.6:1 found in CaA zeolites exchanged at 30 °C indicated that only half of the charge of the Ca\(^{2+}\) cation may be able to bond at one Brønsted acid site of one Al\(^{3+}\). The EDS results also showed that the Si/Al ratio slightly decreased in all the CaA zeolites compared to the parent NaA zeolite. This decrease in Si/Al ratio might be due to the alteration of the structural framework of the zeolite-A. In an attempt to improve the loading % of the Ca\(^{2+}\) cation, the ion-exchange was also carried out at a temperature of 60 °C which samples are discussed in section 4.3.4.2.2 below.

ii. **CaA zeolites exchanged at 60 °C**

The EDS results of CaA zeolites obtained after the ion-exchange at 60 °C with Ca\(^{2+}\) cation are given in Table 7.4 of the appendices and will be discussed in this section in terms of the atomic weight (%) ratios (see Figure 4.21) of the elements.
based on the Al atom which carries the acid site for charge compensating in zeolite-A.

As can be observed in Figure 4.21, the ratios showed that the Na/Al ratios decreased proportionally with the increase of the exchanges (1, 2 and 3) and independently of the contact time (1 hr, 4 hrs and 8 hrs) employed during the ion-exchange. This decrease in Na/Al ratios reached high removal of the host Na atom after three consecutive exchanges (Ca136, Ca436 and Ca836) with an average value approximating 0.038:1. This value represented about 3.9 % of the host Na atom remaining after three consecutive exchanges and this was slightly above the value of 2.8 % obtained at 30 °C for zeolites exchanged three times (Ca133, Ca433, Ca833). This means that the ion-exchange at 30 °C compared to 60 °C may be suitable for displacing the host Na atom with the Ca atom after three exchanges. However as was also discussed in section 4.3.2.1 of the EDS results of CaA zeolites exchanged at 30 °C, the Ca/Al ratios did not show a regular trend.
as the Na/Al ratios decreased. The Ca/Al ratios appeared to be independent of the contact time as well as the exchanges employed during the ion-exchange. The average value for Ca/Al ratios of about 0.5:1 for each contact time (1 hr, 4 hrs and 8 hrs) was slightly lower compared to the value of the Ca/Al ratios obtained at 30 °C. It is known that the Ca/Al ratio in terms of charges compensating is 1:2. Hence the Ca/Al ratio of about 0.5:1 obtained means that only half a charge of the Ca$^{2+}$ cation was able to bond at one Brønsted acid site of one Al$^{3+}$. In addition to the Na/Al and Ca/Al ratios discussed, the Si/Al ratio slightly decreased for all CaA zeolites exchanged at 60 °C. This decrease, as also discussed for CaA zeolites exchanged at 30 °C may indicate that some structural changes of the zeolite-A might have occurred due to the exchange conditions applied.

4.3.3.2.1 Summary of the EDS results obtained from CaA zeolites

The ion-exchange at either 30 °C or 60 °C has shown that Ca$^{2+}$ cation was able to remove a significant amount of the host Na atom compared to the Li$^+$ cation. This removal was independent of the contact time but depended mostly upon the multiple exchanges employed. The amount of Na remaining after three exchanges reached the limit of 2.8 % and 3.9 % at 30 °C and 60 °C respectively. However the ion-exchange of Ca$^{2+}$ cation was found to be suitable at 30 °C with the highest Ca/Al ratios of about 0.6:1 observed and the contact time of 4 hrs was found to be sufficient.

4.3.3.3 MgA zeolites

i. MgA zeolites exchanged at 30 °C

The EDS results of the MgA zeolites obtained after the ion-exchange at 30 °C with Mg$^{2+}$ cation are given in Table 7.5 in the appendices. These results are presented and discussed in Figure 4.22 in terms of the atomic weight (%) ratios of elements based on Al atom which carries the acid site for charge compensating in zeolite-A.
The ratios calculated from the EDS results are given in Figure 4.22. These results indicated that the Mg$^{2+}$ cation was not able to displace a significant amount of the host Na atom as demonstrated by the Na/Al and Mg/Al ratios that showed approximately similar values. Moreover the slight decrease observed in the Na/Al ratios for each set of the contact time as the exchanges increased, did not directly correspond to the increase of the Mg/Al ratios. The Mg/Al ratios for the most exchanged samples (i.e. M133, M433 and M833) could only reach an average of about 0.3:1, which was lower than an average of about 0.6:1 found for Ca/Al ratios. The Mg$^{2+}$ cation which is a divalent cation is known to substitute 2 Na$^{+}$ cations previously occupied at 2 acid sites of 2 Al$^{3+}$ atoms in terms of the charge compensating resulting in the Mg/Al ratio of 1:2. Therefore the Mg/Al ratios found of about 0.3:1, might indicate that there was insignificant charge compensation with Mg$^{2+}$ atom compared to the values obtained at 30 °C for LiA and CaA zeolites respectively discussed in sections 4.3.4.1 and 4.3.4.2 of the EDS.
results. The results have also shown that the Si/Al ratios in the MgA zeolites were nearly similar to the value of 0.97:1 found in the parent NaA zeolite. This may indicate that the structural framework did not alter after the ion-exchange with the Mg$^{2+}$ cation compared to the Ca$^{2+}$ cation. The EDS results were also obtained from the MgA zeolites exchanged at 60 °C and are tabulated in section 4.3.4.3.2.

ii. MgA zeolites exchanged at 60 °C

The EDS results of the MgA zeolites obtained after the ion-exchange at 60°C with Mg$^{2+}$ cation are given in Table 7.6 of the appendices. These results are presented in Figure 4.23 in terms of the atomic weight (%) ratios of elements based on the Al$^{3+}$ atom which carries the acid site for charge compensating in the zeolite-A.

![Figure 4.23: EDS results of atomic weight (%) ratios of Na, Mg, Si and Al before and after the ion-exchange procedure of fly ash NaA zeolite with the Mg$^{2+}$ cation at 60 °C.](image)

<table>
<thead>
<tr>
<th></th>
<th>NaA</th>
<th>Mg11 6</th>
<th>Mg12 6</th>
<th>Mg13 6</th>
<th>Mg41 6</th>
<th>Mg42 6</th>
<th>Mg43 6</th>
<th>Mg81 6</th>
<th>Mg82 6</th>
<th>Mg83 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na/Al</td>
<td>0.972</td>
<td>0.258</td>
<td>0.306</td>
<td>0.262</td>
<td>0.397</td>
<td>0.297</td>
<td>0.25</td>
<td>0.422</td>
<td>0.302</td>
<td>0.226</td>
</tr>
<tr>
<td>Mg/Al</td>
<td>0</td>
<td>0.484</td>
<td>0.386</td>
<td>0.44</td>
<td>0.365</td>
<td>0.401</td>
<td>0.456</td>
<td>0.396</td>
<td>0.438</td>
<td>0.441</td>
</tr>
<tr>
<td>Si/Al</td>
<td>0.979</td>
<td>0.917</td>
<td>0.899</td>
<td>0.901</td>
<td>0.885</td>
<td>0.891</td>
<td>0.887</td>
<td>0.884</td>
<td>0.895</td>
<td>0.853</td>
</tr>
</tbody>
</table>
As can be observed in Figure 4.23, the EDS results obtained from MgA zeolites exchanged at 60 °C showed a slight decrease in terms of the Na/Al ratios compared those obtained at 30 °C. Considering averages in the most exchanged samples (M136, M436 and M836), a significant loading % of the Mg$^{2+}$ cation was observed for all the contact times. It was found that the Na/Al ratio was about 0.2:1. This Na/Al ratio slightly decreased at 60 °C relatively to the value obtained at 30 °C in the same samples (see M133, M433 and M833) and indicated that an additional amount of the host Na atom may be displaced with the increase in temperature during the ion-exchange. Although the Na/Al ratios decreased for MgA zeolites exchanged at 60 °C, only a maximum of about 0.4:1 of the Mg/Al ratio could be obtained. This might indicate that the Mg$^{2+}$ cation was not well exchanged and could not be able to totally occupy two Brønsted acid sites of the Al atoms in terms of charges compensating to achieve Mg/Al ratio of 1:2. Besides the Na/Al and Mg/Al ratios, the Si/Al ratios decreased compared to those obtained in MgA zeolites exchanged at 30 °C and the parent fly ash NaA zeolite (0.979). This decrease in the Si/Al ratios may indicate that the framework structure of zeolite A may be changed after the ion-exchange at 60°C.

4.3.3.3.1 Summary of the EDS results obtained from MgA zeolites

The ion-exchange procedure at either 30 °C or 60 °C with the Mg$^{2+}$ cation at 1 hr, 4 hrs and 8 hrs have shown that, the Mg atom could not replace a significant amount of the host Na atom compared to Ca$^{2+}$ cation. However the ion-exchange at 60 °C was found suitable to exchange the Mg$^{2+}$ cation at 4 hrs and the Mg/Al ratio of about 0.4:1 was found to be the limit. Therefore there was no need to extend the ion-exchange to 8 hrs and, also considering the fact that at high temperature the Si/Al ratio lowered indicating that some structural alteration of the framework of zeolite-A may occur during the ion-exchange at 60 °C.
4.3.3.4 Summary of the EDS analysis from LiA, CaA and MgA zeolites

The overall % ratios of all zeolite samples exchanged at either 30 °C or 60 °C, are respectively summarised in Figures 4.24 and 4.25 below.
Figure 4.24: Comparative atomic ratio trends before (NaA) and after the ion-exchange at 30 °C with Li⁺,Ca²⁺ or Mg²⁺ cations. For sample code, see section 3.8 of Chapter three.
Figure 4.25: Comparative atomic ratio trends before (NaA) and after the ion-exchange at 60 °C with Li⁺, Ca²⁺ or Mg²⁺ cations. For sample code, see section 3.8 of Chapter three.
The EDS results obtained at either 30 °C or 60 °C as can be seen in Figures 4.24 and 4.25 respectively, revealed that the removal of the host Na atom during the ion-exchange was independent of the contact time (1 hr, 4 hrs, 8 hrs) but was mostly influenced by multiple exchanges (1, 2, 3) employed during the exchange for Li\(^{+}\), Ca\(^{2+}\) and Mg\(^{2+}\) cations. Moreover the ion-exchange with the Ca\(^{2+}\) cation displayed the highest removal of the Na atom compared to the exchange with Li\(^{+}\) and Mg\(^{2+}\) cations at either 30 °C or 60 °C. The ion-exchange at 30 °C with three consecutive exchanges was found to be suitable to exchange Ca\(^{2+}\) cation since a Ca/Al ratio 0.6:1 was the limit at both ion-exchange temperatures whereas 60 °C with three exchanges was found to be favourable conditions to exchange Li\(^{+}\) or Mg\(^{2+}\) cations at 4 hrs and a Li/Al ratio of 1:1 but a Mg/Al ratio of only 0.4:1 could be achieved. Finally, as can be seen in Figure 4.25, the ion-exchange at 60 °C for Ca\(^{2+}\) and Mg\(^{2+}\) cations tended to decrease the Si/Al ratios for the ion-exchanged zeolite-A, which decrease indicated that the structure of zeolite-A may be slightly changed.

**PART C: CO\(_2\) ADSORPTION**

**4.4 CO\(_2\)-TPD adsorption**

The part C of this chapter deals with the results obtained after the adsorption of CO\(_2\). The CO\(_2\) adsorption was only carried out on the most exchanged zeolite samples due to instrument access constraint. These samples for both the ion-exchange at 30 °C and 60 °C, were described in part B of this chapter as: Li133, Li433, Li833, Li136, Li436, Li836 (LiA zeolites); Ca133, Ca433, Ca833, Ca136, Ca436, Ca836 (CaA zeolites) and Mg133, Mg433, Mg833, Mg136, Mg436, Mg836 (MgA zeolites). For simplicity, these samples are described in part C as LiA1, LiA4, LiA8 (LiA zeolites); CaA1, CaA4, CaA8 (CaA zeolites) and MgA1, MgA4, MgA8 (MgA zeolites) and in each case the numbering 1, 4 and 8 respectively stood for 1 hr, 4 hrs and 8 hrs of the ion-exchange at either 30 °C or 60 °C.
The Temperature programmed desorption of CO$_2$ (CO$_2$-TPD) is currently one of the most used techniques to assess the interactions (strong or weak) between the CO$_2$ (adsorbate) and adsorbents such as zeolite-A investigated in this thesis. Three interaction sites can be distinguished in the CO$_2$-TPD profiles depending upon the temperature of desorption of the adsorbate. These are namely, weak, medium and strong strength sites respectively at low, medium and high desorption temperature (Bastiani et al., 2004). The physisorption process entails weak interactions (low desorption temperature peaks), and mostly van-der-waals forces whereas chemisorption involves strong interactions (medium and high desorption temperature peaks) (Napolitano et al., 2011). Thus, the CO$_2$-TPD was performed in this study to determine the CO$_2$ capacity and strength of sites of fly ash NaA zeolite and ion-exchanged zeolites. The CO$_2$-TPD was achieved on Micromeritics AutoChem II 2920 as set out in section 3.10.5.1 of chapter three.

Since the thermal conductivity detector (TCD) in this study was only zeroed rather than calibrated due to instrument constraints, the CO$_2$ desorption thermogram profiles generated were integrated using PeakFit v4.12 software (Gaussian assimilation) in order to estimate the relative amount of CO$_2$ adsorbed on each zeolite. An overall comparative discussion will be also given at the end of this section for all the ion-exchanged zeolites as shown in Figures 4.36 and 4.37.
4.4.1 CO$_2$-TPD profile of the parent NaA zeolite

Figure 4.26 shows the full range (40-700 °C) thermogram profile of CO$_2$ desorbed from the parent NaA zeolite.

Figure 4.26: CO$_2$-TPD profile of fly ash based NaA zeolite before the ion-exchange at either 30 °C or 60 °C with Li$^+$, Ca$^{2+}$ or Mg$^{2+}$ cations.

The thermogram profile of CO$_2$ desorbed from NaA zeolite (parent) revealed that the large amount of CO$_2$ was adsorbed at low temperature (40-150 °C) on weak strength sites which entail physisorption. The highest relative amount of about 0.45 a.u was achieved at low temperature whereas in the higher temperature region (150-700 °C), the amount of CO$_2$ did not exceed 0.04 a.u which indicated few medium and strong strength sites for NaA zeolite. The amount of CO$_2$ desorbed from the parent NaA zeolite will be discussed in comparison with other exchanged zeolite in the following sections.
Chapter Four

4.4.2 CO$_2$-TPD profiles of LiA zeolites

4.4.2.1 LiA zeolites exchanged at 30 °C

Figure 4.27 shows the low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash based zeolite NaA before and after the ion-exchange at 30 °C with Li$^+$ cation for 1 hr (LiA1), 4 hrs (LiA4) and 8 hrs (LiA8).

The desorption thermogram profiles of CO$_2$ adsorbed on fly ash NaA zeolite (parent) and LiA zeolites are shown in Figure 4.27. It can be observed that the large amount of CO$_2$ was desorbed from NaA at 63 °C compared to LiA zeolites which shifted slightly to higher temperatures displaying a major desorption peaks at about 80 °C. These desorption peaks in the low temperature region were attributed to physisorbed CO$_2$ on weak strength sites of the zeolites. The relative
amount of CO$_2$ desorbed from the parent NaA zeolite was about 0.45 a.u. while those for LiA zeolites comprised between 0.15-0.25 a.u.

The amount of CO$_2$ desorbed from weak strength sites of LiA1, LiA4 and LiA8 zeolites somewhat tended to decrease with the increase of the contact times used during the ion-exchange at 30 °C and was highest in the case of LiA1 samples. Moreover the decreased amount of CO$_2$ observed on these samples appeared to relate to the variation in Na/Al ratios (amount of Na left after consecutive exchanges) due to the heterogeneity of LiA zeolite samples since no total exchange was achieved (see section 4.3.3). Desorption thermograms of CO$_2$ were also assessed in the region of higher temperatures (150-700 °C) for medium and strong strength sites as shown in Figure 4.28. The thermogram profiles of CO$_2$ desorbed at higher temperature (150-700 °C) from LiA1, LiA4 and LiA8 zeolites revealed a uneven shaped desorption peak between 200 °C and 600 °C with a characteristic peak around 250 °C. The integration of each thermogram profile of CO$_2$ desorbed from LiA zeolites indicated that the highest amount of CO$_2$ was desorbed between 150 °C and 400 °C attributed to medium CO$_2$ strength sites. In this region, the largest amount of CO$_2$ was desorbed from LiA1 zeolite which showed a significant amount of medium strength CO$_2$ adsorption sites compared to the parent NaA zeolite (see full CO$_2$-TPD profile in Figure 4.26), LiA4 and LiA8 zeolites. The relative amount of 0.045 a.u was desorbed from LiA1 and 0.02 a.u for both LiA4 and LiA8. The higher amount of CO$_2$ observed in LiA1 zeolite seems to be related to the slight increment observed in the Li/Al ratios of this sample compared to LiA4 and LiA8 zeolites as discussed in section 4.3.3.1 of the EDS results. Besides the distinctive desorption peak around 250 °C observed in all LiA zeolites, another unique desorption peak was observed between 550 °C and 650 °C. This desorption peak was attributed to CO$_2$ desorbed from strong strength sites which were somewhat significant in LiA1 compared to LiA4 and LiA8 zeolites. In an attempt to improve CO$_2$ adsorption, the ion-exchange was also carried out at 60 °C and the thermogram profiles of CO$_2$ desorbed from LiA
zeolites for both low and high desorption peaks are presented and discussed in section 4.4.2.2.
Figure 4.28: High temperature (100-700 °C) fitted profiles of CO\textsubscript{2} desorbed from LiA1 (1 hr), LiA4 (4 hrs) and LiA8 (8 hrs) zeolites exchanged at 30 °C. For upper curves :(- - - -), is the original profile and (---) the integrated profile with peak Fit.
4.4.2.2  LiA zeolites exchanged at 60 °C

Figure 4.29 shows the low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash NaA zeolite before and after the ion-exchange at 60 °C with Li$^+$ cation at 1 hr (LiA1), 4 hrs (LiA4) and 8 hrs (LiA8).

![Graph showing CO$_2$ desorption profiles](image-url)

Figure 4.29: Low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash NaA zeolite before and after the ion-exchange at 60 °C compared with Li$^+$ cation at 1 hr (LiA1), 4 hrs (LiA4) and 8 hrs (LiA8).

The desorption thermogram profiles of CO$_2$ adsorbed on LiA zeolites obtained after ion-exchange at 60 °C are shown in Figure 4.29. These thermograms, in comparison with those obtained after the ion-exchange at 30°C also displayed a slight shift to higher temperature region. Moreover the amount of CO$_2$ desorbed at low temperature (40-150 °C) was somewhat lower than that of NaA and
reduced in these samples especially for LiA4 zeolite. This might imply that the higher temperature of 60 °C during the ion-exchange might have caused a decrease of weak strength sites of LiA zeolites obtained after the ion-exchange at 60 °C compared to those exchanged at 30 °C. Moreover, the least exchanged LiA1 zeolite tended to dominate with weak strength CO₂ sites compared to LiA4 and LiA8 zeolites. The thermogram profiles of LiA zeolites were also investigated in the region of high temperature (150-700 °C) for medium and strong strength CO₂ sites as shown in Figure 4.30. Thus, the thermogram profiles of LiA zeolites exchanged at 60 °C showed fairly high amounts of CO₂ desorbed from LiA4 and LiA8 zeolites compared to those obtained exchanged at 30 °C discussed in section 4.4.2.1. The amount of CO₂ desorbed from medium strength sites (150-400 °C) compared to those obtained at 30 °C and the parent NaA zeolite (see Figure 4.26), slightly increased with the increase of the contact times. This means that the ion-exchange at 60 °C created additional medium strength CO₂ sites in LiA zeolites responsible for the extra amount of CO₂. The higher increment of CO₂ desorbed from LiA4 zeolite might be as a result of the highest Li loading (%) found in this sample as determined using EDS discussed in section 4.3.3.1. Finally, except in the case of LiA4, all LiA zeolites LiA1 and LiA8 showed relatively equivalent amount of strong strength CO₂ sites between 500 °C and 700 °C with a relative value of 0.025 a.u. This amount remained fairly similar to that obtained for LiA zeolites exchanged at 30 °C.
Figure 4.30: High temperature (100-700 °C) fitted profiles of CO₂ desorbed from LiA1 (1 hr), LiA4 (4 hrs) and LiA8 (8 hrs) zeolites exchanged at 60 °C. For upper curves: (——), is the original profile and (-----) the integrated profile with peak Fit.
4.4.2.3 Summary for CO$_2$ desorbed from LiA zeolites

The desorption thermogram profiles of CO$_2$ for LiA zeolites exchanged at either 30 °C or 60 °C revealed that the weak strength CO$_2$ sites were prevailing. The highest amount of CO$_2$ desorbed at low temperature (40-150 °C), related to the amount of Na cation remaining after the ion-exchange rather than the amount of Li loaded due to the heterogeneity of LiA samples. Furthermore, the parent fly ash NaA zeolite exhibited the highest amount of weak strength CO$_2$ sites with a relative amount of 0.45 a.u compared to maxima of 0.3 a.u and 0.2 a.u respectively for LiA zeolites exchanged at 30 °C and 60 °C. However at high temperature desorption region (150-700 °C), the CO$_2$ essentially desorbed from medium strength CO$_2$ sites (150-400 °C) and was independent of the contact time used during the ion-exchange (1 hr, 4 hrs, and 8 hrs) but depends upon the temperature (30 °C and 60 °C).

4.4.3 CO$_2$-TPD profiles of CaA zeolites

4.4.3.1 CaA zeolites exchanged at 30 °C

Figure 4.31 shows the low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash NaA zeolite before and after the ion-exchange at 30 °C with Ca$^{2+}$ cation at 1 hr (CaA1), 4 hrs (CaA4) and 8 hrs (CaA8).
As can be observed in Figure 4.31, the amount of CO$_2$ desorbed from weak sites at low temperature (40-150 °C) was large in the parent fly ash NaA zeolite compared to all CaA zeolites. The amount of CO$_2$ desorbed from weak sites of CaA zeolites appeared to decrease with the increase in contact time. Thus, the highest amount of CO$_2$ desorbed was found in CaA1 zeolite (exchanged at 1 hr) with a relative amount of 0.35 a.u slightly lower than 0.45 a.u found in the parent NaA zeolite. Furthermore, the amount of CO$_2$ desorbed from weak sites in CaA zeolites exchanged at 30 °C was slightly higher compared to that desorbed in LiA zeolites discussed in section 4.4.2. The thermogram profiles of CO$_2$ desorbed from CaA zeolites are also shown in Figure 4.32 for medium and strong strength CO$_2$ sites in the region of high temperature desorption (150-700 °C).
Figure 4.32: High temperature (100-700 °C) fitted profiles of CO$_2$ desorbed from CaA1 (1 hr), CaA4 (4 hrs) and CaA8 (8 hrs) zeolites exchanged at 30 °C. For upper curves: (——), is the original profile and (---) the integrated profile with peak Fit.
As can be seen in Figure 4.32, the thermogram profiles of CO₂ desorbed at high temperature between 100 °C and 700 °C revealed that the large amount of CO₂ mainly desorbed from the strong sites (400-650 °C) which were more prevalent compared to medium sites (150-400 °C) for all CaA zeolites and far higher than those observed in the parent NaA zeolite (see Figure 4.26). The CO₂ desorption peaks, in particular those between 400-650 °C (strong sites) appeared to be characteristic for all CaA zeolites and may be due to both the inherent characteristic and the location of the Ca²⁺ cation in the framework structure of zeolite-A (see also Figure 2.13) which may result in high CO₂ desorption observed. The highest amount of CO₂ for strong sites was desorbed from CaA8 (8 hrs) with a relative amount of about 0.085 a.u while CaA4 (4 hrs) showed significant amount of medium CO₂ strength sites with about 0.04 a.u. Among other CaA zeolites, CaA8 zeolite tended to display the highest amount of strong CO₂ sites. The large amounts of CO₂ adsorbed at high temperature (100-700 °C) especially those observed on strong sites in all CaA zeolites were assigned to the formation of carbonate like complexes which generally occur above 300 °C (Martin-Calvo et al., 2014). These CO₂ amounts may correspond to the FT-IR vibration bands observed at 1465 cm⁻¹ after the CO₂-TPD analysis cycle in the FT-IR of spectra CaA zeolites as shown in Figure 7.1 (B) of the appendices. Similar FT-IR bands for mono-dental carbonates formation in zeolites were also reported by Stevens et al., (2008). The CO₂ desorption observed at higher temperature for CaA zeolites was due to the strong interactions which exist between the framework structural of CaA zeolite and CO₂ molecule compared to MgA zeolites (Bae et al., 2013). This may explain why MgA and LiA zeolites did not show carbonates bands in the FT-IR spectra after the CO₂-TPD analysis cycle as respectively shown in Figure 7.1 (A) and (C) in the appendices. Moreover, the amount of CO₂ desorbed especially at 450 °C and 550 °C was found to correspond with the Ca loading observed from EDS results discussed in section 4.3.3.2 (see Figure 4.20), which showed higher Ca/Al ratio in CaA8 (0.63:1) compared to CaA4 (0.59:1) and CaA1 (0.56:1). The ion-exchange was also carried
out at 60 °C in attempt to improve Ca$^{2+}$ loading and the thermogram profiles of CO$_2$ desorption from CaA zeolites exchanged at 60 °C are discussed in section 4.4.3.2.

4.4.3.2 CaA zeolites exchanged at 60 °C

Figure 4.33 shows the low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash based zeolite NaA before and after the ion-exchange at 60 °C with Ca$^{2+}$ cation for 1 hr (CaA1), 4 hrs (CaA4) and 8 hrs (CaA8).

Figure 4.33: Low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash based zeolite NaA before and after the ion-exchange at 60 °C with Ca$^{2+}$ cation for 1 hr (CaA1), 4 hrs (CaA4) and 8 hrs (CaA8).

The thermogram profiles of CO$_2$ desorbed from CaA zeolites exchanged at 60 °C compared to those obtained from samples prepared at 30 °C as shown in Figure 4.33 indicated that the large amount of CO$_2$ that was weakly desorbed between 40-150 °C is again observed. Furthermore the amount of weak CO$_2$ sites inversely
increased with decrease in Na/Al ratios discussed in Figure 4.3.3.2 of the EDS. However the relative amount of CO$_2$ desorbed from CaA zeolites exchanged at 60 °C tended to increase with the increase of the contact time and CaA8 (8 hrs) showed the highest amount of weak CO$_2$ strength sites of about 0.4 a.u slightly lower than 0.45 a.u found in the parent NaA zeolite. The slight increment in weak sites observed in CaA zeolites exchanged at 60 °C in particular for CaA8 may imply that additional weak sites might be created on CaA zeolites after the ion-exchange at 60 °C. The thermogram profiles of CO$_2$ desorbed from CaA1, CaA4 and CaA8 Ca zeolites exchanged at 60 °C are also presented in Figure 4.34 for high temperature desorption region.
Figure 4.34: High temperature (100-700 °C) fitted profiles of CO$_2$ desorbed from CaA1 (1 hr), CaA4 (4 hrs) and CaA8 (8 hrs) zeolites exchanged at 60 °C. For upper curves: (____) is the original profile and (——) the integrated profile with peak Fit.
The thermogram profiles of CO\(_2\) desorbed from CaA1, CaA4 and CaA8 zeolites at high temperature are shown in Figure 4.34. These thermograms compared to those obtained at low temperature discussed in section 4.4.3.1 have shown increments for both medium (150-400 °C) and strong (400-600 °C) CO\(_2\) strength sites. The CO\(_2\) desorption peaks between 400-650 °C (strong sites) as discussed also in section 4.3.2.1 may be due to both the inherent characteristic and the location of the Ca\(^{2+}\) cation in the framework structure of zeolite-A (see also Figure 2.13) which may result in high CO\(_2\) desorption observed. The highest amount of CO\(_2\) desorbed from CaA zeolites on medium strength sites that were mainly located between 250 °C and 400 °C. The relative amount of CO\(_2\) desorbed on medium sites comprised between 0.01 a.u and 0.06 a.u with a maximum amount reached in CaA4 that was slightly higher than the maximum amount of 0.04 a.u observed in CaA zeolites exchanged at 30 °C. In addition to the medium CO\(_2\) strength sites (150-400 °C), all Ca zeolite-A samples showed prevalent strong CO\(_2\) adsorption sites between 500 °C and 600 °C. However the amount of CO\(_2\) desorbed in this region compared to that observed in CaA zeolites exchanged at 30 °C was somewhat lower. A maximum relative amount of about 0.085 a.u for CO\(_2\) desorbed on strong sites was reached in CaA zeolites exchanged 30 °C whereas those exchanged at 60 °C only showed a maximum of about 0.065 a.u. The trend shown by CaA zeolites appeared to correspond with the overall Ca loading % that was found to be higher for CaA zeolites exchanged at 30 °C than at 60 °C.

4.4.3.3 Summary for CO\(_2\) desorbed from CaA zeolites

The thermogram profiles of CO\(_2\) desorbed from CaA zeolites exchanged at either 30 °C or 60 °C clearly indicated that physisorption at low temperatures was the major phenomenon that accounted for CO\(_2\) adsorption on CaA zeolites. The significant amount of CO\(_2\) was mostly desorbed at low temperature (40-150 °C) which entails weak sites but was lower than the parent NaA zeolite. However at high temperature (150-700 °C) all CaA zeolites exchanged at either 30 °C or 60 °C
were significantly dominated by strong strength CO$_2$ sites compared to medium strength sites. Both medium and strong strength CO$_2$ sites observed at high temperature region were ascribed to the formation of carbonate like materials.

4.4.4 CO$_2$-TPD profiles of MgA zeolites

4.4.4.1 MgA zeolites exchanged at 30 °C

Figure 4.35 shows the low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash based zeolite NaA before and after the ion-exchange at 30 °C with Mg$^{2+}$ cation for 1 hr (MgA1), 4 hrs (MgA4) and 8 hrs (MgA8).

![Graph showing CO$_2$ desorption profiles](image)

Figure 4.35: Low temperature (40-150 °C) profiles of CO$_2$ desorbed from fly ash based zeolite NaA before and after the ion-exchange at 30 °C with Mg$^{2+}$ cation at 1 hr (MgA1), 4 hrs (MgA4) and 8 hrs (MgA8).
The thermogram profiles of CO$_2$ desorbed from fly ash NaA zeolite before and after the ion-exchange at 30 °C with Mg$^{2+}$ cation are presented in Figure 4.35. These thermograms compared to those obtained in LiA and CaA zeolites discussed in sections 4.4.2 and 4.4.3 respectively, and in particular LiA zeolites also revealed a slight shifting to higher temperature region. Moreover the large amount of CO$_2$ was mainly physisorbed on the MgA zeolites exchanged at 30 °C which may be due to the relative amount of Na$^+$ cations left after consecutive exchange. This amount of CO$_2$ appeared to decrease with the increase of the contact time employed during the ion-exchange. A relative amount of about 0.15 a.u was found in MgA8 (8 hrs) while about 0.4 a.u was found in MgA1 and MgA4 zeolites. The amount of about 0.4 a.u found in MgA1 and MgA4 was similar to that obtained in CaA zeolites in the region of low temperature (40-150 °C). This may indicate that the ion-exchange at 30 °C maintained the number of weak strength CO$_2$ adsorption sites with Mg$^{2+}$ cation relatively to the parent NaA zeolite. The thermograms of CO$_2$ desorbed from MgA zeolites exchanged at 30 °C are also shown in Figure 4.36 for the region of high temperature CO$_2$ desorption (150-700 °C) in order to evaluate the medium and strong strength CO$_2$ sites. Thus, at high temperature the medium strength sites (150-600 °C) in MgA zeolites, dominated the overall CO$_2$ adsorption as in LiA zeolites compared to the parent NaA zeolite (see full profile in Figure 4.26) and CaA zeolites. The desorption peak observed at 350 °C appeared to be characteristic in all MgA zeolites and may be due to both the inherent characteristic and the location of the Mg$^{2+}$ cation in the framework structure of zeolite-A (see also Figure 2.13) which might resulted high CO$_2$ desorption observed at this temperature. The relative amount of CO$_2$ desorbed from medium strength sites region ranged between 0.03 a.u and 0.045 a.u and the highest amount of CO$_2$ was desorbed from MgA8 zeolite. This higher amount corresponded to high loading (%) of Mg which was found to be higher in MgA8 zeolite through the EDS analysis discussed in section 4.3.3.3.1. Finally, in contrast with the thermogram profiles of CO$_2$ obtained from CaA zeolites, the MgA zeolites did not display a significant amount of CO$_2$.
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desorbed from strong CO$_2$ adsorption sites (400-700 °C). This means that CO$_2$ mainly adsorbed on medium sites in MgA zeolites rather than strong sites. This performance demonstrated by MgA zeolites was interesting in terms of the regeneration energy compared to CaA zeolites which tended mainly to display strong CO$_2$ adsorption sites.
Figure 4.36: High temperature (100-700 °C) fitted profiles of CO$_2$ desorbed from MgA1 (1 hr), MgA4 (4 hrs) and MgA8 (8 hrs) zeolites exchanged at 30 °C. For upper curves: (---), is the original profile and (—) the integrated profile with peak Fit.
The ion-exchange with Mg\textsuperscript{2+} cation was also performed at 60 °C in attempt to improve the adsorption capacity of CO\textsubscript{2} and the thermograms of CO\textsubscript{2} desorption from MgA zeolites exchanged at 60 °C are discussed in section 4.4.4.2 below.

### 4.4.4.2 MgA zeolites exchanged at 60 °C

Figure 4.37 shows the low temperature (40-150 °C) profiles of CO\textsubscript{2} desorbed from fly ash NaA zeolite and MgA1, MgA4 and MgA8 zeolites obtained through the ion-exchange procedure at 60 °C after 1 hr, 4 hrs and 8 hrs respectively.

As can be seen in Figure 4.37, these results indicated that the amount of CO\textsubscript{2} desorbed from weak sites at low temperature (40-125 °C) decreased as a function of the temperature of the ion-exchange as well as the contact time. This is shown by a low amount of weak CO\textsubscript{2} sites in MgA8 (low desorption peak) compared to
MgA1 and MgA4 zeolites (intense desorption peak). The variation the lower temperature peak in these samples corresponded to the decrease observed in the Na/Al ratios (remained Na\(^+\) cation after exchanges) which were discussed in section 4.3.3.3 of the EDS. In contrast with the thermogram profiles of CO\(_2\) obtained at low temperature (40-150 °C) for MgA zeolites exchanged at 30 °C, the amount of weak CO\(_2\) sites slightly decreased in MgA1 and MgA4 zeolites and remained approximately constant for MgA8 zeolite. This means that the increase in temperature at 60 °C during the ion-exchange appeared to modify the surface of the MgA zeolites by reducing the number of weak CO\(_2\) strength sites. The relative amount of CO\(_2\) desorbed from MgA zeolites ranged between 0.15 a.u and 0.3 a.u. This amount was slightly lower than the range of 0.15 a.u and 0.4 a.u found in MgA zeolites exchanged at 30 °C. The thermogram profiles of CO\(_2\) desorbed from MgA zeolites were also assessed at high temperatures (150-700 °C) for medium and strong strength CO\(_2\) sites as shown in Figure 4.38.
Figure 4.38: High temperature (100-700 °C) fitted profiles of CO$_2$ desorbed from MgA1 (1 hr), MgA4 (4 hrs) and MgA8 (8 hrs) zeolites exchanged at 60 °C. For upper curves: (—) is the original profile and (— — ) the integrated profile with peak Fit.
As can be seen in Figure 4.38, the thermogram profiles of CO$_2$ desorbed from MgA zeolites at high temperatures showed prominent medium CO$_2$ desorption sites between 250 °C and 400 °C compared to the amount CO$_2$ observed in the parent NaA zeolite (see full profile of NaA in Figure 4.26). The peak observed at 350 °C as also discussed in section 4.4.4.1 may be due to both the inherent characteristic and the location of the Mg$^{2+}$ cation in the framework structure of zeolite-A (see also Figure 2.13) which might have resulted in higher CO$_2$ desorption observed at this temperature. The MgA8 zeolite tended to demonstrate a higher amount of medium strength CO$_2$ sites compared to MgA1 and MgA4 zeolites. The relative amount of CO$_2$ desorbed at 350 °C was about 0.035 a.u for MgA1 and MgA4, and was about 0.06 a.u. in MgA8 zeolite. The amount of CO$_2$ desorbed in MgA8 prepared at 60 °C slightly increased compared to that obtained for MgA8 zeolite exchanged at 30 °C. This means that additional medium strength CO$_2$ adsorption sites may be created after the ion-exchange at 60 °C. This amount of medium sites was somewhat equivalent to the amount obtained in CaA4 zeolite prepared at 60 °C (highest) and was lower compared to LiA4 also prepared at 60 °C. Finally, all MgA zeolites exchanged at 60 °C once again, did not demonstrate significant amount of strong CO$_2$ sites compared to CaA zeolites exchanged at either 30 °C or 60 °C. This shows that the desorption of CO$_2$ from MgA zeolites exchanged at either 30 °C or 60 °C occurred essentially on medium strength sites making these fly based zeolites to some extent suitable in terms of their regeneration with lower energy cost compared to CaA zeolites.

4.4.4.3 Summary for CO$_2$ desorbed from MgA zeolites

The thermogram profiles of CO$_2$ desorbed from MgA zeolites exchanged at either 30 °C or 60 °C revealed that, the physisorption which entails weak interactions (weak sites) was the major phenomenon observed in MgA zeolites. The main amount of CO$_2$ was desorbed in the least exchanged MgA zeolites (MgA1 and MgA4) at low temperatures (40-150 °C) at either 30 °C or 60 °C but this was also less than the amount desorbed from the parent NaA zeolite. However at high
temperature region (150-700 °C), all the MgA zeolites did not display remarkable strong CO\textsubscript{2} sites compared to Ca zeolite-A. The medium strength CO\textsubscript{2} sites dominated and increased with the increase of the contact time at either 30 °C or 60 °C in all the MgA zeolites.

4.4.4.4 Summary of CO\textsubscript{2}-TPD analysis

The thermogram profiles of CO\textsubscript{2} desorbed from various cation exchanged fly ash based zeolites are compared and summarised in Figures 4.39 and 4.40 for samples exchanged respectively at 30 °C and 60 °C. The peak areas reported in Figures 4.39 and 4.40 were determined using Peak Fit v4.12 technique.

Figure 4.39: Share of CO\textsubscript{2} desorbed from weak strength sites (WSS); medium strength sites (MSS) and strong strength sites (SSS) of NaA zeolite (parent) and LiA, CaA and MgA zeolites exchanged at 30 °C.
The conclusion drawn was that the adsorption of CO$_2$ on LiA, CaA and MgA zeolites was mostly induced by the inherent characteristic of each cation rather than the contact time and the temperature. The integration of peak area of the thermograms was employed using Peak Fit v4.12 technique to evaluate the amounts of CO$_2$ adsorbed (Bastiani et al., 2004, Yu et al., 2014). The results from the integration of peak areas of CO$_2$ desorption profiles for LiA, CaA and MgA zeolites exchanged at either 30 °C or 60 °C, are compared in Figures 4.39 and 4.40 and indicated that the physisorption process was the major phenomena observed rather than chemisorption for all cations. This implies that LiA, CaA and MgA
zeolites exchanged at either 30 °C or 60 °C may be suitable for low temperature swing adsorption application since the highest amounts of CO$_2$ were desorbed from weak strength sites (WSS) at low temperature but NaA had the highest capacity for low temperature adsorption of CO$_2$. Besides the amounts of CO$_2$ desorbed from WSS at low temperature, only a small amount of CO$_2$ desorbed at higher temperature in all cases of either 30 °C or 60 °C. CO$_2$ desorption at higher temperature essentially occurred at strong strength sites (SSS) for all CaA zeolites while LiA and MgA zeolites were dominated with medium strength sites (MSS). The CO$_2$ desorption peaks observed on MSS and SSS tended to relate to the inherent characteristic and the location (framework structure of zeolite-A) of each cation exchanged. The temperatures at which CO$_2$ desorbed from MSS and SSS especially for CaA and MgA zeolites indicated the formation of carbonate like complexes (Martin-Calvo et al., 2014). Considering the amount of CO$_2$ chemisorbed upon MSS and SSS, the CaA zeolites displayed the highest amount of CO$_2$ capture and the following desorption order was observed: CaA > MgA > LiA ≈ NaA. The conclusion drawn was that, CaA zeolites were the most suitable for chemisorption and longer term sequestration of CO$_2$ due to the high amount of CO$_2$ captured and only released at high temperature but it could require much more energy in terms of short term CO$_2$ storage compared to NaA or LiA and MgA exchanged zeolites.
5. GENERAL CONCLUSIONS

This chapter gives a general summary of the main findings of this work which are answers to the questions and the objectives set in this thesis. Some recommendations will also be laid out for future work regarding this topic.

5.1 Conclusions

This study has reaffirmed that pure phase NaA zeolite can be prepared from South African class F fly ash sourced from Arnot coal power plant since its chemical composition is predominated by Al₂O₃ and SiO₂. The NaA zeolite was used as starting material for the ion-exchange. In this study the NaA zeolite obtained from the hydrothermal synthesis was subjected to a series of ion-exchange protocols with Li⁺, Ca²⁺ or Mg²⁺ cations in order to improve the adsorption of CO₂. This study aimed to develop zeolite-A adsorbents from South African coal fly ash for CO₂ adsorption or sequestration that can be applied in power station flue gas plants. In order to address the aims and objectives set in this study, some research questions were set in section 1.8 of chapter one and their answers are drawn in the conclusions of this study. The questions set were as follows:

Q1: What impact do different selected cations have on the structure of fly ash based zeolite? And does the respective cation (Na⁺, Li⁺, Ca²⁺, and Mg²⁺) influence this?

This study has shown through the X-ray diffraction patterns and IR spectra that the structural integrity of fly ash based zeolite-A was maintained at all conditions applied except for some slight changes noted at high temperature and extended
times for Ca$^{2+}$ and Mg$^{2+}$ cations as noted on FT-IR spectra. However each cation revealed unique structural modifications which were independent of applied temperatures, contact time and consecutive exchanges employed during the ion-exchange process. The changes observed on the ion-exchanged zeolites-A, were mainly induced by the intrinsic characteristic of Li$^+$, Ca$^{2+}$ and Mg$^{2+}$ cations. The XRD and IR results demonstrated that a bigger cation in terms of the atomic radius resulted in a decrease of the XRD peak intensities of fly ash based zeolite-A. This was shown by higher peak intensities observed for LiA zeolites and followed this order: LiA > MgA > CaA. In addition, the decrease in intensity was shown to correspond to the changes observed by FT-IR in the D4R and S6R region of zeolite-A for CaA and MgA zeolite samples. Furthermore, LiA zeolite displayed a characteristic peak shifting between 2θ peak values 20-60° for either 30 °C or 60 °C compared to CaA and MgA zeolites. The vibration at 677 cm$^{-1}$ was characteristic to each cation and was shown to significantly increase (LiA > MgA ≈ NaA > CaA) with the decrease in atomic radius of the cation loaded.

Q2: Can the ion-exchange procedure using different cations be optimized for fly ash based zeolite-A?

This study has shown that the ion-exchange was mostly driven by the inherent characteristic of the cation. The temperature of 60 °C and 4 hrs was found to be suitable condition to exchange either Li$^+$ or Mg$^{2+}$ cation whereas Ca$^{2+}$ cation demonstrated good loading at lower temperature of 30 °C for 4 hrs. The multiple exchanges employed during the ion-exchange significantly contributed to the removal of the host Na$^+$ but did not always correspond to higher loading of the guest cation. The longer period of 8 hrs during the ion-exchange did not correspond to higher exchange of either Li$^+$, Ca$^{2+}$ or Mg$^{2+}$ cation and was found to be energy and time consuming compared to 1 hr and 4 hrs which were minimum but effective. The optimum condition of cation exchange procedure was observed at 4 hrs with three consecutive exchanges for all cations. However 60 °C as mentioned above was suitable in the case of Li$^+$ and Mg$^{2+}$ cations and 30
°C for Ca\(^{2+}\) cation. However in no case was the Na\(^{+}\) cation entirely removed. This is probably due to its location at different sites in the pseudo cell of zeolite-A as was discussed in section 2.9.2.3 of chapter two.

Q3: To which extent, and under which conditions can the host cation Na\(^{+}\) be exchanged with Li\(^{+}\), Ca\(^{2+}\) or Mg\(^{2+}\) cations in fly ash based zeolite-A and, what is the optimum cation uptake capacity?

The EDS was chosen as the main technique of elemental analysis because of its availability and also due to the instrument constraint met for ICP analysis in this study. The loading of cations were expressed in terms of percentage of exchange and ratios. The study revealed that the Li, Mg atoms were not able to displace much of the host Na atom compared to the Ca atom which caused the highest removal of the Na atom from the parent fly ash NaA zeolite. The temperature of 60 °C during the ion-exchange was found to be the optimum condition to exchange Li and Mg at 4 hrs with three consecutive exchanges whereas 30 °C for 4 hrs was the optimum for Ca exchange. The highest Li/Al ratios of 1:1 were found after the ion-exchange at 60 °C whereas about 0.4:1 and 0.6:1 were the limit reached in this study for Mg/Al and Ca/Al ratios respectively for either 30 °C or 60 °C. These ratios were often found to be half of 1:2 ratios commonly cited for divalent cation substitution in zeolite. The conclusion drawn was that, the type and valence of the divalent cations affected the amount taken up and also the remaining Na\(^{+}\) cation might have caused heterogeneity due to poor removal of the host cation. Thus finding the best conditions for the ion-exchange is imperative. The study has shown that ion-exchange protocols required careful optimization for each guest cation to be fully exchanged.

Q4: Is CO\(_2\) adsorption onto fly ash based exchanged zeolite-A, a physisorption or chemisorption process?

The CO\(_2\)-TPD thermogram profiles of the fly ash NaA zeolite and ion-exchanged zeolites-A investigated in this study, indicated that both physisorption and
chemisorption of CO$_2$ were occurring due to heterogeneity caused by incomplete or partial exchange observed after the ion-exchange. However, the highest amount of CO$_2$ for each cation loaded onto zeolite-A was weakly adsorbed at low temperature between 40-150 °C (physisorption). The parent fly ash NaA zeolite showed the highest amount of weak strength CO$_2$ sites at low temperature compared to all the ion-exchanged zeolite-A samples and was suitable for PSA. Finally at temperatures between 150-650 °C, it was found that LiA and MgA zeolite samples were dominated by medium adsorption strength sites (< 400 °C) which showed significant CO$_2$ desorption peaks between 150-400 °C whereas CaA zeolite samples prevailed with strong strength sites (400-650 °C). The small amount of CO$_2$ desorbed between 150-650 °C from both medium and strong strength sites were attributed to the formation of carbonate like complexes (chemisorption). The carbonate band which appeared at 1465 cm$^{-1}$ in the FT-IR spectra after the CO$_2$-TPD analysis cycle were significant in CaA zeolites compared to MgA and LiA zeolites which did not show carbonate bands (see Figure 7.1 in the appendices).

Q5: Which cation (Na$^+$, Li$^+$, Ca$^{2+}$, and Mg$^{2+}$) allows the greatest CO$_2$ capture in terms of physisorption or chemisorption?

Apart from the amounts of CO$_2$ adsorbed at lower temperature (40-150 °C) where the parent fly ash NaA zeolites prevailed; the ion-exchanged zeolites-A only demonstrated distinguishing CO$_2$ adsorption thermograms at higher temperature (150-700 °C) where medium and strong interactions occurred. Thus, Gaussian integration of CO$_2$-TPD thermogram profiles at higher temperature (150-700 °C) using PeakFit software revealed that CaA zeolite samples displayed the highest peak areas in this region which indicated that a considerable amount of CO$_2$ was chemisorbed on CaA zeolite samples rather than upon other modified zeolites. The increase in peak areas which corresponds to the amount of CO$_2$ desorbed at higher temperatures follows the order: CaA > MgA > LiA ≈ NaA. The conclusion drawn was that, CaA zeolites were the most suitable for
chemisorption and sequestration of CO$_2$ due to the high amount of CO$_2$ captured but only released at high temperature. However CaA could require much more energy in terms of short term CO$_2$ storage for the regeneration process compared to LiA and MgA zeolite samples. The study showed also that, NaA zeolite does not need modification and can be used as made most effectively if the goal is CO$_2$ capture for separation and recovery.

### 5.2 Novelty of the findings

The results of this study have proved that:

- The peak intensities of the fly ash NaA zeolite increases with the decrease of the atomic radius of cation exchanged.
- The longer contact time during the ion-exchange (8 hours) does not improve the loading capacity of cations.
- The temperature is not the main force driving the ion-exchange but rather the intrinsic characteristic of the cation.
- The multiple exchanges contributed to the degree of removal of the host Na$^+$ cation. The Ca$^{2+}$ cation was found to be suitable for the removal of host Na$^+$ cation in NaA zeolite.
- The CO$_2$ adsorption in fly ash based Na, Li, Ca and Mg zeolites-A is essentially predominated by physisorption (weak strength sites) rather than chemisorption (medium and strong strength sites) and fly ash based NaA zeolite did not need modification to be useful in this application.

### 5.3 Recommendations and future work

The narrow scope of this study has left areas where further research is needed regarding this topic.

The ion-exchange procedure was carried out in a comparative set of 1 hr, 4 hrs and 8 hrs in this study. This has confirmed that the longer exchange of 8 hrs was
time and energy consuming and 1 hr and 4 hrs were found to be suitable conditions for the ion-exchange depending upon the type of the cation. A similar investigation should be done in order to optimize these contact times and extend the study to other cations than Li\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) to improve the CO\(_2\) adsorption capacity. Three repeated exchanges improved the removal of the Na\(^+\) cation but as it was still not completely removed, the possibility exists that further exchanges may be needed.

Having investigated and confirmed CO\(_2\) loading capacity through TPD using Gaussian integrations for Li, Ca and Mg based zeolite-A thermogram profiles between 40-700 °C; a similar investigation should be done using the same conditions used in this study for CO\(_2\)-TPD system with TCD calibrated to determine the absolute concentration (mol/L) of CO\(_2\). This has to confirm also whether the CO\(_2\) capacity calculated (peak surface integrations) for NaA, LiA, CaA and MgA fly ash based zeolites using Gaussian approach can or not be correlated to the amount of CO\(_2\) in the system with TCD calibrated.

For future work, the fly ash based Na, Li, Ca and Mg zeolite-A catalysts prepared in this study should be analysed by NMR to investigate the extra-framework Al cation after the ion-exchange. Moreover the ion-exchanged zeolite samples should be tested for a cyclic process (regeneration) and also for a mixture of gases in order for them to be applied in a power plant station for CO\(_2\) separation and adsorption. This step will also need an up scaling system where considerable amount of fly ash based zeolite-A can be pumped in a column and tested under conditions relevant to post-combustion flue gases. The negative effect of moisture in CO\(_2\) uptake is documented and the NaA zeolite could also be used to dry the flue gas stream prior to CO\(_2\) capture, thus its uptake capacity for moisture should be determined.
6. REFERENCES


Chapter Six


Chapter Six


Chapter Six


Intergovermental panel for climate change (IPCC) Special Report on Carbon dioxide Capture and Storage. 2007


Chapter Six


Chapter Six


Chapter Six


Richard’s Bay Coal Terminal (www.rbct.co.za)


Chapter Six


Chapter Six


Weiland RH, Dingman JC, Cronin DB. (1997). Heat capacity of aqueous monoethanolamine, diethanolamine, N-methylidethanolamine, and N-
methyltriethanolamine-based blends with carbon dioxide; *Journal of Chemical Engineering*. 42:1004-1006.


www.worldcoal.org (world coal institute, 2009).


www.undp.org


7. APPENDICES

7.1 Calculations of ratios

For all the fly ash based NaA, LiA, CaA and MgA zeolites investigated in this study in order to obtain the ratios discussed, consider: row 1, 2 and 4 over row 2 from table 7.1-7.6.

A. LiA based zeolites

Table 7.1: EDS results obtained from LiA zeolites exchanged at 30 °C

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<th>Raw</th>
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<th>Li433</th>
<th>Li813</th>
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<th>Li833</th>
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<td>Li</td>
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<td>15.9</td>
</tr>
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<td>14.7</td>
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<td>14.5</td>
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<td>15</td>
<td>14.9</td>
<td>14.9</td>
<td>15.7</td>
</tr>
</tbody>
</table>

(*): The parent fly ash zeolite NaA before the ion-exchange at either 30 °C or 60 °C with Li⁺ cation. The numbering next to Li respectively indicates the contact time (1 h, 4 hrs, 8 hrs), the exchanges (1, 2, 3) and the temperature (3=30 °C and
6=60 °C). These EDS results were obtained in duplicate and in each case an average of six spots analysis on zeolite specimen was calculated to obtain the current values.

B. CaA based zeolites

Table 7.3: EDS results obtained from CaA zeolites exchanged at 30 °C

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<td>12.93</td>
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Table 7.4: EDS results obtained from CaA zeolites exchanged at 60 °C

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(*): The parent fly ash zeolite NaA before the ion-exchange at either 30 °C or 60 °C with Ca$^{2+}$ cation. The numbering next to Ca respectively indicates the contact time (1 h, 4 hrs, 8 hrs), the exchanges (1, 2, 3) and the temperature (3=30 °C and
6=60 °C). These EDS results were obtained in duplicate and in each case an average of six spots analysis on zeolite specimen was calculated to obtain the current values.

C. MgA based zeolites

Table 7.5: EDS results obtained from MgA zeolites exchanged at 30 °C

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Table 7.6: EDS results obtained from MgA zeolites exchanged at 60 °C

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(*): The parent fly ash zeolite NaA before the ion-exchange at either 30 °C or 60 °C with Mg$^{2+}$ cation. The numbering next to Mg respectively indicates the contact time (1 h, 4 hrs, 8 hrs), the exchanges (1, 2, 3) and the temperature (3=30 °C and 6=60 °C). These EDS results were obtained in duplicate and in each case an average of six spots analysis on zeolite specimen was calculated to obtain the current values.
7.2 Calculations of % XRD crystallinity (I: intensity of XRD peaks)

\[
\% \text{ XRD(crystallinity)} = \frac{\Sigma I \text{ (sample)}}{\Sigma I \text{ (standard)}} \times 100 \%
\]  

(7-1)

Figure 7.1: FT-IR spectra of fly ash based zeolite-A samples obtained after CO₂-TPD analysis on samples exchanged at 30 °C (A) or 60 °C (B) and NaA (parent).