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Review of Carbon Dioxide Capture and Storage With Relevance to the South African Power Sector

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Abstract

The issue of carbon dioxide emissions and its link to climate change is currently a major discussion point in government and amongst the public at large in South Africa, especially due to the country's heavy reliance on fossil fuels for electricity production. This paper provides a review on the current situation regarding carbon dioxide (CO₂) emissions in the South African power generation sector, and potential process engineering solutions to reduce these emissions. Estimates of CO₂ emissions are presented, with the main sources of emissions identified and bench-marked to other countries. A promising mid-term solution for mitigation of high CO₂ emissions, known as carbon dioxide capture and storage (CCS), is reviewed. The various aspects of CCS technology and techniques for CO₂ capture from pulverised coal power plants are discussed, which include processes such as gas absorption, hydrate formation, cryogenic separation, membrane usage, sorbent usage, enzyme-based systems, and metal organic frameworks. The latest power plant designs which optimise CO₂ capture are also discussed and include integrated gasification combined cycle (IGCC), oxy-fuel combustion, integrated gasification steam cycle (IGSC), and chemical looping combustion. Each CO₂ capture technique and plant modification is presented in terms of the conceptual idea, the advantages and disadvantages, and the extent of development and applicability in a South African context. Lastly, CO₂ transportation, storage, and potential uses are also presented. The main conclusions of the review are that gas absorption using solvents is currently most applicable for CO₂ capture and that enhanced coal bed methane recovery could provide the best disposal route for CO₂ emissions mitigation in South Africa.

Keywords: Carbon Dioxide; Capture; Storage; Emissions; South Africa

1. Introduction

There has been a nearly 100% increase in worldwide CO₂ emissions since 1971. This is of great concern to scientists, governments, and the public in general as there is general consensus from the greater scientific community that CO₂, which is a greenhouse gas, is one of the main contributors to rapid climate change^[1] experienced globally, especially in the last few decades.

Globally, almost 78–83% of CO₂ emissions can be attributed to electricity generation using fossil fuels^[2]. In South Africa the situation is no different with almost 93% of the country's electricity needs provided by fossil fuels; with 77% specifically provided by coal power plants^[3,4]. Due to the country's abundant coal reserves, the use of relatively inexpensive coal-derived power is unlikely to cease in the next 200 years^[3]. Coal power plant operations have resulted in South Africa's power sector being the 9th highest CO₂ emitting power sector in the world, with an estimated 218 mega tonnes (Mt) of CO₂ emitted each year^[4,5]. Eskom Ltd., the country's primary electricity utility, is currently the 2nd highest CO₂ emitting company in the world, due to its utilisation of pulverised coal (PC) combustion plants.

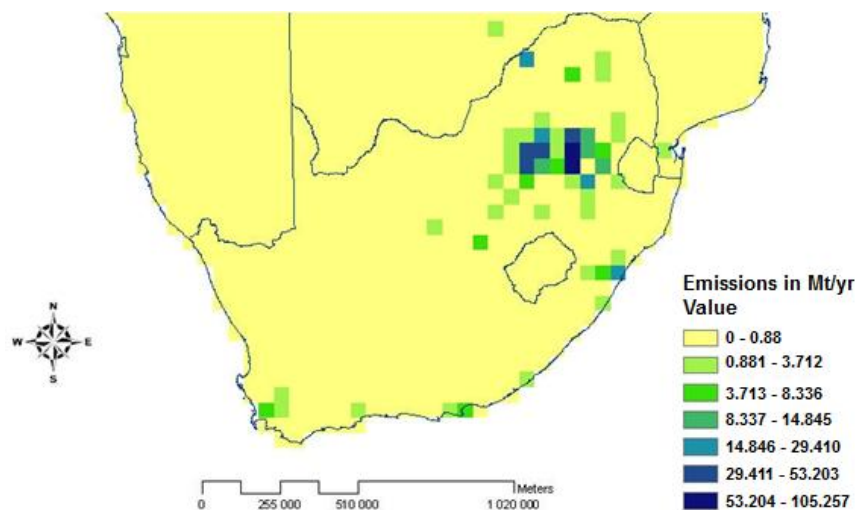


Figure 1: Main CO₂ emission point sources in South Africa^[6]

As can be seen in Figure 1, the most significant CO₂ emission sources in South Africa are situated in the Gauteng, Mpumalanga, and Free State provinces. It is not surprising as this is the heart of South Africa's coal mining sector and the regions in which most of coal power plants are situated. Figure 1 however, does not limit the CO₂ emission data to just coal power

plants, but also includes coal-to-liquids (CTL) industries, gas-to-liquids (GTL) industries, and oil refining processes.

In an effort to reduce CO₂ emissions and encourage a move towards a cleaner energy strategy, the South African government is considering proposing a CO₂ emissions tax that would be levied on all CO₂ emission sources. Recent debates have estimated that a tax rate of R75 to R200 per tonne of CO₂ emitted; with the most recent and currently applicable cost being R120/tonne CO₂ in line with international standards^[7]. Considering that South Africa's energy industry emits well over 200 Mt of CO₂ per annum, the proposed levy will result in significant increases in operating costs for companies in this sector. With Eskom having over the last few years almost doubled its electricity tariff, the proposed carbon dioxide emission tax will further add to the need for Eskom to increase its tariff if it passes on this cost to the consumer. It is therefore imperative that solutions to reduce CO₂ emissions be found.

Carbon capture and storage (CCS) is a promising mid-term solution to reduce CO₂ emissions. This strategy involves capturing CO₂ at power plants and other industries before they are emitted, transporting CO₂ to suitable disposal locations, and either storing CO₂ underground or utilising CO₂ to retrieve high value products.

This review shall concentrate on coal power plant operations and their suitability for CCS technology. Techniques that are potentially applicable to CO₂ capture in coal power plants are presented, along with some discussion on CO₂ transportation, storage, and potential uses with specific relevance to South Africa.

2. Coal Power Plant Operations

Currently, South Africa possesses 14 pulverised coal (PC) power plants, seven of them being in the top 30 highest CO₂ emitting power plants in the world^[3,5].

A simplified schematic of a typical PC power plant is shown in Figure 2. In a PC power plant, coal is transported to a pulveriser via conveyor belts and crushed into a powder with a particle diameter of approximately 50 µm. Hot air then blasts the coal into a boiler where it is burnt. The heat generated is used to heat tubes containing water. These tubes can be kilometres long, but coiled in order to be compact^[8]. The water in the heat exchanger tubes is converted into superheated steam at high pressure. The steam is used to drive turbine blades

which spin the turbine. The turbine shaft is linked to a generator rotor, which generates electricity using an electromagnet^[8]. The electricity flows through transmission lines and transformers to reach consumers at the required voltages. The used steam is then cooled and condensed in cooling towers, and recycled to the boilers for reheating.

The gases that are released during the coal combustion are filtered using bag filters, to remove ash. If the gas mixture contains substantial sulphur and nitrogenous emissions, particularly SO_x and NO_x compounds, then desulphurisation and denitrification processes are also installed to remove them. The remaining gases are emitted through a stack as flue gas. Flue gas composition varies according to coal composition and power plant flue gas treatment processes. Typical composition of flue gases are approximately 13 vol% CO_2 , 68 vol% N_2 , 16 vol% water, 3 vol% O_2 , 200ppm SO_2 , 60ppm NO_x , and 60 ppm hydrocarbons, and the flue gas is typically emitted at pressures ranging from 1 to 1.7 bar and temperatures of 363.15–412.15 K^[9,10].

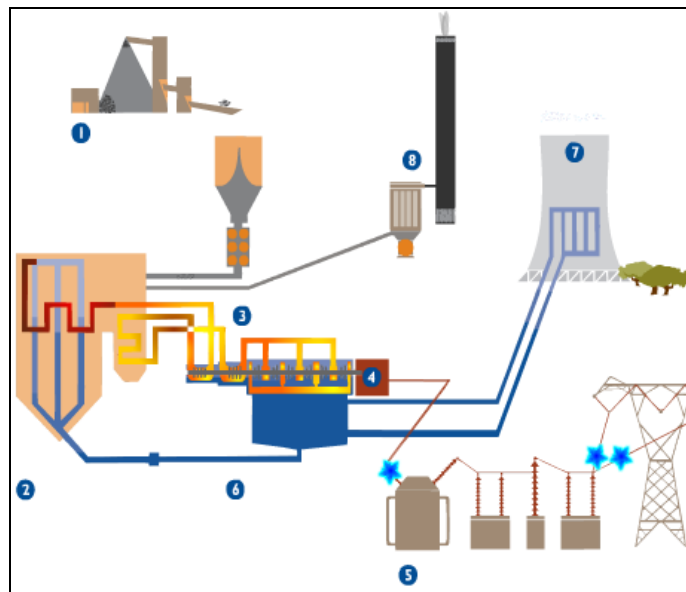


Figure 2: Pulverised coal (PC) power plant^[8]. 1- Coal heap; 2- Boilers; 3- Superheated steam in turbine; 4- Generator rotor; 5- Transmission lines; 6- Condensed H_2O ; 7- Cooling tower; 8- Stack

CO_2 removal from PC power plants entails retrofitting the power plant with a CO_2 capture process to treat the flue gas for selective CO_2 removal before it is emitted through the stack. This mode of CO_2 capture is known as post-combustion capture, since CO_2 capture occurs after coal combustion.

PC combustion is a well developed and common power plant process that requires a lower investment cost compared to newer technologies. However, CO₂ capture and compression is expensive since the flue gas to be treated is available at unfavourably low pressure and high temperature.

3. Techniques of Capturing CO₂ from PC Power Plants

Currently, there are many gas separation techniques under investigation for post-combustion CO₂ capture from PC power plants. This section explains the unique properties of CO₂ and presents CO₂ capture techniques which exploit these properties for efficient gas separation, despite the unfavourable conditions of post-combustion flue gas at the stack.

3.1 Solubility and pH of CO₂ in H₂O

The solubility of CO₂ in water is 0.9 vol CO₂/vol H₂O at 293.15 K^[11], forming weak carbonic acid. This however may change the pH of water to as low as 5.5^[12]. This is an important finding, as it suggests that CO₂ is more likely to act as an acid in acid-base reactions. This is vital information in the selection of solvents or sorbents which may be used to absorb or adsorb CO₂.

3.1.1 Gas Absorption using Solvents

The acidic nature of dissolved CO₂ in water dictates the types of physical and chemical solvents that would potentially be successful for efficient CO₂ absorption. Applicable chemical solvents include amine solvents and solutions, which result in CO₂ absorption by zwitterion formation and easy deprotonation by a weak base^[13]. Promising potential physical solvents include Amisol and Rectisol solvents^[2], and ionic liquids which consist purely of cations and anions. Huang and R  ther^[14] discovered that a Lewis-acid type interaction occurs between CO₂ and anions, with CO₂ acting as a Lewis acid and anions acting as a Lewis base.

The selective absorption of CO₂ can be achieved by passing the flue gas through an absorber through which solvent flows counter-currently. CO₂ is selectively absorbed into the solvent and leaves through the bottom, while other flue gas components are passed out through the top of the absorber.

The solvent loaded with CO₂ is then heated and sent to a stripping column where desorption occurs. CO₂ is released, while the unloaded solvent is recycled to the absorber.

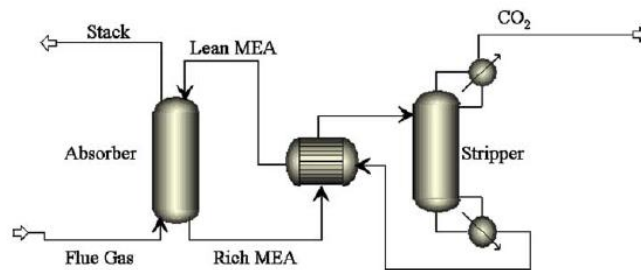


Figure 3: A Typical Solvent Absorption Process^[2]

The advantage of this strategy is that the process is well developed as it is already in use for other gas treatment requirements such as desulphurisation and denitrification processes. There are many possible solvents and solvent mixtures that are under investigation for CO₂ absorption, including amine and carbonate solvents, as well as ionic liquids.

The disadvantage is the high energy penalty associated with solvent regeneration in the stripping column. CO₂ absorption increases with decreasing temperature, yet flue gas is available at a relatively high temperature of up to 413 K^[15]. There is on-going research on finding suitable solvents that are easily regenerated with a much lower energy penalty.

Pilot plants for processes of this type have already been set up in Austria and Netherlands in 2008^[16,17]. South Africa's first CO₂ capture plant that would likely include solvent absorption is scheduled to be set up by 2020^[18].

3.1.2 CO₂ capture using dry regenerable sorbents

Figure 4 illustrates a sorbent adsorption process. Flue gas is first cooled and then sent to a carbonation reactor, which is a packed or fluidised sorbent bed reactor. CO₂ is absorbed or adsorbed into the sorbents. This may be a physical or reactive process. The sorbent, now loaded with CO₂, is then transferred to a regenerator where it is heated to release the CO₂. Sorbent is then recycled to the carbonation reactor^[15].

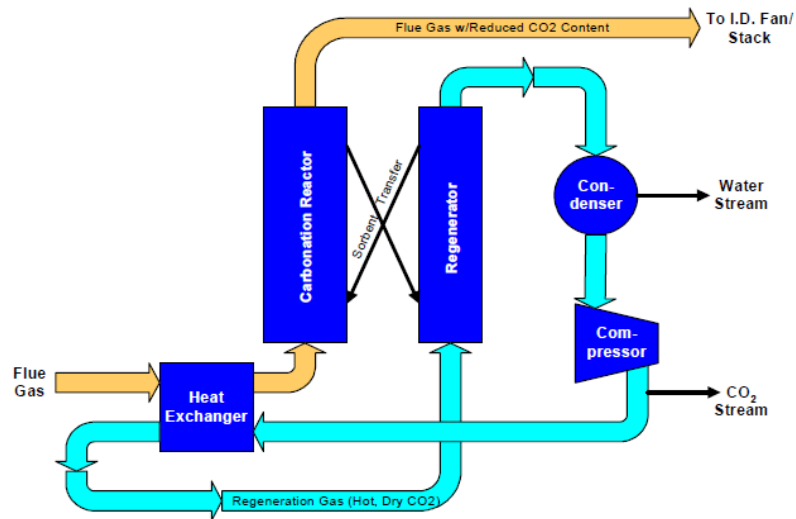


Figure 4: Sorbent Capture Process^[19]

Packed bed reactors are popular for inherently porous activated sorbents while sorbents occurring as pellets, flakes, or fine particulate matter are used in a fluidised bed reactor. The process operates in continuous or batch mode, depending on the efficiency of solids handling and the CO₂ removal capacity of the process.

Common sorbents under investigation for CO₂ capture include activated coal, sodium carbonate, potassium carbonate, and calcium carbonate^[15]. CO₂ capture is efficient even at low CO₂ concentrations in the flue gas. Depending on the sorbent and process design, lower regeneration energy requirements can be achieved than absorption using amine solvents^[15,19]. The low attrition resistance of many sorbents is a fundamental setback to its implementation as a CO₂ capture technique. While single-cycle results seem promising, many sorbents are not robust enough to be used in multi-cycle operation with conventional solids handling techniques. Sorbent pellets may erode or become caked and lose shape. High water content in the flue gas results in further attrition and sorbent caking. Moreover, the expensive nature of solids handling, including conveyor belts and compressed air blast loops which require maintenance, also reduces the feasibility of sorbents as a CO₂ capture technique.

Research is being conducted to overcome the current challenges facing sorbents, especially with the introduction of additives and sorbent supports, and hybrid processes that combine sorbents with solvents. Details of a pilot plant setup and usage are provided by Manovic et al.

[20], whom utilised a fixed bed reactor. Fluidised bed pilot projects have also been considered in Canada and Korea [21,22].

3.2 CO₂ molecular size

The CO₂ properties presented by AIGA [11] shows the CO₂ molecule to be compact, possessing a carbon atom double bonded to two oxygen atoms. The molecule is either linear or angular in shape, with a bond length of 116.18 pm. Figure 5 provides an illustration of the molecule.

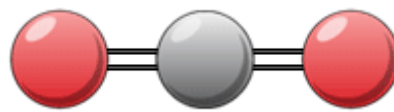


Figure 5: The CO₂ molecule

The small size of the CO₂ molecule in relation to other flue gas components facilitates not only the use of sorbents, but also the use of conventional membrane filtration systems, enzymatic membranes, and metal organic frameworks.

3.2.1 Membrane filtration

Figure 6 illustrates a typical membrane contactor. Flue gas enters into a membrane filtration unit. CO₂ selectively permeates through the membrane while other flue gas components do not. Flue gas passes out as stack gas, while CO₂ is recovered and compressed on the other side of the membrane.

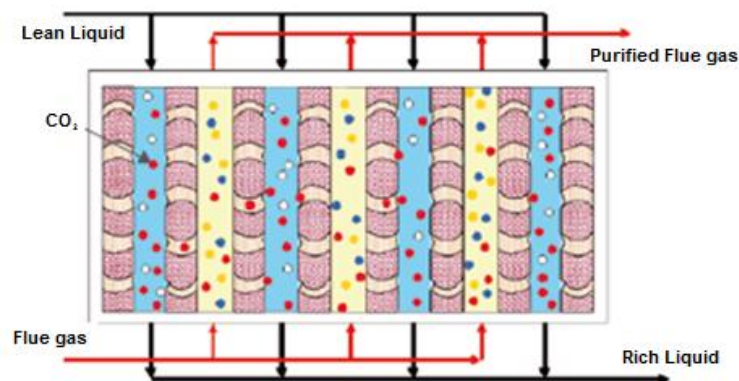


Figure 6: An Illustration of a Membrane Contactor with solvent [23]

While membranes can be used on their own, increased efficiency is noted when solvents are used as a sweep fluid to accelerate mass transfer and recover CO₂ on the other side of the membrane. Some solvents, such as ionic liquids are combined into the membrane pores to increase CO₂ permeability through the membrane^[2].

Common membrane material includes zeolite, ceramic, polymer, and silica material. More fragile membranes are supported by alumina to increase robustness. Depending on the type of filtration unit, the process can operate in batch or continuous mode.

The advantage of membranes is that CO₂ can potentially be recovered at high purity. Filtration units are well developed and there is high scope of study regarding membrane types and solvent combinations. If no solvent is used, then no solvent regeneration and recycle is required.

The challenge in implementing membrane separation for CO₂ capture is the high pressure that the process demands. The flue gas needs to be compressed before undergoing filtration in order to achieve a high CO₂ removal rate, which amounts to a high energy penalty. Moreover, many types of membrane material cannot satisfy optimum CO₂ permeability and selectivity constraints and are not robust enough for long term operation. Satisfying these requirements forms part of ongoing research.

A pilot plant in the Netherlands was constructed in 2008 which accommodates CO₂ capture using membranes combined with solvents^[17].

3.2.2 Enzyme based systems

Instead of using conventional membranes as previously described, enzymes can be used as a liquid membrane suspended between hollow fibre supports for rigidity. As shown in Figure 7, flue gas passes through the liquid membrane. CO₂ is hydrated and permeates as carbonic acid (HCO₃) at a faster rate than N₂, O₂ and other flue gas components. CO₂ is recovered under pressure or using a sweep gas on the other side^[2].

A popular enzyme for CO₂ capture is carbonic anhydrase (CA). CO₂ recovery can potentially be as high as 90%^[2]. 600000 molecules of CO₂ are hydrated by one molecule of CA^[24]. A further advantage is that the heat of absorption of CO₂ into CA is comparatively low.

Disadvantages include limitations at the membrane boundary layers, long term uncertainty, and sulphur sensitivity of the enzyme^[24], prompting ongoing research on new enzymes.

Research in this technique has not gone beyond lab studies on CO₂ permeability and selectivity^[24,25].

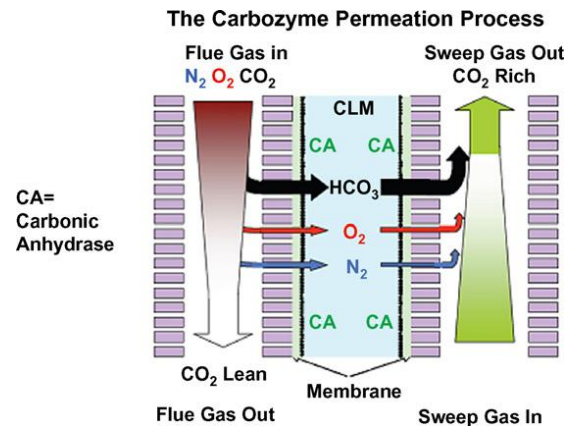


Figure 7: CO₂ Separation using Carbonic Anhydrase Enzyme^[2]

3.2.3 Metal Organic Frameworks

Metal organic frameworks (MOFs) are hybrid organic/inorganic structures containing metal ions geometrically co-ordinated and bridged with organic bridging ligands^[26]. This arrangement increases surface area for adsorption, enabling them to be used as sorbents or as nanoporous membranes.

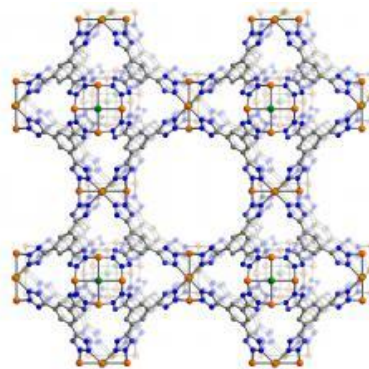


Figure 8: Structure of a typical metal organic framework (MOF)^[27]

MOFs possess enormous potential since there are hundreds of possible MOFs that can be developed using various combinations of metal ions and organic ligands. They can be tailor-made to suit a particular application such as CO₂ capture. MOFs containing zinc and

magnesium ions provide higher CO₂ adsorption and are hence being thoroughly investigated^[28,29]. Another advantage is that regeneration energy required is lower than that for conventional sorbents and solvents^[2].

The study of metal organic frameworks is still in its infancy, with investigations being made primarily on a laboratory scale.

3.3 CO₂ phase behaviour

The critical point and triple point of CO₂ are 304.25 and 216.55 K respectively^[11], and the phase behaviour of CO₂ shown in Figure 9 also allows for CO₂ capture from flue gas by changing conditions of temperature and pressure. Figure 9 shows a wide range of temperature and pressure conditions for the conversion of CO₂ from the gas phase into liquid phase, as well as into the solid phase for storage.

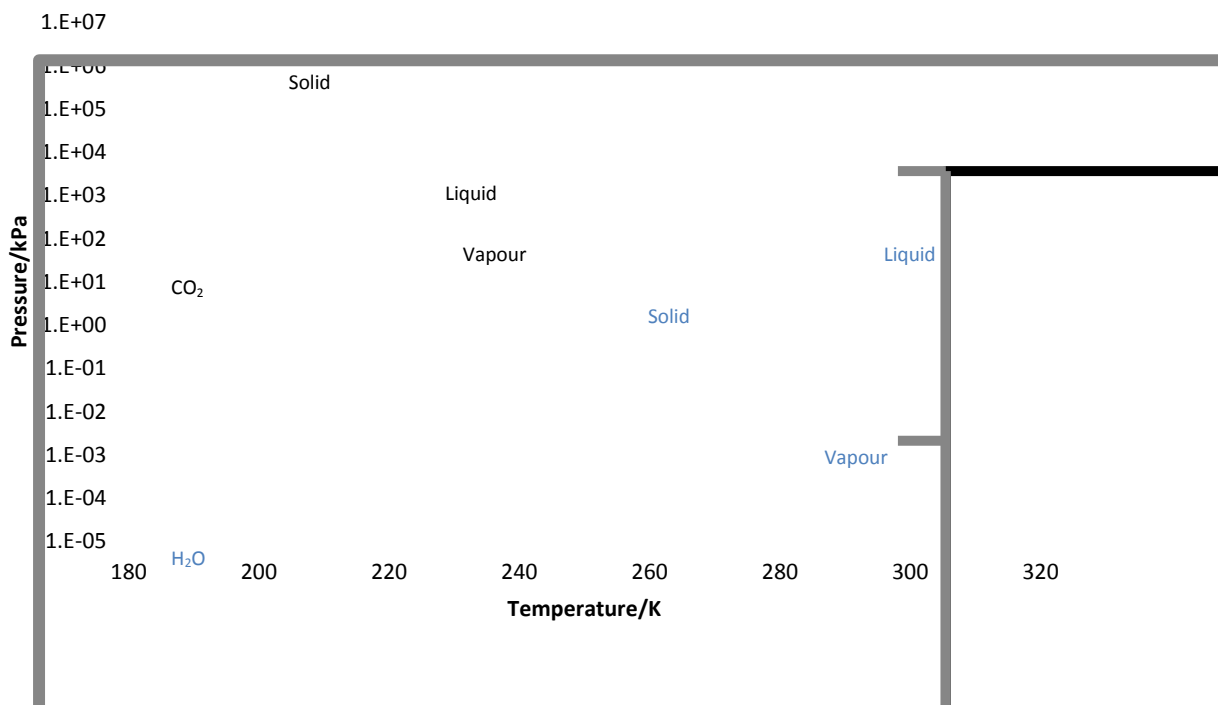


Figure 9: H₂O and CO₂ Phase diagram^[11,30]

Separation processes that make use of the phase behaviour of CO₂ include cryogenic separation and hydrate formation.

3.3.1 Cryogenic Separation

Cryogenic separation entails the separation of CO₂ from flue gas by a phase change, specifically through cooling flue gas until CO₂ exists in the liquid or solid phase. Figure 9 indicates that vapour-liquid phase change can occur at temperatures between 217 and 304 K and pressures from 630 to 7396 kPa. In the case of recovering CO₂ in the solid phase at lower temperature, the process is also popularly referred to as CO₂ anti-sublimation.

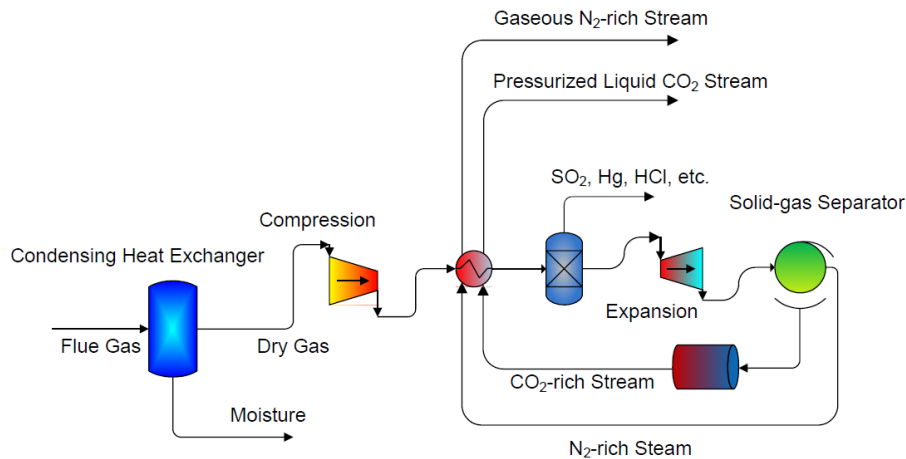


Figure 10: Cryogenic CO₂ Capture^[31]

As shown in Figure 10, flue gas is cooled in a heat exchanger and moisture is removed. The resultant dry gas contains CH₄, CO₂, N₂, O₂, and trace components such as Hg, SO₂, and HCl. The dry flue gas is moderately compressed and sent to a heat exchanger where its temperature is lowered to just above the CO₂ solidification point. This temperature varies depending on the operating pressure, which depends on the flue gas conditions from the coal power plant.

SO₂ and other trace compounds from the flue gas are removed using a flash unit. The flue gas then passes through an expander, which causes further cooling and partial precipitation of CO₂. CO₂ is thus separated from the flue gas, which at this point consists primarily of N₂ gas. The CO₂ rich stream is further pressurised and recycled, together with the N₂ rich stream, to the heat exchanger to cool incoming dry flue gas. The CO₂ rich stream undergoes a temperature increase during heat exchange which results in CO₂ being produced in the liquid phase at elevated pressure. N₂ remains in the gaseous phase and is recovered separately.

As an alternative to applying high pressure to compress the flue gas, simulations have proved CO₂ liquefaction to be more energy efficient and cost effective. This entails cooling the flue gas instead of compressing it. Energy costs associated with gas compression are reduced, and operating and investment costs for circulation equipment are also reduced^[32].

The advantage of cryogenic separation is that CO₂ can potentially be recovered at 99% purity. Refrigeration processes are already well established. Refrigerants such as n-butane, propane, ethane, and methane, and others, or a blend of each can be used^[33].

The disadvantage is the high energy penalty associated with cooling flue gas by refrigeration. Flue gas needs to be cooled to 136–194 K^[33,34], depending on the concentration of CO₂ in the flue gas. There are also mixed results by various studies on the energy penalty and resultant efficiency of cryogenic separation as a CO₂ capture method. Some studies suggest that cryogenic separation possesses an 11–27% energy penalty and is 40% more efficient than conventional absorption^[33,34]. However, other studies estimate that the efficiency of cryogenic separation is 3% lower than absorption and membrane processes^[35]. This depends on the CO₂ composition in the flue gas and degree to which pinch technology can be applied. The CATO programme in Netherlands, has developed a pilot plant that also accommodates the study of cryogenic separation^[16].

3.3.2 Hydrate formation

A separation process which makes use of CO₂ and H₂O phase behaviour, as well as molecular size and bond lengths, is hydrate formation. This technique entails passing flue gas through a unit containing chilled water at optimum temperature and pressure, causing some components of the flue gas to freeze together with water molecules to form hydrates, which are ice-like crystals where the gas molecules are trapped inside a cage of water molecules, formed through hydrogen bonding. Figure 11 shows a wide range of temperature and pressure that can result in hydrate formation.

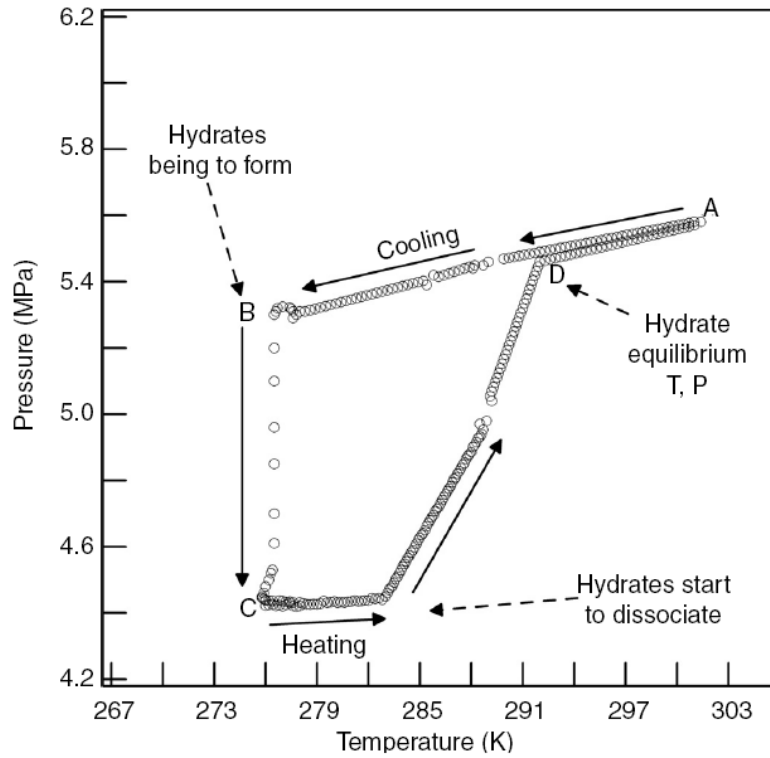


Figure 11: Pressure-temperature diagram for formation and dissociation of hydrates via isochoric pressure-search method. A-B: hydrate induction period, B-C: catastrophic growth period, D – complete hydrate dissociation^[36]

The specific formation of CO₂-water hydrates industrially can require low temperatures of 268.15-298.15 K, and very high pressures of 3000–50000 kPa^[37]. Hydrate formation pressure decreases substantially at temperatures lower than 273 K. Figure 12 shows various hydrate structures. The structures differ depending on the guest molecule. A structure I hydrate is formed with CO₂, due to the quadrupole nature of the CO₂ molecule.

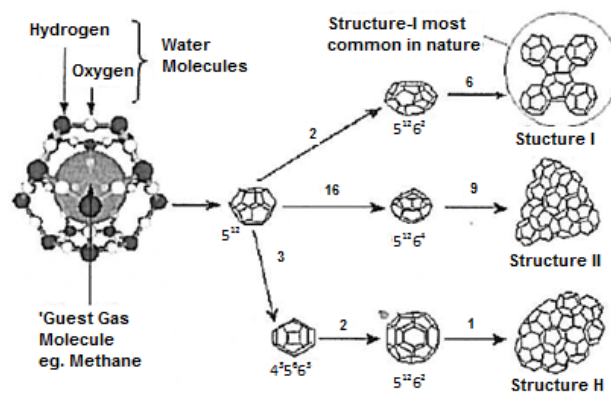


Figure 12: Guest Molecule Trapped inside Water Molecule, forming Hydrates^[37]

CO₂-water hydrates would form and exist as ice crystals in a slurry of water, while other flue gas components remain in the vapour phase and are recovered. CO₂ is thereafter recovered by heating the ice crystals and releasing the CO₂ molecules

Due to the size of the CO₂ molecules and the resultant ease of hydrate formation, an advantage of this process is its high selectivity. 99 % CO₂ recovery can be achieved^[38]. Water is used as an inexpensive recyclable solvent.

The disadvantage is the low temperature and very high pressure required for hydrate formation. Studies are currently being conducted on additives and hydrate formation promoters to reduce the required pressure for hydrate formation, so as to improve the feasibility of the process. Moreover, the handling of slurries results in maintenance problems such as pipeline plugging.

Hydrate formation as a CO₂ capture technique is relatively under-developed. There are plans however, to set up a pilot plant in the U.S.A. which caters for hydrate formation^[39].

4. CO₂ Mitigation Through the Design of New Coal Power Plants

The CO₂ capture techniques described above are investigated primarily for their ability to capture CO₂ from conventional PC power plants. These techniques are intended to be retrofitted in post-combustion mode to existing PC power plants. However a further option for future coal power plants is to design the coal combustion process in a manner that would result in favourable flue gas composition and conditions, and hence result in more efficient CO₂ capture, from a cost and energy point of view. The main alternative coal combustion processes currently under investigation are Integrated Gasification Combined Cycle (IGCC), Oxy-Fuel combustion, Integrated Gasification Steam Cycle (IGSC), and Chemical looping combustion.

4.1 Integrated Gasification Combined Cycle (IGCC)

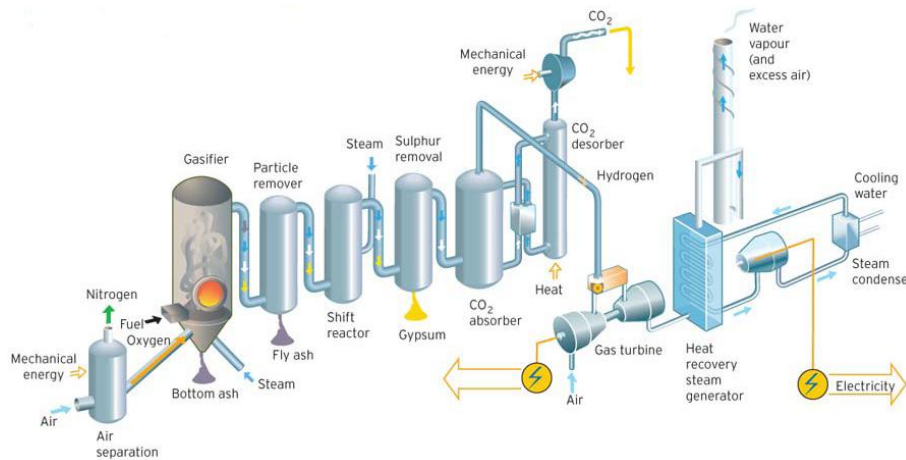
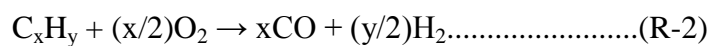
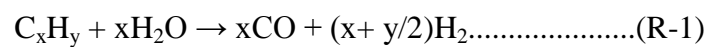


Figure 13: IGCC power plant, including CO₂ capture unit^[40]

A new alternative power plant process is the integrated gasification combined cycle (IGCC) process. While there are currently no such power plants in South Africa, the process has some advantages over PC power plants and is a more environmentally friendly alternative for new power plant construction.

A simplified schematic of an IGCC power plant is shown in Figure 13. In this process, nearly pure oxygen (O₂) is produced using an air separation unit. The O₂ is sent to a gasifier together with coal. Combustion in the presence of nearly pure O₂ occurs. Coal is partially oxidised to produce a mixture of CO, CO₂, and H₂, collectively known as syngas^[15]. The gasifier operates at 35–70 bar and 1255–1644 K. The reactions occurring in the gasifier are:^[41]



After particulate removal, the syngas is sent to a shift converter to undergo a water gas shift reaction:



Steam is utilised in the converter as a reactant. A gas mixture of CO₂, H₂, sulphurous and nitrogenous compounds leave the converter. Unreacted steam is often removed as water.

Desulphurisation and denitrification processes are then employed depending on sulphur and nitrate content. The resulting gas mixture contains approximately 50 vol% H₂, 40 vol% CO₂, 2 vol% CO and other trace elements. The gas occurs at 27 bar and 310 K^[9].

At this point in the process, CO₂ may be removed using a feasible CO₂ capture technique. CO₂ may then be compressed and stored. After CO₂ capture, H₂ is burned to generate steam at approximately 12400 kPa^[43] which is used to drive the turbines and hence generate electricity.

The electricity generated by the turbine is used to power the gasifier, shift convertor, air separation and compression operations. The remaining electric energy is then available for commercial use.

IGCC processes are estimated to require higher investment costs than PC processes. However, upon integration of CO₂ capture into the plant, the total investment cost is lower for IGCC processes than PC processes which are retrofitted for CO₂ capture. IGCC processes also introduce the prospect of pre-combustion capture after shift conversion. CO₂ is captured from flue gas at higher pressure, reducing CO₂ compression costs. It is these advantages that make IGCC an attractive option if the capacity of coal power in South Africa is expanded.

4.2 Oxy-fuel combustion

This technique is a modification of the PC power plant. It involves burning coal in nearly pure oxygen.

Oxygen is cryogenically separated from air in an air separation unit (ASU). Other air components are emitted into the atmosphere while oxygen is used in the boiler for coal combustion. The resulting heat converts water to superheated steam, for use in steam turbines. The resulting flue gas from combustion is treated for ash and sulphur removal, and thereafter contains CO₂ and water vapour. Water is separated from CO₂ by cooling the flue gas. A schematic of the process is shown in Figure 14.

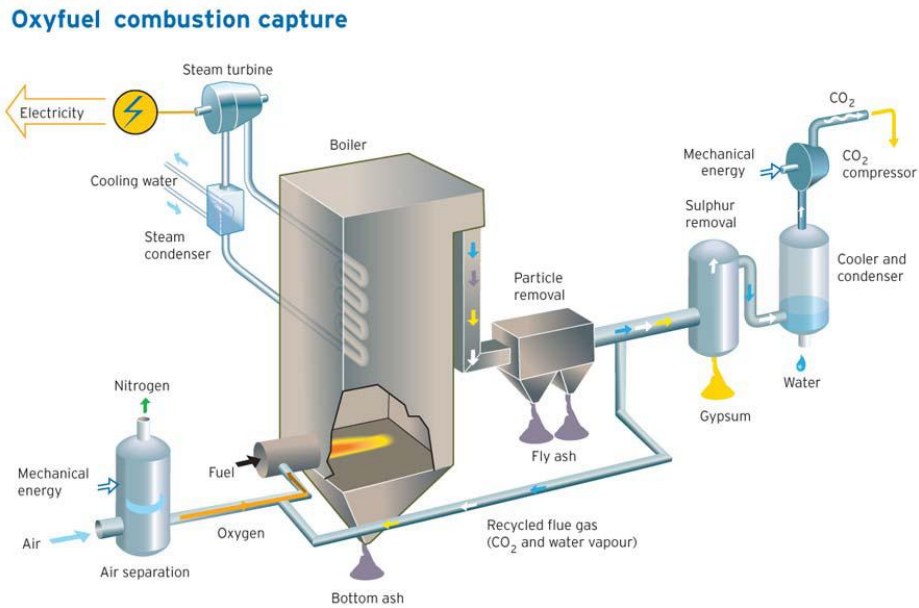


Figure 14: Oxy-fuel combustion capture^[40]

The main advantage of the process is that the flue gas is available at a high CO₂ concentration of approximately 75.7 mol%^[44], thereby reducing compression costs and facilitating efficient CO₂ removal^[2]. Moreover, CO₂ is easily separated from H₂O. The modification of PC to oxy-fuel combustion is also easier than constructing an IGCC process. Oxy-fuel combustion is estimated to inherently result in lower CO₂ emissions than IGCC and conventional PC processes^[44].

The disadvantage is the high flaming temperature at which coal burns in the presence of pure oxygen, which puts much strain on the material of construction^[40]. To mitigate this, flue gas is recycled to enable temperature control, as shown in Figure 14. Captured and cooled CO₂ streams may also assist in lowering the temperature of the boiler. Moreover, ASUs require high amounts of energy to obtain pure oxygen from air. Cryogenic methods are also presently accompanied with high energy penalties.

4.3 Integrated gasification steam cycle (IGSC)

A U.S. consortium consisting of Siemens Ltd., MAN Ltd., CO₂ Global, Imperial College London, and Jacobs Consultancy has conducted research into a modified IGCC coal combustion process called Integrated Gasification Steam Cycle (IGSC), in order to minimise the energy penalty associated with coal power plants possessing CO₂ capture. As seen in

Figure 15, waste energy is efficiently utilised through a relatively complex system of recycle streams and turbines of varying pressure.

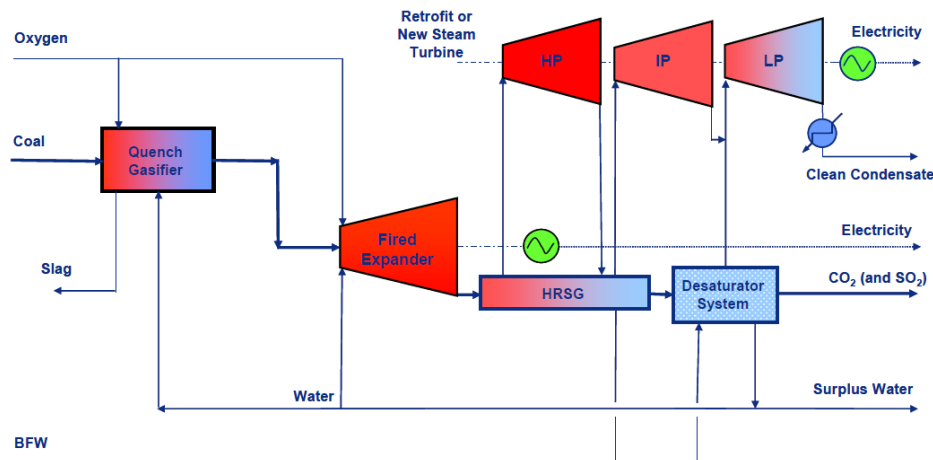


Figure 15: Integrated Gasification Steam Cycle^[45]

The process consists of a two-stage combustion system. Coal is gasified in a quench gasifier, which utilises water for temperature control. The resultant syngas contains carbon monoxide, hydrogen gas, and oxygen gas, which is passed through a fired expander to generate power. The expander consists of a burner connected to a turbine. Combustion is completed in the expander at temperatures over 1000 K.

The exhaust heat is used to raise high pressure steam in a heat recovery steam generation (HRSG) system, which is then used to power an additional turbine retrofitted to the process. Resultant gases, containing primarily H₂O, CO₂, and trace SO₂, are then cooled in a desaturator to remove H₂O and recover CO₂ in post-combustion mode. The desaturator utilises recycled cooling water and if optimised, can drive a low-pressure turbine, generating additional power^[45].

The advantage is that the process can potentially obtain 100% CO₂ recovery and increase power plant output by 60%^[46]. Conventional turbines can be used and CO₂ is available at high pressure.

The capital cost of IGSC processes is the main drawback, due to the air separation units required to provide oxygen to the gasifier. A desulphurisation unit may also be required for coal possessing high sulphur content.

Research on IGSC is limited solely to the consortium that invented it, barring all possibility of finding data from other independent sources. There is however, abundant information available from the consortium itself^[45].

4.4 Chemical looping combustion

This technique is a further modification of oxy-fuel combustion. Instead of utilising oxygen from an ASU for coal combustion, oxygen derived from metal oxides is used^[47]. As shown in Figure 16, two fluidised bed reactors are used, the air reactor (1) and fuel reactor (3). Particulate metal or metal oxide is oxidised in the air reactor using air, thereby acting as an oxygen carrier. A cyclone (2) is used to separate the carrier from unreacted components of air, which are emitted as flue gas. The particulate oxygen carrier is transferred into the fuel reactor (3). The oxygen carrier is reduced in a combustion reaction with coal and recycled to the air reactor. Flue gas from the fuel reactor contains H₂O and CO₂, and can be used to drive a turbine before being separated by cryogenic means.

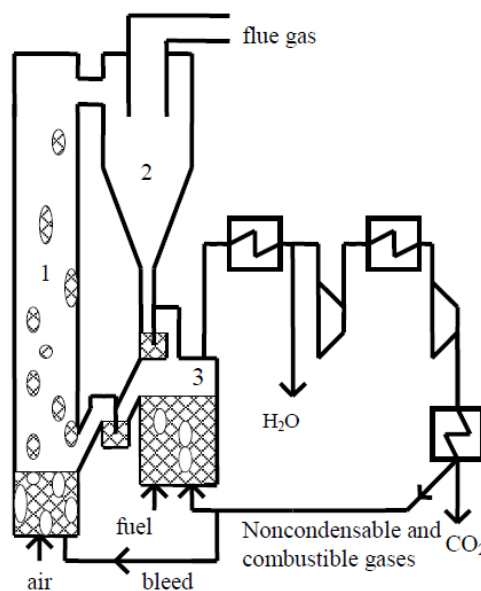


Figure 16: An illustration of Chemical Looping Combustion^[47]

The oxygen carrier is reduced in a combustion reaction with coal and recycled to the air reactor. Flue gas from the fuel reactor contains H₂O and CO₂, and can be used to drive a turbine before being separated by cryogenic means.

The reactions occur typically at 1173.15–1573.15 K^[48]. Different metal oxides can be used as the oxygen carrier, such as Fe₂O₃/CuO and MgAl₂O₄, nickel, manganese and calcium oxides^[49,50].

The advantage of chemical looping combustion is that no ASU is required, and flue gas contains primarily CO₂ and H₂O, with CO₂ available at 31wt% in the flue gas, which is higher than conventional PC power plant flue gas^[23].

The current disadvantage of chemical looping is the high investment cost required for the technology, which deters research and implementation. Another fundamental challenge to implementation is choosing an ideal oxygen carrier. Current studies show the conversion rate under oxidising conditions, using conventional oxygen carriers to be very fast (nearly 100%/min^[47]). However the occurrence of side reactions with undesirable products are yet to be minimised^[51].

Most research on chemical looping that is currently underway is on the finding of a suitable oxygen carrier^[42]. Despite this, a pilot plant has been developed in Sweden to investigate the industrial operation of chemical looping^[47,48].

5. CO₂ TRANSPORTATION

After the removal of CO₂ from coal power plants and other industrial sources, CO₂ needs to be transported to locations whereby it is stored or alternatively used in various processes. CO₂ can be transported via ship or pipeline. In both cases, the required compression pressure can be 100–300 bar^[52], depending on the distance and intended disposal or use of CO₂.

6. CO₂ STORAGE

The relatively high heat of formation of CO₂ of -393.5 kJ/mol^[53] provides great difficulty in converting CO₂ to high value products, despite current and recent efforts^[54]. Moreover, the sheer amount of CO₂ emitted necessitates alternative disposal methods for this gas.

The term “sequestration” describes the storage of CO₂ and the increase in carbon stock in underground reservoirs rather than the atmosphere^[55]. The strategy involves injecting CO₂ at least 800m underground where ambient pressure and temperature are sufficient to result in liquid or supercritical CO₂, and no substantial leakage may occur^[52].

CO₂ can be stored in geologic formations such as former natural gas, oil or brine fields (saline formations), and un-minable coal beds which contain porous rock and cavities. There is also the possibility of storing CO₂ in offshore formations of the same nature, but this option

is more hazardous and expensive. A well sealed cap rock, containing a layer of shale and clay is preferable to prevent upward CO₂ migration and leakage^[56]. A good knowledge of the underground reservoir size is needed to account for horizontal migration of CO₂ and ensure ultimate trapping by geochemical means, such as carbonate formation from reactions with CO₂ and the host rock^[52,56].

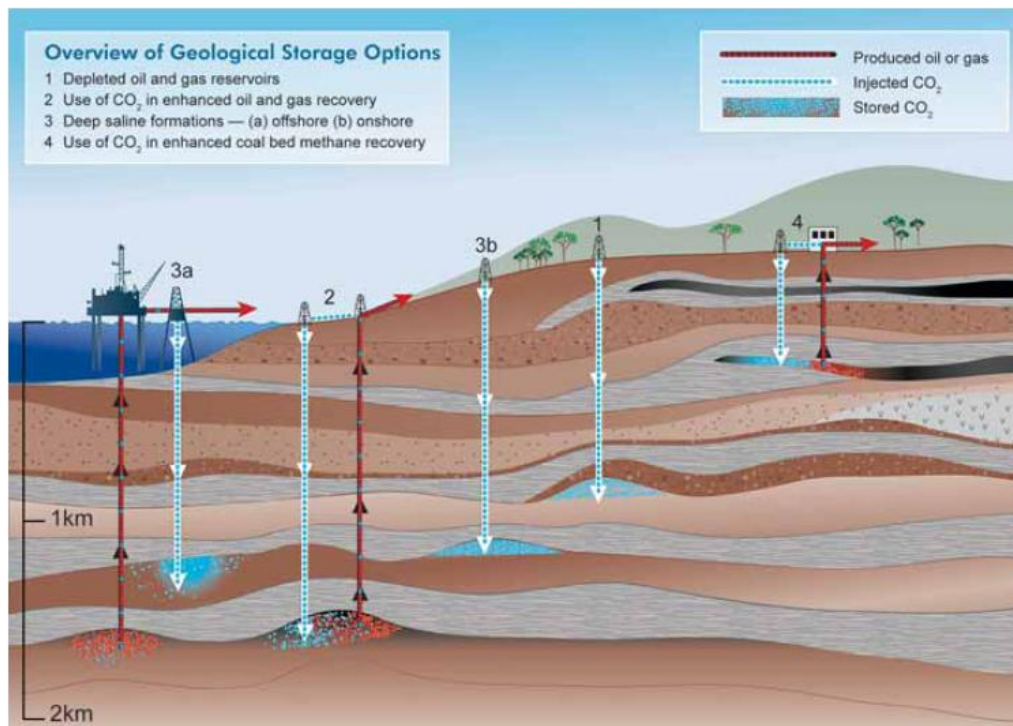


Figure17: Geological storage options^[56]

While CO₂ capture is relatively underdeveloped for commercial use, CO₂ sequestration is already prevalent in oil, gas, and coal industries in Canada, Algeria, U.S.A., Norway, Netherlands, China, Japan, Poland, and Australia^[56].

Viljoen^[57] presents areas in South Africa where CO₂ can be stored. These include saline formations, gas reservoirs and depleted coal mines. The closest area to many of Eskom's operations, and most CO₂-emitting industries in general, are parts of the Northern Karoo, which possesses free saline formations, as well as depleted coal mines. Further formations are shown in Figure 18 below, which includes large offshore storage opportunities as well.

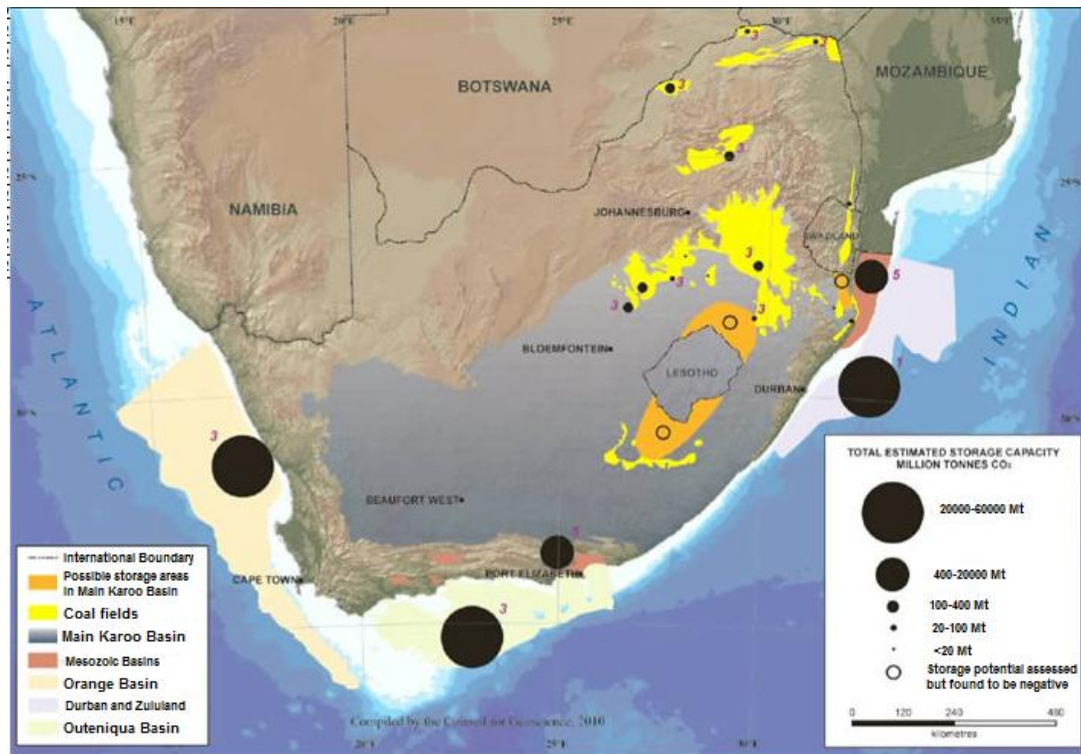


Figure 18: Potential areas for CO₂ storage in South Africa^[58]

It is encouraging to find that many possible storage sites shown in Figure 15 are relatively close to the CO₂ emitting sources shown in Figure 1. CO₂ compression and transportation costs via pipelines would be reduced. CO₂ storage attempts are currently being planned in South Africa, with a test being scheduled for 2016. If CO₂ storage tests are successful, CO₂ capture implementation tests hope to reach completion by 2020^[18].

7. USES OF CO₂ STORAGE

In addition to CO₂ storage in empty reservoirs, CO₂ may be injected underground to assist in the recovery of high value resources such as oil, natural gas, and methane. These are more feasible solutions that can partially or completely recover the cost of CO₂ capture and storage. Below are a few options for CO₂ storage. Refer to Figure 17 for illustrations.

7.1. CO₂ Enhanced oil recovery

Enhanced oil recovery (EOR) refers to the strategy of injecting CO₂ into nearly depleted oil wells to pressurise the well and force the remaining oil upwards. Once all oil is depleted, CO₂ shall be sealed off underground. Two channels are drilled, one for injecting CO₂ and the other to allow the upward migration of oil. EOR can increase the recovery rate of oil by 8–15%,

and can ultimately increase the recovery of oil by up to 50% of the total oil originally able to be recovered^[52].

A major EOR project using CO₂ has been conducted in Canada^[56]. EOR projects using other gases such as N₂ and hydrocarbon gas mixtures are also a mature technology.

7.2 CO₂ Enhanced gas recovery

Enhanced gas recovery (EGR) refers to the extraction of natural gas from nearly depleted gas reservoirs, using CO₂. Natural gas is a mixture composed of methane and various hydrocarbon gases. After conventional extraction, gas reservoirs still contain 10–20% of their initial capacity^[52]. Due to reduced pressure in the reservoir, conventional extraction becomes unfeasible. CO₂ injection increases the pressure in the reservoir. Moreover, CO₂ is denser than natural gas and sinks to lower regions of the reservoir, forcing natural gas upwards. In this way, the reservoir can be completely emptied of all natural gas. An EGR system is in operation in Netherlands^[56].

7.3 CO₂ Enhanced coal-bed methane recovery

Enhanced coal bed methane (ECBM) recovery involves the extraction of methane gas from coal seams using CO₂. The process of extraction is similar to EGR but is done with coal seams. CO₂ is injected into a depleted or un-minable coal bed and methane is forced up through a drilled outlet channel. Conventional extraction techniques recover 50% of methane in coal beds. The use of CO₂ in ECBM has the potential to increase methane recovery to 90% or even 100%^[52].

The main concern with ECBM recovery is the potential for CO₂ leakage which might occur due to the relatively shallow depth of extraction and the permeability of coal seams that are required. While shallow depth and permeable rock facilitate efficient methane recovery, it is conducive to permanent, stable CO₂ storage.

Moreover, for leakage to be prevented and for predictable channelling of methane and CO₂ to occur, the coal bed has to be sufficiently thick, which requires an amount of coal to be left un-mined and the mine must be rendered un-minable. A thorough feasibility analysis is required to ensure that ECBM is worth the cost of un-mined coal.

ECBM operations are currently underway in Canada, China, Japan, and Poland^[56]. Of all the options of CO₂ usage during storage, ECBM has the most potential in South Africa, due to the vast number of coal beds in the country. However, coal beds offer the least amount of storage potential worldwide due to their shallow depth and capacity compared to other types of potential storage reservoirs.

8. CONCLUSIONS

Seven main CO₂ capture techniques have been identified which show great promise as industrial CO₂ emissions mitigation solutions. The technique of CO₂ absorption using solvents was identified as currently the best option for industrial implementation as a capture technique. It is the only technique currently included in the South African CCS schedule, with a view to be implemented in 2020. Other techniques, while potentially more efficient than the use of solvents, still require substantial research to bring them to the stage of industrial implementation.

Four power plant modifications or alternative process designs have been identified and are currently at the pilot plant stage of research. No country has yet issued a full roll out of these technologies and it remains unclear as to when these designs would be implemented on an industrial scale.

The potential areas of CO₂ storage have been mapped out, with a test injection due to commence in 2016. Three uses of CO₂ storage have been identified, with ECBM recovery posing great benefit particularly for South Africa's depleted coal mines.

9. REFERENCES

1. International Energy Agency (IEA). Key World Energy Statistics – 2010, France; International Energy Agency; 2010.
2. Figueroa J.D., Fout T, Plasynski S. et al. Advances in CO₂ capture technology—The U.S. department of energy's carbon sequestration program, *Int. J. Greenh. Gas Con.* 2008; 2: 9—20.
3. Eskom Power Generation. Eskom – coal power; South Africa; Eskom Ltd.; [updated 2011; cited 28 February 2011]; Available from: http://www.eskom.co.za/live/content.php?Item_ID=279
4. Carbon Monitoring for Action (CARMA). The 10 largest CO₂ emitting power sectors in the world by country; U.S.A.; CARMA - a division of the Centre for Global Development, [updated 2009; cited 4 July 2011]; www.carma.org
5. Carbon Monitoring for Action (CARMA). Top 30 CO₂-emitting power plants in the world; U.S.A.; CARMA - a division of the Centre for Global Development; [updated 2007; cited 4 July 2011]. www.carma.org
6. Surridge T. South African activities related to carbon capture and storage – September 2005; South Africa; Department of Minerals and Energy: Carbon Sequestration Leadership Forum; [updated 2005; cited 28 January 2009]. http://www.cslforum.org/documents/pg_RomeMinutespublic.pdf.
7. National Treasury. Reducing greenhouse gas emissions: The carbon tax option. Discussion paper for public comment; South Africa; Department of National Treasury; [updated 2010; cited 5/09/2011]; <http://www.treasury.gov.za/public%20comments/Discussion%20Paper%20Carbon%20Taxes%2081210.pdf>
8. Eskom Ltd. Eskom coal power animation; South Africa; Eskom Ltd.; [updated 2011; cited 25 May 2011]. <http://www.eskom.co.za/content/Coal.swf>
9. National Energy Technology Laboratory (NETL). DoE/Netl advanced carbon dioxide capture r&d program: Technology update; U.S.A.; National Energy Technology Laboratory; [updated 2010; Cited 25 May 2011]. <http://www.netl.doe.gov/technologies/coalpower/ewr/pubs/CO2%20Capture%20Tech%20Update%20Final.pdf>
10. Brennecke J.F. and Gurkan B.E. Ionic liquids for CO₂ capture and emission reduction, *J. Phys. Chem. Lett.* 2010; 1: 3459–3464

11. Asia Industrial Gases Association. Carbon Dioxide – Globally Harmonised Document, 7th Edition, Singapore, Compressed Gas Association, [updated 2009, cited 12 February 2012].
12. Lentech Water Treatment Solutions. What is carbon dioxide and how is it discovered?, Netherlands; Lentech BV, [Updated 2009; Cited 14 February 2012]. <http://www.lentech.com/carbon-dioxide.htm>
13. Ma'mun S. Selection and characterisation of new absorbents for carbon dioxide capture, Norway, Faculty of Natural Science and Technology, Department of Chemical Engineering, NTNU. [updated 2005, cited 30 June 2011].
14. Huang J. and Rüther T. Why are ionic liquids attractive for CO₂ absorption? An overview, Aust. J. Chem., 2009, vol. 62, pg. 298-308.
15. Osman K. Carbon dioxide capture methods for industrial sources: A literature review, energy efficiency and feasibility study; South Africa; University of KwaZulu Natal; 2010.
16. Vierde Nationaal Symposium (VNS) CCS, CATO CO₂ catcher, a CO₂ capture plant treating real flue gas, Netherlands; EON Ltd.[updated 2008; cited 12 February 2011] <http://www.co2-cato.nl/modules.php?name=CATO&page=79&symposium=true>
17. Knudsen J.N., Vilhelmsin P.J., Jensen J.N et al. Performance review of Castor pilot plant at Esbjerg; Austria; Dong Energy; 2008;
18. Surridge T. Personal correspondence with Dr. Tony Surridge, South African National Energy Research Institute (SANERI), and Head of the South African Centre for Carbon Capture and Storage (SACCCS), South Africa, 2011.
19. Green D.A., Turk B.S., Portzer J.W. et al. Carbon dioxide capture from flue gas using dry regenerable sorbents. U.S.A.; U.S. Department of Energy, National Energy Technology Laboratory, NETL, 2004.
20. Manovic V., Anthony E.J., Lu D.Y. Sulphation and carbonation properties of hydrated sorbents from a fluidized bed CO₂ looping cycle reactor, Fuel 2008; 87: 2923-2931.
21. Yi C., Jo S., Seo Y. et al. Continuous operation of the potassium-based dry sorbent CO₂ capture process with two fluidized-bed reactors, Int. J. Greenh. Gas Con. 2007; 1: 31-36.
22. Lu D.Y., Hughes R.W., Anthony E.J. Ca-based sorbent looping combustion for CO₂ capture in pilot-scale dual fluidized beds, Fuel Proc. Tech. 2008; 89: 1386-1395
23. National Energy Technology Laboratory (NETL). [Chemical looping process in a coal to liquids configuration], U.S.A.; Department of Energy; [updated 2007; cited 29 January 2009]. Available from: <http://www.netl.doe.gov/energy-analyses/pubs/DOE%20Report%20on%20OSU%20Looping%20final.pdf>

24. Trachtenberg M.C., Tu C.K., Landers R.A. et al. Carbon dioxide transport by proteic and facilitated transport membranes, *Int. J. Earth Space* 1999; 6: 293-302.
25. Ge J.J., Cowan R.M., Tu C.K., et al. Enzyme-based CO₂ capture for ALS, U.S.A.; Carbozyme Ltd.; [updated 2002; cited 4 August 2011]. <http://www.carbozyme.us/publications/P5.pdf>
26. Plasynski S., Lang D.A., Richard W. Carbon dioxide separation with novel microporous metal organic frameworks, U.S.A.; National Energy Technology Laboratory (NETL); [updated 2008; cited 4 August 2011]; <http://www.netl.doe.gov/publications/factsheets/project/Proj315.pdf>
27. Long J. New metal organic frameworks in action for capturing carbon dioxide, U.S.A.; The Green Optimistic, [updated 2010; cited 4 August 2011]. <http://www.greenoptimistic.com/2010/06/02/metal-organic-frameworks-carbon-dioxide-capture/>
28. Yazaydin A.O., Snurr Q., Park T.H. et al. Screening of metal-organic frameworks for carbon dioxide capture from flue gas using a combined experimental and modelling approach, *J. Am. Chem. Soc.* 2009; 131: 18198-18199
29. Simmons J.M., Wu H., Zhou W. et al. Carbon capture in metal-organic frameworks – A comparative study, *EnergyEnv. Sci.* 2011; 4: 2177-2185
30. Chemicalogic. Steamtab, U.S.A., Chemicalogic Corporation [updated 1999, cited 14 February 2012]. http://www.chemicalogic.com/download/phase_diagram.html
31. Burt S., Baxter A., Baxter L. Cryogenic CO₂ capture to control climate change emissions, U.S.A.; Brigham Young University; [updated 2009; cited 21 June 2011] <http://www.sustainablees.com/documents/Clearwater.pdf>
32. Xu G., Li L., Yang Y. et al., A novel CO₂ cryogenic liquefaction and separation system, *Energy*, 2012, Vol. 42, pg. 522-529.
33. Clodic D., Hitti R., Younes M. et al. CO₂ capture by anti-sublimation: thermo-economic process evaluation, U.S.A., 4th Annual Conference on Carbon Capture and Sequestration; 2 –5 May 2005; Alexandria; 2005
34. Baltus R.E., Culbertson B.H., Dai S. et al. Low-pressure solubility of carbon dioxide in room-temperature ionic liquids measured with a quartz crystal microbalance, *J. Phys. Chem. B* 2004; 108: 721-727.
35. Gottlicher G. And Pruschek R., Comparison of CO₂ removal systems for fossil-fuelled power plant processes, *Eng. Conv. Manage.*, 1997, vol. 38, pg. 173-178.

36. Sloan E.D., Koh C. Clathrate Hydrates of Natural Gases, 3rd Edition, U.S.A., CRC Press 2012.
37. Jadhawar P., Mohammadi A.H., Yang J. et al. Subsurface carbon dioxide storage through clathrate hydrate formation, United Kingdom, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh, 2006.
38. Chatti I., Delahaye A., Fournaison L. et al. Benefits and drawbacks of clathrate hydrates: a review of the areas of interest, Eng. Con. and Manage. 2005; 46: 1333–1343
39. Tam S.S., Stanton M.E., Ghose S. et al. A High Pressure Carbon Dioxide Separation Process for IGCC Plants; U.S.A.; National Energy Technology Laboratory, Department of Energy; [updated 2000; cited 29 July 2011]. http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/1b4.pdf.
40. Arshad M.W. CO₂ capture using Ionic Liquids; Denmark; Department of Chemical and Biochemical Engineering, Technical University of Denmark; [updated 2009; cited 28 March 2011]; http://docs.google.com/viewer?a=v&q=cache:uF9eKE4Xeg0J:orbit.dtu.dk/getResource%3FrecordId%3D240068%26objectId%3D1%26versionId%3D1+Non+fluorinated+Ionic+Liquids+%2B+CO2+capture&hl=en&pid=bl&srcid=ADGEESg9aXin_GbLKmM6LyI0ZwZISYo9jdm6WoHXOZShMxVHKwcdqJ9348xr_ET4DibAHbAcF09sbUcIgJSDpEtHdGpt8LdGo4lv02MgmONX0xD9Dj8r9vXvxaAYZI1cbkOF3ovX0axf&sig=AHIEtbRXq7UJoi74_T-CVBR3d5zuDcG5EQ
41. Steeneveldt R., Berger B., Torp. T.A. CO₂ capture and storage. closing the knowing-doing gap, Chem. Eng. Res. Des., 2006; 84: 739-763.
42. Kanniche M., Bouallou C. CO₂ capture study in advanced integrated gasification combined cycle, App. Therm. Eng. 2007; 27: 2693-2702
43. Department of Energy. Cost and Performance Baseline for Fossil Energy Plants, Bituminous Coal and Natural Gas to Electricity, U.S.A., National Energy Technology Laboratory, 2007, Vol. 1[Updated 2007, cited 30 September 2012]
44. Davison J. Performance and costs of power plants with capture and storage of CO₂, Energy. 2007; 32: 1163–1176
45. Karmarkar M., Griffiths J., Russell A. et al. Industrial and utility scale IGSC coal power stations; U.S.A.; Department of Energy and Climate Change; [updated 2009; cited 3 August 2011]. <http://webarchive.nationalarchives.gov.uk/+http://www.berr.gov.uk/files/file52638.pdf>

46. Kent R. New Power Cycles with Carbon Capture and Sequestration; U.S.A.; Sempra Energy Utilities, Waste Management Association; [updated 2009; cited 3 August 2011]. <http://www.wcsawma.org/sitebuildercontent/sitebuilderfiles/34.pdf>
47. Mattisson T., Lyngfelt A. Applications of chemical-looping combustion with capture of CO₂, Sweden; Department of Energy Conversion, Chalmers University of Technology, [updated 2001; cited 8 August 2011]. <http://www.entek.chalmers.se/~anly/symp/01mattisson.pdf>
48. Mattisson T., Chemical looping combustion using gaseous and solid fuels, Sweden; International Energy Agency (IEA) Greenhouse Gas R&D Programme; [updated 2007; cited 8 August 2011]. [http://www.co2captureandstorage.info/docs/oxyfuel/MTG2Presentations/Session%2006/2%20-%20T.%20Mattisson%20\(Chalmers%20University\).pdf](http://www.co2captureandstorage.info/docs/oxyfuel/MTG2Presentations/Session%2006/2%20-%20T.%20Mattisson%20(Chalmers%20University).pdf)
49. Wang S., Wang G., Jiang F. et al. Chemical looping combustion of coke oven gas by using Fe₂O₃/CuO with MgAl₂O₄ as oxygen carrier, *Energy Env. Sci.* 2010; 3: 1353-1360.
50. Fang H., Haibin L., Zengli Z. Advancements in development of chemical-looping combustion: A Review, *Int. J. of Chem. Eng.* 2009; 2009: 1-16.
51. Wall T., Liu Y., Chemical looping combustion and CO₂ capture: Status and developments, Australia; Co-operative Research Centre for Coal in Sustainable Development (CCSD), University of Newcastle; [updated 2008; cited 8 August 2011]. http://www.ccsd.biz/publications/files/TN/TN%2032%20Chem%20looping%20updated_web.pdf
52. International Energy Agency (IEA). Prospects for CO₂ capture and storage, France; International Energy Agency; [updated 2004; cited 5 March 2009]. <http://www.iea.org/textbase/nppdf/free/2004/prospects.pdf>
53. Perry R.H., Green D.W. Perry's Chemical Engineers' Handbook, U.S.A., 7th Edition, McGraw Hill, 1997.
54. L'Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME), Panorama des voies de valorisation du CO₂, l'Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME), 2010, France. Report made available by Dr. Christophe Coquelet of Mines-Paristech, France.
55. Teng F., Tondeur D. Efficiency of carbon storage with leakage: physical and economical approaches, *Energy* 2006; 32: 540-548
56. Intergovernmental Panel on Climate Change (IPCC). Carbon Dioxide Capture and Storage: Summary for Policy Makers and Technical Summary; Spain; Intergovernmental

Panel on Climate Change; [updated 2005; cited 26 January 2011].http://www.climnet.org/EUenergy/IPCC_CCS_0905.pdf

57. Viljoen J.H.A., Stapelberg F.D.J., Cloete M. Technical report on the geological storage of carbon dioxide in South Africa, South Africa; Council for Geoscience, Department of Energy; [updated 2010; cited 30 June 2011].
http://www.ccsconference.co.za/images/presentations/thinus_cloete.pdf

58. Cloete M. Atlas on geological storage of carbon dioxide in South Africa, South Africa; Council for Geoscience, Department of Energy; [updated 2010; cited 30 June 2011]. <http://www.sacccs.org.za/wp-content/uploads/2010/11/Atlas.pdf>