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Site Trials of Novel CO_2 Capture Technology at Delta Electricity

Final Report

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Abstract

Growing concerns for global warming and climate change have attracted widespread efforts to develop efficient and cost-effective technologies for Post-combustion CO_2 Capture (PCC) from large point sources, such as coal-fired power plants. Among various PCC technologies for CO_2 capture from flue gas, use of porous solid sorbents offers a promising solution as it has the potential to be highly cost-effective and has less impact on the environment. From January 2006, CSIRO began to develop a new CO_2 capture process by developing nano-structured monolithic carbon fibre composite adsorbents, which are fabricated in a honeycomb structure. This structure enables CO_2 capture in a dry process in dusty environments with low pressure drop. Compared with conventional solvent process, the carbon adsorbent CO_2 capture exhibits the following advantages: no degradation and secondary emissions, high resistance to NO_x and SO_x in the flue gas, no need for flue gas pre-treatment, use of waste heat from the flue gas for CO_2 desorption due to high thermal conductivity. For the carbon adsorbents for the post combustion CO_2 capture, studies so far have been carried out only using simulated flue gas and under laboratory conditions. Hence, the site trials and demonstration of the carbon composite adsorbents for CO_2 capture at the power station through this CINSW project is a pioneering research in the world to study the adsorbent stability, the capture performance and captured gas quality using real flue gas.

A large scale solid sorbent CO_2 capture-regeneration prototype unit, previously designed and built by CSIRO, was modified and integrated with a dedicated pre-treatment system to form the carbon adsorbent test facility at the power station site. Then, the site trials and demonstration of the carbon fibre composite solid sorbent CO_2 capture prototype unit were successfully carried out at the power station. Over 200 adsorption and regeneration tests were performed using real flue gas to evaluate the performance of the adsorbents, and key performance data and operational experience were obtained. The experimental results showed that the CO_2 adsorption efficiency of the solid sorbents was found to be consistently over 98%, which means that most CO_2 in the flue gas was captured during an adsorption process. The captured CO_2 onto the solid sorbents needs to be released by a desorption process whose CO_2 desorption efficiency was found to be between 90-95%. As the CO_2 capture performance of the solid sorbents was maintained even after more than 200 tests, it was first time demonstrated that the solid sorbents were very stable towards real flue gas without any noticeable impact of SO_x and NO_x on their CO_2 capture performance.

All the project objectives were successfully accomplished through this study. The important experimental data and site operational experience obtained at the power station form a base for further development of this carbon composite adsorbent CO_2 capture technology towards its application at fossil fuel fired power stations.

Executive Summary

Growing concerns for global warming and climate change have attracted widespread efforts to develop efficient and cost-effective technologies for Post-combustion CO_2 Capture (PCC) from large point sources, such as coal-fired power plants. Post-combustion carbon capture has the greatest near-term potential for reducing emissions and can be retrofitted to existing coal-fired power plant infrastructure without requiring substantial changes to the combustion process. Among various PCC technologies for CO_2 capture from flue gas, use of porous solid sorbents offers a promising solution as it has the potential to be highly cost-effective and has less impact on the environment. From January 2006, CSIRO began to develop the new CO_2 capture process by developing nano-structured monolithic carbon fibre composite adsorbents, which are fabricated in a honeycomb structure. This structure enables CO_2 capture in a dry process in dusty environments with low pressure drop. Compared with conventional solvent process, the carbon adsorbent CO_2 capture exhibits the following advantages: no degradation and secondary emissions, high resistance to NO_x and SO_x in the flue gas, no need for flue gas pre-treatment, use of waste heat from the flue gas for CO_2 desorption due to high thermal conductivity. For the carbon adsorbents for the post combustion CO_2 capture, studies so far have been carried out only using simulated flue gas and under laboratory conditions. Hence, the site trials and demonstration of the carbon composite adsorbents for CO_2 capture at the power station through this CINSW project is a pioneering research in the world to study the adsorbent stability, the capture performance and captured gas quality using real flue gas.

The large scale solid sorbent CO_2 capture-regeneration prototype unit, designed and built by CSIRO, was modified and integrated with a dedicated pre-treatment system to form the carbon adsorbent test facility besides the ammonia absorption process pilot plant at the power station site. The development of the pre-treatment system enables the adsorbent CO_2 capture test facility to operate independently to the ammonia pilot plant and carry out its own pre-treatment of flue gas to remove SO_x, some NO_x and dust, though it was beyond the original project scope. Two main experimental scenarios were planned for testing. First, to conduct CO_2 adsorption and desorption tests using pre-treated flue gas. Pre-treatment of flue gas includes removal of SO_x and particulates. Second set of study was to use the flue gas with minor pre-treatment, i.e., removal of particulates alone and no SO_x and NO_x removal. The site trials and demonstration of the carbon fibre composite solid sorbent CO_2 capture prototype unit was successfully carried out using real flue gas at the power station. Over 200 adsorption and regeneration tests were performed on-site using real flue gas. Various operating parameters were varied during the course of testing to evaluate the performance of the adsorbents, and key performance data and operational experience were obtained.

The fully constructed CO_2 capture test facility with a control and monitoring system was transported to the site in October 2012. Pre commissioning of the CO_2 capture prototype unit was performed using simulated flue gas during November/December 2012 and March 2013, and the unit was fully functional at the site and ready for trialling actual flue gas. After addressing the strict safety requirements of Delta Electricity in relation to the pre-preparations for the supply of real flue gas, the flue gas to the solid sorbent test unit was provided on 29th May 2013. Following this, the next twelve months involved over 200 adsorption and regeneration tests performed on-site using real flue gas. For each test, the pressure, temperature, flow rate and gas compositions (O_2, CO_2, SO_2, NO, NO_2 and CO) at various points were monitored in real time. Various operating parameters were tested to evaluate the performance of the adsorbents, and key performance data and operational experience were obtained.

Under the study conditions, the CO_2 adsorption efficiency of the solid sorbents using real flue gas from the coal fired power station was found to be consistently over 98%, which means that most CO_2 in the flue gas was captured during an adsorption process. The captured CO_2 onto the solid sorbents needs to be released by a desorption process and the CO_2 desorption efficiency was found to be between 90-95%. As the CO_2 adsorption performance of the solid sorbents was maintained even after more than 200 tests, it was for the first time demonstrated that the solid sorbents were very stable towards real flue gas without any noticeable impact of SO_x and NO_x on their CO_2 adsorption performance, and this was the most significant outcome achieved for this project.

A five-stage CO_2 capture-regeneration process configuration was designed for the honeycomb monolithic carbon composite adsorbent based PCC process and HYSYS process simulation was conducted on the designed process configuration to estimate energy consumption. A preliminary life cycle assessment (LCA) study was carried out based on a case study of 350 MW power plant. As the flue gas waste heat is not sufficient to achieve the regeneration duty for processing the entire flue gas generated, extra auxiliary heat will be required. Two scenarios were investigated in the LCA: Scenario 1 was referred to as partial flue gas treatment, where only a fraction of the flue gas generated from the 350 MW unit was processed relying on the flue gas waste heat for adsorbent regeneration. When treating the complete flue gas stream generated, extra auxiliary heat will be taken from the steam plant of the power plant resulting in loss of electricity. This was considered as Scenario 2 referred to as complete flue gas treatment.

All the project objectives set out were successfully accomplished through this study. The important experimental data and site operational experience obtained at the power station form a base for further development of this carbon composite adsorbent CO_2 capture technology towards its application at fossil fuel fired power stations.

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1 Introduction

1.1 Background

In 2012, Australia's emissions were 555 MtCO_2-e, and electricity generation contributed just over one-third of total emissions (193 MtCO_2-e) [1]. NSW emissions in 2010 were 157 million tonnes CO_2-e, and nearly half of all NSW emissions in 2010 were from the stationary energy sector, primarily from public electricity production. Coal combustion alone produces 62 million tonnes of emissions annually or nearly 40 per cent of all NSW greenhouse gas emissions [2].

Growing concerns for global warming and climate change has attracted widespread efforts to develop efficient and cost-effective technologies for Post-combustion CO_2 Capture (PCC) from large point sources, such as coal-fired power plants. Post-combustion carbon capture has the greatest near-term potential for reducing emissions and can be retrofitted to existing coal-fired power plant infrastructure without requiring substantial changes to the combustion process. Among various PCC technologies for CO_2 capture from flue gas, use of porous solid sorbents offers a promising solution as it has the potential to be highly cost-effective and has less impact on the environment.

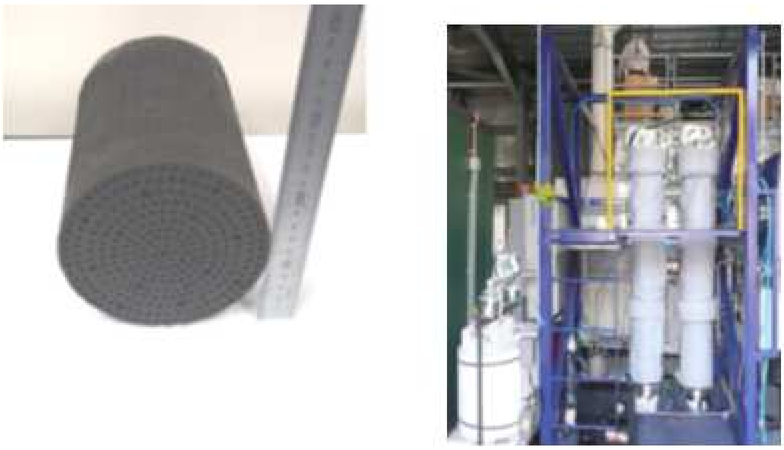
From January 2006, CSIRO began to develop the new CO_2 capture process by developing nano-structured monolithic carbon fibre composite adsorbents, which are fabricated in a honeycomb structure. This structure enables CO_2 capture in a dry process in dusty environments with low pressure drop. Hence, our process based on solid carbon adsorbents is advantageous over the solvent process in the following aspects:

- There are no degradation issues and secondary emissions using carbon adsorbents unlike amine process, and therefore the solid sorbent process is more environmentally friendly.
- The carbon composite adsorbents have very high resistance to NO_x and SO_x in the flue gas from coal fired power station, and our process could avoid the flue gas pre-treatment prior to CO_2 capture, thereby avoiding the expensive facilities (e.g. flue gas de-nitrification, flue gas de-sulphurisation) required to clean up the flue gas before it enters the CO_2 capture unit. This is a very important factor for coal fired power stations in Australia as there are no de-sulphurisation and flue gas de-nitrification facilities.
- It is a dry process. No large volumes of waste water and sludge are produced from the process.
- The energy efficiency is expected to be high. In other words, energy penalty for CO_2 capture is low mainly due to:
    - The open monolith structure leading to a low pressure drop through the adsorption column; consequently the operational power consumption is low.
    - This material possesses very high thermal conductivity and hence waste heat of the flue gas at 120-160^{o}C can be used for CO_2 desorption or in a combination with vacuum swing. Hence, no high quality energy will be extracted from the coal fired power stations.
    - This novel CO_2 capture process is carried out at room temperature and atmospheric pressure, so almost no energy is required for chilling and compression.

The State of the Art review of post combustion CO_2 capture by using solid adsorbents is presented in the next Chapter. The honeycomb shaped nano-structured monolithic carbon fibre composite adsorbents developed and patented by CSIRO have been demonstrated under laboratory test conditions to effectively adsorb over 95% of CO_2 from simulated flue gas with the pure component CO_2 capture capacity of 0.2 g/g at 0^{o}C. With proper choice of carbon fibre type and fabrication conditions these honeycomb carbon fibre adsorbents are tailor made to achieve a high portion of micropores less than 0.7nm, which are more relevant to CO_2 capture at coal fired post-combustion capture conditions (10-15% CO_2 at 25°C). It has been demonstrated that these carbon fibre composites are twice more effective than conventional activated carbons in adsorbing CO_2 [3]. The higher the adsorption capacity is, the lesser the energy required for the regeneration in terms of per unit of captured CO_2, smaller the footprint of the PCC plant, and lower the capital and operating costs.

1.2 Technology description

Since 2008, large sized carbon fibre composites and the large scale CO_2 adsorption coupled with regeneration test unit have been designed and developed (Figure 1a and b) to evaluate CO_2 capture performance using simulated flue gas with a maximum throughput of 200 L/min. Under laboratory test conditions, experimental results have shown these carbon fibre composites can effectively adsorb over 97% of CO_2 from simulated flue gas. Carbon dioxide capture or adsorption was performed at ambient conditions at a flue gas temperature of 25^{o}C and atmospheric pressure. Regeneration or desorption is carried out by applying heat and vacuum. The waste heat from the flue gas can be utilised for the thermal regeneration of sorbents at about 110-120^{o}C. It has been demonstrated, under laboratory conditions that combined thermal and vacuum swing regeneration of these materials, after adsorption, have produced desorbed CO_2 gas quality of up to 100% with overall capture efficiency of over 95%. Portion of the CO_2 product is used to purge the adsorbents before desorption so as to enrich the CO_2 concentration during regeneration.



(a) Adsorbent (b) large scale test unit

Figure 1: Large scale CO_2 capture adsorbent and adsorption and regeneration test unit

1.3 Scope of this project

In 2011, the Coal Innovation NSW (CINSW) awarded the project of Delta CO_2 capture site trials to CSIRO, to evaluate the performance of large size novel honeycomb carbon fibre composite adsorbents with actual flue gas. This carbon composite site trial and demonstration project was carried out at Delta Electricity power station. The large scale solid sorbent CO_2 capture-regeneration prototype unit, designed and built by CSIRO, was modified and then installed (besides another pilot plant unit using ammonia absorption process) at the power station site. Two main experimental scenarios were planned for testing. First, to conduct CO_2 adsorption and desorption tests using pre-treated flue gas. Pre-treatment of flue gas includes removal of SOx and particulates. Second set of study was to use the flue gas with minor pre-treatment, i.e., removal of particulates alone and no SO_x and NO_x removal. The originally proposed scope of the project was to test the performance of the solid honeycomb monolithic adsorbents at power station using the pre-treated flue gas obtained from the aqueous ammonia pilot plant. However, due to rescheduling of the time lines of the aqueous ammonia pilot unit relocation, the overall scope of this project was expanded and the time lines for the completion of project milestones were extended by two Quarters. The overall scope of the project is given below and the rescheduled timelines of the project milestones are given in Table 1.

- Design and construct a dedicated pre-treatment system to remove SO_2, NO_2 and dust to treat the real flue gas from the stack before entering the solid sorbents column for CO_2 capture.
- Carryout modifications to the existing large scale CO_2 capture system to suit operation with the flue gas available under site conditions.
- Conduct experiments as planned to test the effect of actual flue gas characteristics on the operation and performance of the CO_2 capture unit and to demonstrate this new CO_2 capture process at the power station site.
- Obtain operational performance data and experience, which will be used for further scale up of a pilot scale CO_2 capture plant.

Table 1: Timelines for the completion of various project milestones

No.	Timelines	Milestone
1	Q1, 2011	Execution of Agreement
2	Q2, 2011	Complete power station site investigation and project plan.
3	Q4, 2011	Complete site infrastructure design
4	Q1, 2012	Begin site infrastructure construction;
5	Q2, 2012	Complete site infrastructure construction; prototype unit transported to power station site
6	Q3, 2012	Complete installation of prototype unit at the site. Submission of Year 1 Annual Progress Report
7	Q2, 2013	Commission prototype unit; commence site trials and prototype unit demonstration
8	Q3, 2013	Commence data processing and analysis.
9	Q4, 2013	Complete site trials and prototype unit demonstration
10	Q1, 2014	Complete data processing and analysis; complete final project report including GHG LCA

2 State of the Art

2.1 Basic routes for CO_2 capture

Among the greenhouse gases CO_2 is the largest contributor to global warming. It is emitted into the atmosphere from various sources, mainly from the combustion of fossil fuels used in power generation, transportation and industrial processes. As the demand for electricity is projected to increase both in developed and developing countries, power generation will account for almost half the increase in global emissions between 2000 and 2030 [4]. On the other hand, Canadell et al. [5,6] have reported a declining trend in the long-term efficiency of the natural sinks in absorbing atmospheric CO_2 , with major implications for current and future growth of atmospheric CO_2. With fossil fuels as the primary source of energy (meeting over 90% of the increase in demand to 2030) for a foreseeable future [7,8], concerted action is necessary in order to stabilise the atmospheric level of CO_2. CO_2 capture and storage (CCS) have been receiving significant attention in recent years and are being recognized as promising options for CO_2 emission reductions [9].

Generally speaking, there are three basic CO_2 capture routes [10,11,12,13,14,15]: (1) pre-combustion capture (via oxygen-blown gasification) (e.g. integrated gasification combined cycle technology); (2) oxy-fuel combustion, i.e. removing nitrogen before combustion (e.g. oxy-fuel gas turbine technology); and (3) post combustion capture, i.e. capturing CO_2 from flue gas. Figure 2 illustrates the three basic CO_2 capture routes.

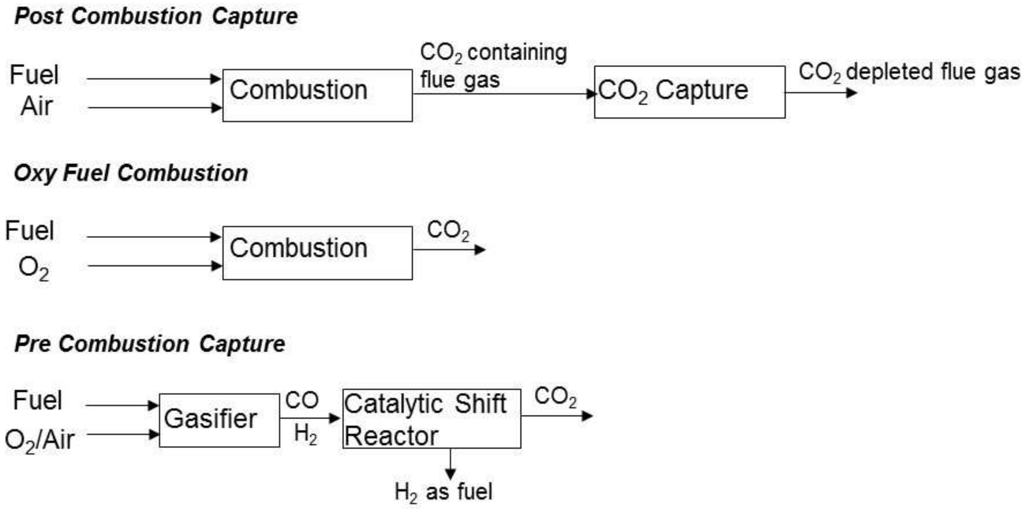


Figure 2: Three basic routes of CO_2 capture

Pre-combustion capture involves reacting a fuel with oxygen or air and in some cases with steam or CO_2 to produce a gas mainly composed of carbon monoxide and hydrogen, which is known as synthesis gas (syngas) or fuel gas. In a gasification reactor, the amount of oxygen available inside the gasifier is carefully controlled so that only a portion of the fuel burns completely. This ''partial oxidation'' process provides the heat necessary to chemically decompose the fuel and produce syngas. The carbon monoxide formed is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as furnaces, gas turbines, engines and fuel cells. This route needs long-term development in a number of enabling technical areas including syngas cleaning, gas separation, hydrogen turbine and fuel cells to achieve targeted efficiency towards a hydrogen economy.

In oxy fuel combustion, nearly pure oxygen is used for combustion instead of ambient air, thereby eliminating nitrogen and this results in a flue gas that is mainly CO_2 and H_2O. If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO_2 and/or H_2O-rich flue gas can be recycled to the combustor to lower the flame temperature. Oxygen is usually produced by low temperature (cryogenic) air separation [16,17], and novel techniques to supply oxygen to the fuel, such as membranes (e.g. oxygen permeable ceramic membranes) have been researched [18,19,20,21]. The major disadvantages of oxy-fuel combustion are the high capital cost and large electric power requirement inherent in conventional cryogenic air separation units required to produce oxygen. Chemical looping cycles [22] are being investigated as an alternative means.

The principle of post combustion capture is to remove CO_2 from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates/captures most of the CO_2. Adopting the post combustion capture route avoids the potentially long development times required to develop cost-effective coal-derived syngas separation technologies, hydrogen turbine technology, and fuel-cell technology etc. In particular, post combustion capture eliminates the need for substantial modifications to the combustion process and provides a means for near-term CO_2 capture for new and existing stationary fossil fuel-fired power plants. It has been suggested that the major bulk (two-thirds) of the cost involved in carbon sequestration process is the cost of CO_2 capture [23].

2.2 Post combustion CO_2 capture technologies

To date, there are several post combustion gas separation and capture technologies being investigated [24], namely; (a) absorption, (b) cryogenic separation, (c) membrane separation, (d) micro algal bio-fixation, and (e) adsorption. Figure 3 summarizes various technology options for post combustion CO_2 capture.

2.2.1 Absorption (i.e. solvent scrubbing)

This is a wellestablished CO_2 capture system primarily used in the chemical and oil industries. Physical absorption is temperature and pressure dependent with absorption occurring at high pressures and low temperatures. These processes are used when the partial pressure of CO_2 is high (>525 kPa). For lower CO_2 concentrations, chemical absorption is more widely applied. Chemical absorption of CO_2 from gaseous streams such as flue gases depends on acid-base neutralization reactions using basic solvents [25,26]. The preferred solvents for CO_2 removal for post combustion capture are amines (e.g. monoethanolamine MEA) [27,28] and ammonia solution [29,30], and for pre-combustion CO_2 capture Selexol (dimethylethers of polyetheleneglycol) [31], Rectisol (chilled methanol) [32], fluorinated solvents [33] etc are used. The exhaust gas is first cooled, then treated to remove particulates and other impurities before being fed to the absorption column, where the amine solvent absorbs CO_2 by chemical reaction. The CO_2-rich solution is fed into a stripper column where the temperature is increased (to about 120°C) in order to release the CO_2. The released CO_2 is compressed and the regenerated absorbent solution is recycled to the absorption column. Absorption based processes for CO_2 capture are closest to being commercialised. However, the solutions are corrosive, produce chemical by-products and are energy intensive due to large thermal losses in the absorption process [34].

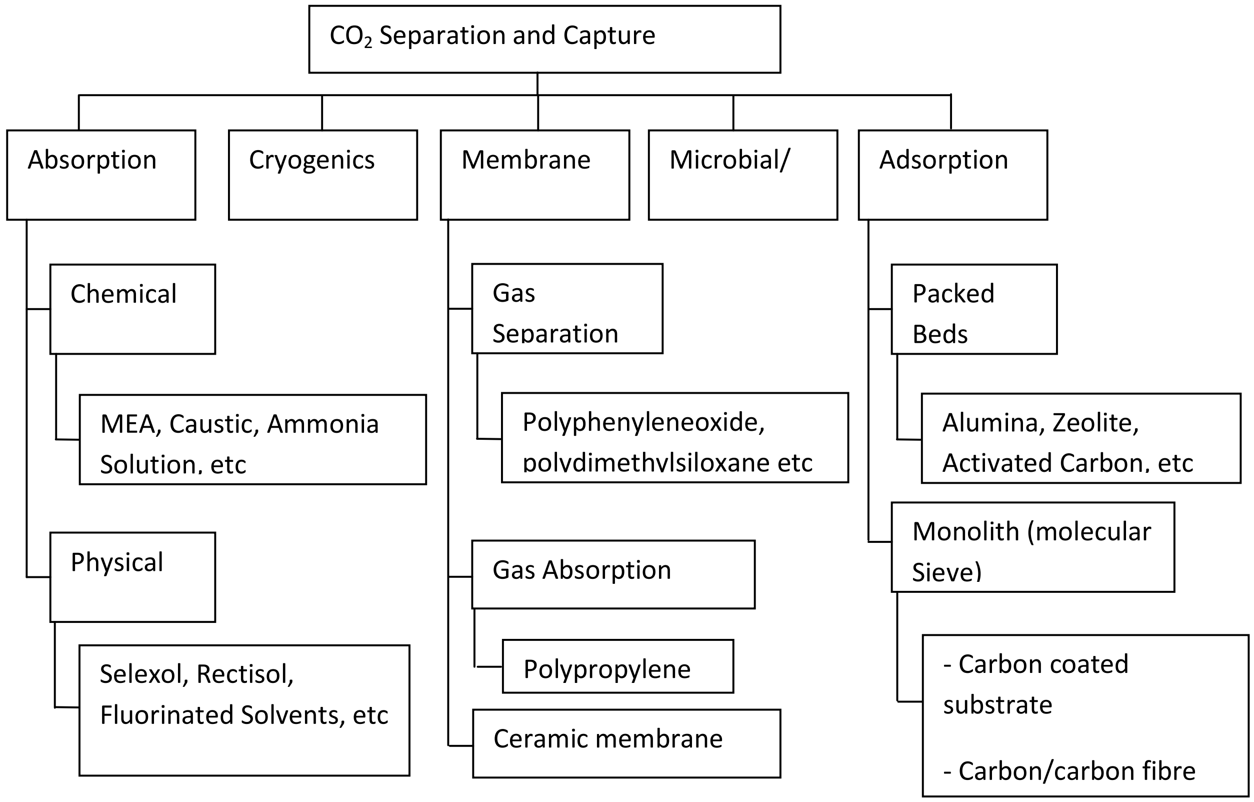


Figure 3: Different technologies for CO_2 removal (modified from [24])

2.2.2 Cryogenics

This process operates in the principle of separation based on cooling and condensation [35]. This method is applied for CO_2 capture where the gas stream contains high CO_2 concentration. It is presently not applied to more dilute CO_2 streams as those encountered with typical power generation plants. This technique also requires significant amount of energy for separation.

2.2.3 Membranes

The operation of membranes is based on the selective permeation of certain gases, allowing one component in the gas stream to pass through the membrane faster than the other. The membrane modules can either be used as conventional membrane separation units or as a gas absorption column [36, 37, 38, 39, 40]. In the former case, CO_2 removal is achieved due to the intrinsic selectivity of the membrane between CO_2 and other gases involved, while in the latter case, the CO_2 removal is accomplished by the gas absorption where the membranes, usually microporous, hydrophobic and non-selective, are employed as a fixed interface for CO_2 transfer. This method of gas separation using membrane is relatively new and the selectivity is generally low. The energy consumption is high. According to Corti et al. [38], membrane technology for flue gas application can be competitive only if CO_2 flue gas concentration is higher than 10%.

2.2.4 Use of microbial/algae

Apart from physicochemical methods of CO_2 removal, biological methods using algae, bacteria and plants [41, 42, 43, 44, 45] have also been adopted. Microalgal bio-fixation of carbon dioxide in photo bioreactors has recently gained renewed interest for CO_2 mitigation. Insufficient illumination would limit the micro-organism growth and hence would reduce the CO_2 removal. Chemoautotrophic micro-organisms which uses inorganic chemicals instead of light energy for CO_2 removal have also been attempted [46].

2.2.5 Adsorption

Adsorbents development for CO_2 capture can be classified broadly based on two main adsorption mechanisms: Physical adsorption and chemical adsorption [47, 48, 49, 50]. In physisorption gas molecules are adsorbed on the pore surface of the adsorbent due to weak electrostatic van der Waals forces, where as in chemisorption, target gas molecules undergo chemical reaction to bind to the sorbents. In physisorption the sorbents are generally stable even over 200°C, while chemisorbents tend to degrade over 120°C. Also, chemisorbents can permanently bind certain species thereby decreasing the capacity of sorbents. Our focus on the solid sorbents for post combustion CO_2 capture application has been on physisorbents.

A variety of solid physical adsorbents such as activated carbons [51, 52, 53, 54], zeolites [55, 56, 57] and mesoporous silicates [58], alumina [59, 60] metal oxides framework [61,62] have been extensively investigated for CO_2 separation. To be competitive with other available technologies, solid sorbents must offer substantially greater adsorption capacities and selectivity for CO_2 than currently available physical sorbents, be less sensitive to toxic materials like SOx, NOx and moisture in the gas stream, readily able to be regenerated without compromising on the performance during repeated capture and discharge operations and possess good thermal and mechanical properties. Zeolite based adsorbents have been extensively studied in CO_2 separation processes next to activated carbon [63 64]. However, carbon based adsorbents presents some key advantages over zeolites, such as hydrophobicity, significantly lower adsorbent cost, lower energy for regeneration (lower isosteric heat of adsorption of CO_2 for activated carbon, which nearly half that of zeolite, means lower amount of energy needed for regeneration)[52, 65]. Comparing the estimates from the studies by Radosz et al. [66] and Ho et al. [67],the total capture cost of US$27-44 per tonne of CO_2 avoided using carbon adsorbents has been reported as compared to US$51 for Zeolite adsorbents.

In a US DoE funded study [68, 69] over 100 different potential CO_2 sorbents were evaluated. The adsorbent materials were highly varied in their chemical and physical properties, and divided into three categories: carbon based, amine supported materials and zeolites. They were tested under the same conditions including using real flue gas of 10-12% CO_2, saturated moisture (90% relative humidity), 5-6% O_2, 100-120ppm NOx, and 50-250ppm SO_2. The study identified that carbon-based materials showed a working CO_2 capacity between 0.3 to 1.1 wt% both in the laboratory and in the field conditions with superior repeatability and stability. The supported amine based sorbents had a higher working CO_2 capacity between 1.3 to 7.5 wt%, but showed degradation in the field conditions. Zeolites had up to 1.6 wt% CO_2 capacity, but its performance degraded quickly by the presence of moisture. In summary, carbon-based sorbents had a low CO_2 capacity, but exhibit superior cyclic stability and a resistance to poisoning by flue gas constituents. Supported amines had exhibited high CO_2 capacities and low theoretical regeneration energies, but they were not cyclically stable and can be negatively affected by flue gas constituents. Zeolites showed an extreme affinity to moisture that makes their use for CO_2 capture unlikely. In another study, a synergistic negative effect on CO_2 adsorption by zeolite material was noticed due to the presence of water and SO_2 [70].

2.3 Carbon composite adsorbents for CO_2 capture

2.3.1 Developments on carbon composite adsorbents

Over the last 15 years several researchers have attempted to make the activated carbon materials in monolithic composite type to improve adsorption capacity [71, 72]. A composite adsorbent is a heterogeneous combination of two or more materials (reinforcement material and resin binders), differing in form or composition and their combination results in a material that has properties that cannot be achieved with either of constituents acting alone. They can be made in many shapes including cylindrical, flat plate or block shaped [73] or structured channel opening also known as honeycomb structures [3]. Activated carbon pellets or milled activated carbon powders or carbon precursors (e.g. phenolic resins) mixed with binders or fillers or others have been fabricated (extrusion) into composites of desired shapes [74,75]. Honeycomb structure refers to any structure having a plurality of openings or passages of any desired size or shape extending all through the composite (as flow through channels). Introduction of a honeycomb shaped carbon fibre composite adsorbents not only allow distribution of the process fluid through a plurality of flow-through channels with minimal channel blocking, but also enable uniform carbonisation and activation during the adsorbent fabrication. This shape is known to have a very high geometric surface area to volume ratio [76]. Structured porous monolith materials made from carbon fibres, which have the ability to selectively adsorb gases due to its molecular sieving characteristics, have been investigated [77, 78, 79, 80, 81, 82, 83, 84, 85, 76, 86]. More recently, carbon fibre composites have been investigated as adsorbents for gas separation and storage [3, 76, 85, 86, 87]. Carbon fibre composite in monolith form reduce the interparticle voids and maximize bulk density, thereby increasing the adsorption capacity of the material. These carbon fibre monolith adsorbents have a large portion of micropores depending on the pyrolysis and activation steps involved in the manufacturing process. The molecular sieving ability of these carbonaceous adsorbents can be controlled during their fabrication process to make them be preferential to a gas (e.g. CO_2) adsorption based on the difference in the shape and size of the adsorbing molecule.

For example, US Pat. No. 6,030,698 to Burchell et al. [88] describes the manufacture of carbon fibre composite molecular sieve (CFCMS) material from pitch based carbon fibre and phenolic resin. The composite material is vacuum moulded into a plate (or cylinder) shape. Klett and Burchell [89] prepared a carbon fibre composite material as a flat plate (12 inches length, 12 inches width and 2 inches thickness) using polyacrylonitril (PAN) based fibre and phenolic resin. US Patent No. 5925168 to Judkins et al. [90] indicates that the composite characteristics like strength, thermal conductivity, pore size distribution, density and electrical properties can be modified or controlled with the appropriate carbon fibre or blend of carbon fibres. US Patent No. 6090477 to Burchell et al. [91] describes the use of two types of pitch based carbon fibres (isotropic and mesophase), to enhance the thermal conductivity of the monolith. The bulk (typically cylindrical) or flat plate carbon (fibre) monoliths have been formed with carbonizable binding materials and subsequently dried, cured, carbonised and activated. The formed monolithic material is quite porous, and can therefore be used for adsorbing a component or components from a fluid by passing the fluid through the monolith. However, this type of structure has several problems, in particular, a high pressure drop across the monolith. In addition, these monoliths also have a tendency for the pores to become blocked, should there be any dust or other particular matter in the fluid passing through the monolith. Both of the above problems tend to lead to a reduction in the efficiency of the monolith.

Another type of the structured honeycomb monoliths comprises of substrate coating or impregnation with carbon materials which are subsequently dried, cured, carbonised and activated. Since about 1980, more than 90 % of the monoliths use substrates, which are made from ceramic material, cordite [92,93,94]. A major disadvantage of ceramic supports is their high cost. Monolith materials also use various metal substrates. However, base metals are more susceptible to loss of performance through poisoning by sulphur, trace lead etc. In addition, the carbon coating may erode from the substrate, creating uneven surfaces inside the monolith which can lead to blockages [95, 96, 97, 98, 99, 100, 101].

To develop more efficient high performance adsorbents to capture CO_2, CSIRO devised the honeycomb shaped nano-structured monolithic carbon fibre composite adsorbents, and these carbon fibre composites are twice more effective than conventional activated carbons in adsorbing CO_2 as compared in Figure 4 [3]. In the past a few years CSIRO has made a continuous effort, and made further significant progress in developing new generation carbon composites using carbon nanotubes (CNT) modified carbon fibre composites [102] and macadamia nutshell (MNS) derived biomass carbon composites [103]. Both the CNT and MNS based carbon composites have shown further enhancement in CO_2 adsorption capacities (at 25°C and 1 atm) compared to originally developed carbon fibre composite adsorbents (Figure 5). Further improvements in CO_2 adsorption capacities with these new carbon composites, offer great potential for their application in the post-combustion CO_2 capture.

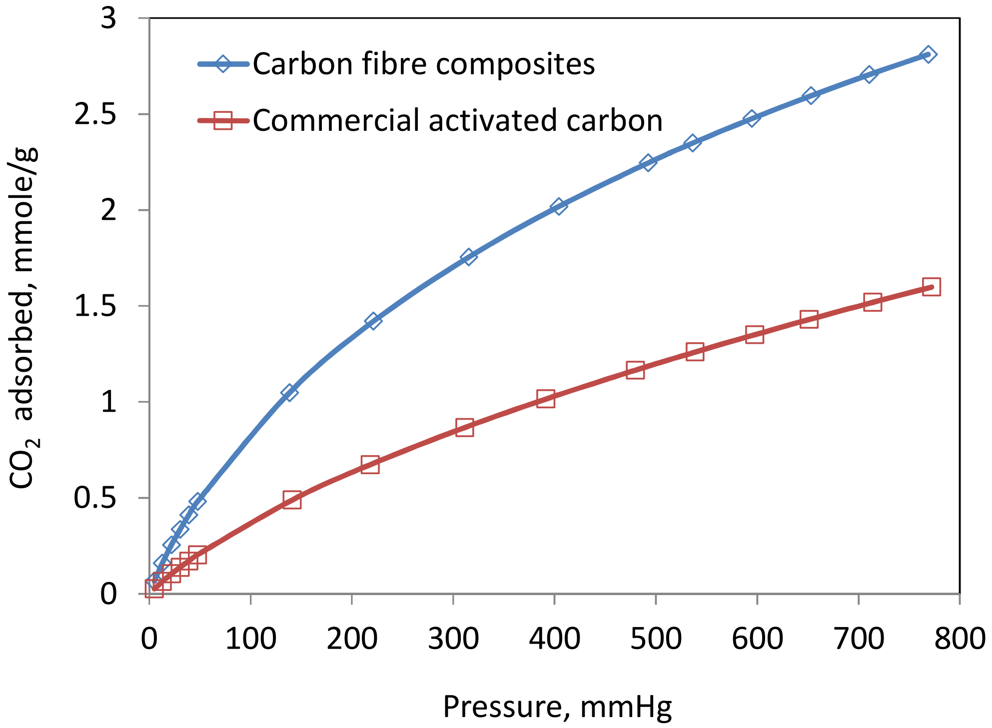


Figure 4: Comparison of CO_2 adsorption performances between CSIRO developed carbon fibre composite and activated carbon pellets

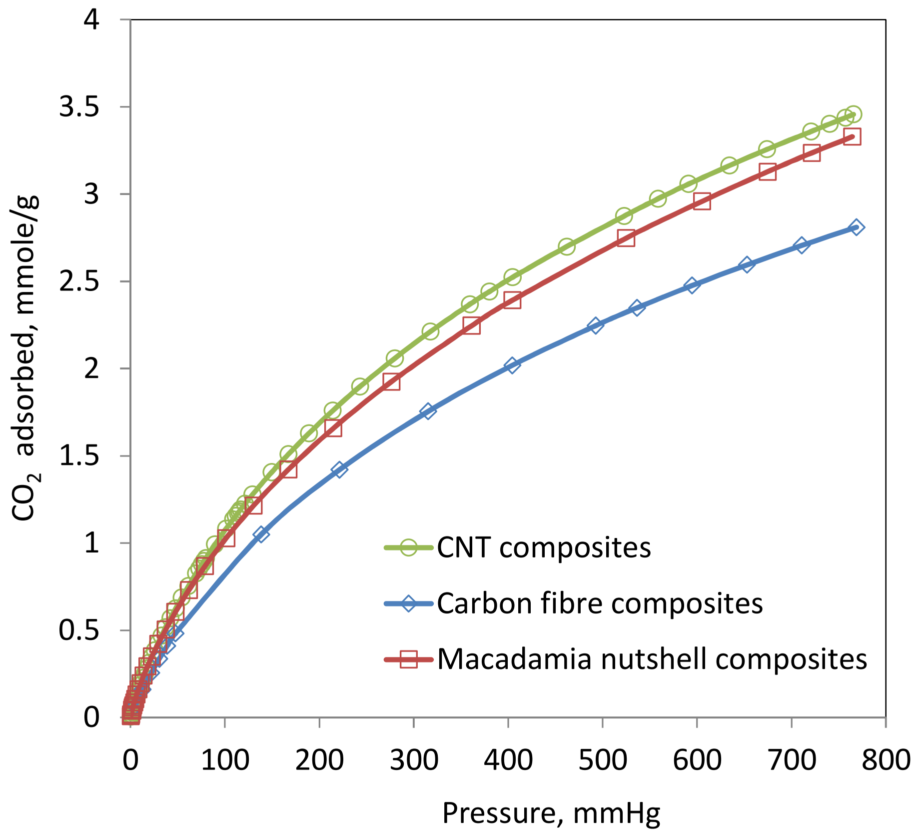


Figure 5: Advancement in carbon based composites performance with improved CO_2 adsorption capacities

To the best of our knowledge, the CO_2 adsorption capacities achieved by CSIRO composites are among the highest, compared to other porous carbon based solid adsorbents in the world that are produced by physically activation. Physical activation is normally carried out by heating the adsorbents using steam or CO_2, after carbonisation. Chemical activation is generally carried out using various activation agents or chemicals like $ZnCl_2$, KOH, K_2CO_3 etc [104]. Although some chemically activated carbon adsorbents have reported higher CO_2 adsorption capacities at saturation pressure (760 mm Hg and ambient temperature 298 K) [105,106], at pressures of 114 mmHg (corresponding to 15% of CO_2), which are of more relevance for flue gas applications, CSIRO composites have found to have very high CO_2 adsorption capacities. Moreover, chemical activation method is an expensive and complex process, requiring additional steps for washing to remove residual inorganic material, which causes secondary problems of pollution, where as physical activation is simple, environmentally benign, provide better control of micropore formation and more suitable for carbon adsorbents [107]. So our focus of research on carbon composite adsorbent development is by fabrication using physical activation.

2.3.2 Types of CO_2 capture adsorbers using carbon adsorbents

Gas adsorption is a cyclical continuous operation involving multiple beds in which at least one bed remains active with capture mode whilst the others are in regeneration mode by either the temperature swing (TSA) or the pressure swing (PSA) or vacuum swing (VSA) methods [47]. In TSA, adsorption is carried out at atmospheric pressure and the regeneration is achieved by heating the adsorbents using hot air or steam. Similar to TSA, electric swing adsorption (ESA) is referred to that the solid sorbents are heated by the Joule effect of applying electricity to the sorbents [108]. In PSA, adsorption is performed at pressures higher than atmospheric pressure, while desorption is performed at atmospheric pressure. In VSA, adsorption operates at atmospheric pressure and ambient temperature and desorption operates at lower pressures. In a post-combustion application, the flue gas would pass through a bed of solid sorbents and the CO_2 would be preferentially adsorbed. The regeneration energy requirement for CO_2 capture using dry solid adsorbents is significantly reduced compared to the aqueous amine-based process because of the absence of large amount of water [109].

The adsorption process used for solid sorbents for CO_2 capture from flue gas can be broadly differentiated as fixed bed, moving bed and honeycomb. Fixed bed or packed bed adsorbers are by far the most commonly used adsorption system, using adsorbents like activated carbon pellets packed in reactor vessels. In a fixed bed adsorption system, the feed gas generally flows downwards (as upward flow would result in fluidisation of fine sorbents) through the stationary adsorbent packing. For the conventional packed bed reactors, the inherent limitations, such as, high pressure drop, low mass and heat transfer characteristics, are not favourable for its application in the post combustion CO_2 capture. Due to the high pressure drop associated with fixed bed and given the huge volume of flue gas, moving bed reactor operates with adsorbent particles moving in the opposite direction as the gas while the gas flows either counter current or across the sorbents. The adsorbent material circulates between adsorption section and regeneration section. It provides greater mass transfer efficiency, as the adsorbents leave the adsorption section when it is essentially at equilibrium with the feed gas. Fluidised bed is also one form of moving bed reactor where the gas moves upwards and the sorbent enters at the top of the bed and leaves the adsorber in the bottom of the bed. Honeycomb structure refers to the unit having a plurality or matrix of openings or passages of any desired size or shape extending all through the material (as flow through parallel channels) and so the drawbacks of the fixed bed adsorber are avoided. The structured honeycomb shaped adsorbents by their nature are immobilized, so fluidisation of adsorbents is nonexistent. The honeycomb shaped adsorbents are placed inside the reactor vessel with flue gas able to enter from the top or bottom of the reactor. Generally flue gas enters from the bottom of the reactor and leaves from the top of the reactor. As the flue gas pass through the adsorbent channels, the adsorbate from the bulk gas phase are adsorbed onto the adsorbent surface. The honeycomb type reactors are more suited than fixed bed reactors for flue gas application as it allows the use of dust laden flue gas at high flow rates without large pressure drop as it pose minimum obstruction to particulate matter. It also provides greater geometric surface area (which leads to better gas solid contact) and ease of scale-up compared to packed bed. Another important aspect of the honeycomb carbon fibre composite adsorbents developed by CSIRO [110] is that the whole adsorbent comprise of reactive carbon monolith, unlike other systems such as carbon coated honeycomb material [111, 112], having inert substrate coated (about 10% of volume) with active material on the inner walls of the channel, which would result in gradual reduction in its performance.

2.3.3 Laboratory and site trials of CO_2 capture using carbon adsorbents

Table 2 provides an overview of available literature of carbon based adsorbents studied for CO_2 capture from flue gas. As it can be seen from the Table 2, to our best of our knowledge for carbon adsorbents, so far studies have been carried out only using simulated flue gas and under laboratory conditions. Only one study by Wang et al. [113] a site trial at the power station was carried out with activated carbon. However, the CO_2 concentration in the flue gas to the activated carbon adsorbent was 70-80% and was not subjected to actual flue gas conditions. Experiences from actual site trial studies are very critical for the development of the solid sorbent CO_2 capture technology. A number of large-scale demonstration plants (equipped with a capture capacity of 1 $MtCO_2$/year) for the post-combustion capture of CO_2 from coal-fired power plants planned for operation in the next decade are solvent based [114].

To our knowledge, this carbon fibre composite solid sorbent site trial and prototype unit demonstration for CO_2 capture from real coal fired station flue gas using a combined thermal and vacuum swing regeneration is by far the first of its kind in the world. The developmental stage in the solid sorbent studies using honeycomb carbon fibre composite for flue gas CO_2 capture has already advanced ahead of other research works with carbon based adsorbents around the world, as we have completed our evaluation of the performance of these honeycomb carbon fibre composite solid sorbents under laboratory scale from 2006 to 2008 and under large scale using simulated flue gas between 2008-2011 and then with this site trial from 2011-2014 using real flue gas. The CSIRO devised honeycomb shaped carbon fibre composite adsorbents are novel and exhibits unique features of high CO_2 adsorption capacity, low pressure drop, good mechanical properties, handle dust containing gas streams, thermally conductive and selective adsorption of gases. The site trial studies aimed to provide information about the stability and performance of these carbon composite adsorbents under actual field conditions subjected to real flue gas containing mixture of various gas constituents for an extended period of time, which is very important for the development of this novel CO_2 capture technology.

Table 2: Analysis of literature for carbon adsorbents used for CO_2 capture from flue gas

Adsorbent Type	Scale/ Adsorber Type	Gas composition	CO_2 adsorption capacity		Regeneration			Ref.
			Analysis Condition	mmole g^{-1}	Method	Max CO_2 conc., %	Capture efficiency, %	
Pitch based activated carbon	Lab Scale/fixed bed	Simulated flue gas, 15% CO_2 in N_2	Pure CO_2 @15kPa, 30°C	1.1	TSA, VSA-ESA	75-80	76~100	115
Activated carbon	Lab Scale/fixed bed	Simulated flue gas, 17% CO_2 , 79% N_2, 4% O_2	Pure CO_2 @15kPa, 25°C	0.75	PSA	99.8	34	116
Norit activated carbon	Lab Scale/fixed bed	Simulated flue gas, 17% CO_2 in N_2	17 v% CO_2, bal N_2, 30 °C	0.77	TSA VSA VTSA	43	40 87 97	52
Pitch based activated carbon	Field/ fixed bed	Enriched flue gas 74.5% CO_2	Pure CO_2 @15kPa, 30°C	0.7	VPSA	95.6	90.2	113
Commercial activated carbon pellets	Lab Scale/fixed bed	Simulated flue gas, 15% CO_2 in N_2	15 v% CO_2, bal N_2, 47°C	0.09	-	-	-	70
Biomass Activated carbon	Lab Scale/fixed bed	Simulated flue gas, 14% CO_2 in N_2	Pure CO_2 @15kPa, 25°C	1.02-1.08	-	-	-	51
Norit activated carbon	Lab Scale/sound assisted fluidised bed	Simulated flue gas, 15% CO_2 in N_2	15 v% CO_2, bal N_2, 25°C	0.37-0.55	-	-	-	117
CSIRO carbon nanotube composite	Lab scale/ Honeycomb monolith fixed bed	Simulated flue gas, 12% CO_2, 5% O_2, bal N_2	Pure CO_2 @15kPa, 25°C	1.18	-	-	-	102
CSIRO carbon fibre composite	Large scale/ Honeycomb monolith fixed bed	Simulated flue gas, 13-15% CO_2, 5-6% O_2, bal N_2	Pure CO_2 @15kPa, 25°C	0.92	TSA & VSA	~100	96	110

3 Development of Site Test Facility

The major activities involved in the development of site test facility are listed below:

- Site investigation
- Design of the pre-treatment system
- Modifications to the existing large scale CO_2 prototype unit
- Development of assembly design drawings
- Development of control and monitoring system for the site test unit
- Construction of pre-treatment system and integration with the CO_2 capture unit
- Connection of the test unit to flue gas.

3.1 Site investigation

3.1.1 Plant layout

The first line of activity after the project commencement was the power station site investigation. In May 2011, the project team from CSIRO visited Delta Electricity power station for studying the location of the solid sorbent prototype test unit near the stack and the on-site infrastructure requirements. The positioning of the flue gas extraction and return points on the duct to supply flue gas to aqueous ammonia CO_2 capture pilot scale plant and the solid sorbent prototype test unit were identified (Figure 6).

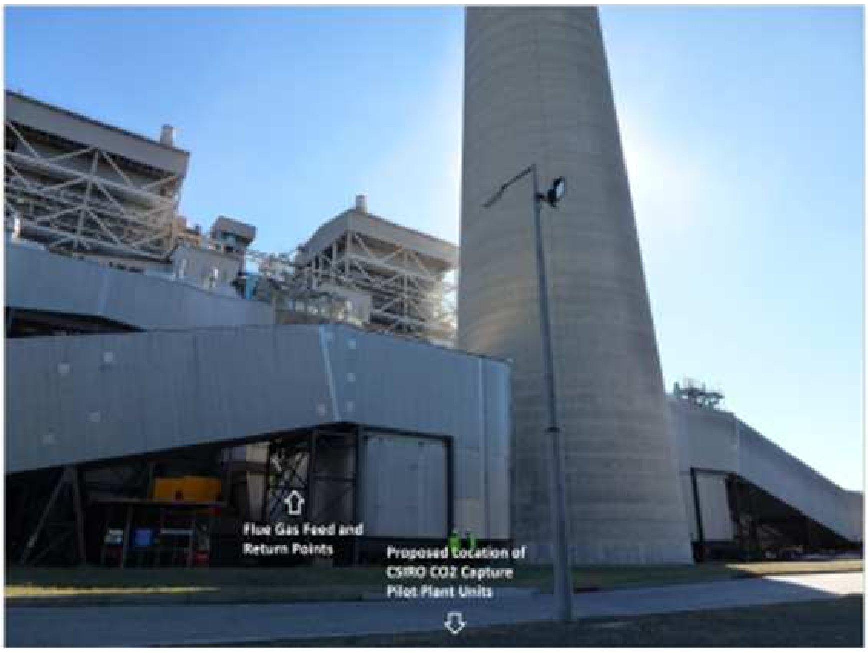


Figure 6: Illustration of the proposed flue gas extraction and return points and the position for CO_2 capture pilot plant units

According to the original project plan, the prototype test unit was to be installed alongside the ammonia pilot scale plant, and during the study period flue gas will be supplied by the ammonia pilot plant from a split stream pipeline connecting the pilot scale plant and the power station. The sketch of a top view showing the approximate locations of the CSIRO test units is given in Figure 7. A bounded concrete area of about 18m x 15m was marked to carry out the CSIRO's CO_2 capture testing at Delta Electricity's power station. Out of this area, about 14m x 15m accommodated the aqueous ammonia and solid sorbent test units. The space allocated for the large scale solid adsorbent prototype unit was about 6.5m x 4m. The solid sorbent test unit required a pre-treatment system installed with the adsorbent columns. The flue gas inlet lines from the main flue gas duct and the return line are also represented in Figure 7. The distance from the stack to the flue gas inlet line would be about 11m. The estimated flue gas inlet slip stream to the solid sorbent pre-treatment system will be approximately 7-10m.

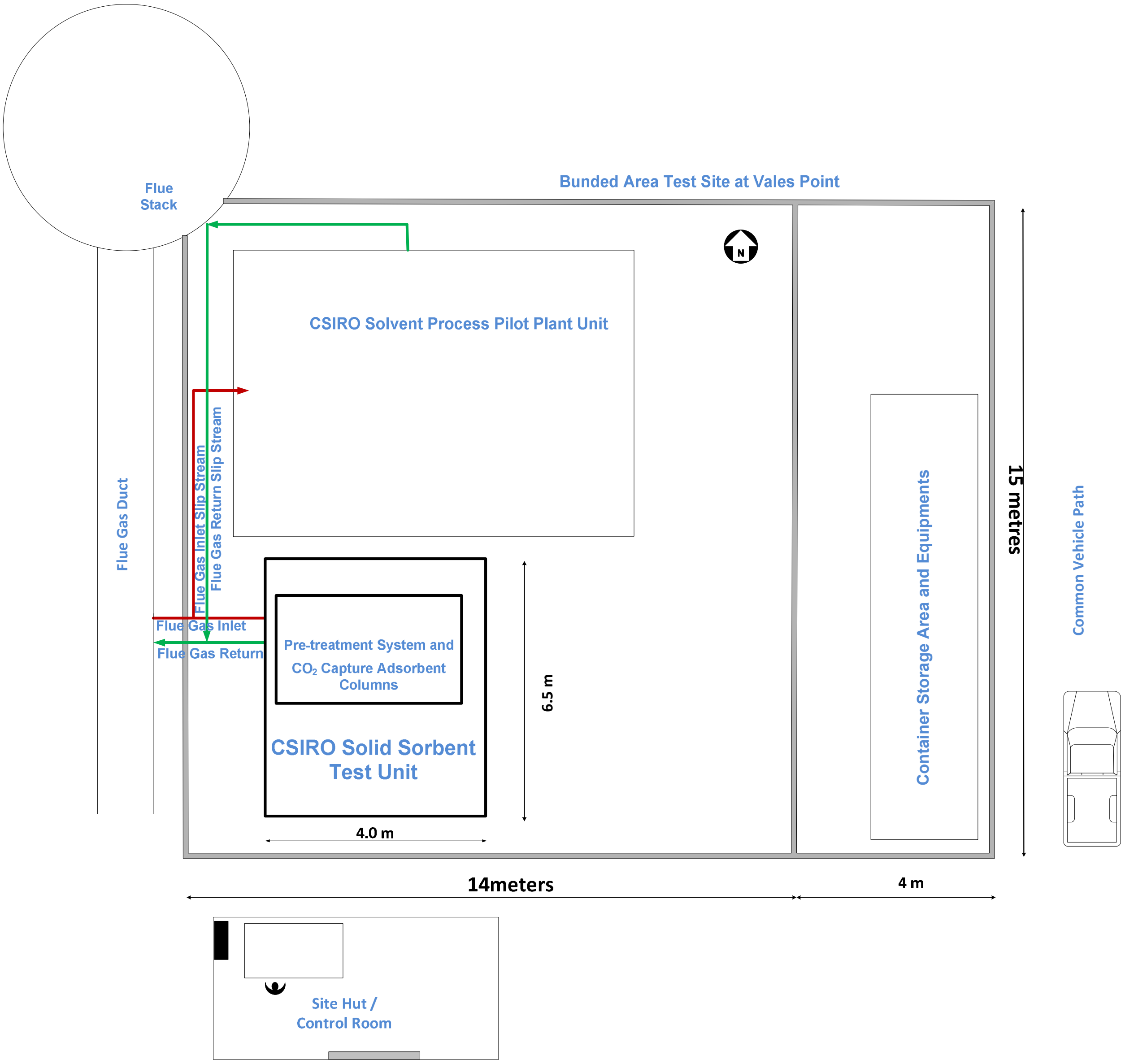


Figure 7: Plant layout at the power station for the CO_2 capture site trial using large scale carbon fibre composite solid adsorbent prototype unit

3.1.2 Flue gas characteristics

Typical flue gas composition of the raw flue gas and the coal properties used are summarised in Table 3 and Table 4.

Table 3: Characteristics of raw flue gas

Parameter	Unit	Values (Range)
Flow rate	Dry gas, 1 atm, m^3/s	160-172
Pressure	bar	0.97-0.99
Temperature	^oC	115-152
Gas composition		
N_2 + Ar	vol%	75.9
CO_2	vol %	9.9-13.0
O_2	vol %	5.5-8
H_2O	vol %	6.0
CO	ppmv	9-19
SO_2	ppmv	100-300
NOx	ppmv	200-300
Dust	mg/m^3 (dry)	2.5

Table 4: Properties of coal used

Proximate analysis (a.d. %)		Ultimate analysis (d.a.f. %)	
Moisture	2.4	Carbon	84.4
Ash	15.6	Hydrogen	5.09
Volatile matter	28.4	Nitrogen	1.74
Fixed carbon	53.6	Oxygen	8.4
		Sulphur	0.39
Ash (%)			
SiO2	56.6	TiO_2	1.1
Al2O3	31.9	Mn_3O_4	0.07
Fe_2O_3	3.0	SO_3	2.10
CaO	3.5	P_2O_5	0.91
MgO	0.3	BaO	0.06
Na_2O	0.31	SrO	0.14
K_2O_3	0.22	ZnO	<0.01

3.2 Pre-treatment system

During the site investigation, it was found that the pre-treated flue gas cannot be supplied from the ammonia pilot scale CO_2 capture plant for the solid adsorbent CO_2 capture trials on time as planned originally due to its relocation time issue. Hence, we had to extend the project scope by developing a flue gas pre-treatment system. This standalone test facility is capable of independent operation in terms of extraction of flue gas from the stack and able to pre-treat the gas to remove SO_2 and dust. The typical composition of flue gas from the power station, given in Table 3, formed a basis for the design of the infrastructure. The flue gas composition has majority N_2 of 75.9%, CO_2 10.9%, O_2 6.7%, moisture 6.0% (volume) and other constituents like SO_x, NO_x and dust. Although the temperature of the flue gas at the stack has been recorded to be over 115°C, under our study conditions with the amount of flue gas extracted by operating the prototype solid sorbent unit alone being less than 85kg/hr, the flue gas temperature at the inlet to the solid sorbent test unit would be close to ambient temperature (25-35^{o}C).

Provision of a dedicated pre-treatment system enabled the operation of solid adsorbent CO_2 capture system independently to aqueous pilot plant unit. The schematic of the pre-treatment system is shown in Figure 8. The pre-treatment system designed was able to provide two flue gas streams. One stream (denoted in red) provides raw hot gas to the adsorption columns for thermal regeneration of adsorbents and the other stream (denoted in green) provides pre-treated flue gas (or bypass caustic scrubber pre-treatment) to the adsorption column for CO_2 capture at 25^{o}C. The schematic for the adsorption column system is shown in Figure 9. Therefore, this allows us to conduct CO_2 adsorption and desorption tests using pre-treated flue gas. The flue gas goes through the cartridge dust filter to remove particulates and then through the caustic scrubber pre-treatment mainly to remove SO_2. Alternatively, planned experiments can also be conducted using raw flue gas for adsorption with particle removal only. During the study period, flue gas was only extracted by the solid sorbent test unit and the ammonia pilot plant was not extracting the flue gas. CO_2 capture was generally carried out at ambient conditions (25°C and 100 kPa).

The high temperature variable speed blower (BLH-01) draws the flue gas from the main flue gas duct to stack, and heated up in a furnace (FUR-01) to about 200^{o}C and then sent through the adsorbent column to heat the solid adsorbent material for regeneration or CO_2 desorption. A coiled tube arrangement (shown in Section A of Figure 8) was made inside the furnace to obtain the desired flue gas temperature at the outlet of the furnace. In real operation, the waste heat from the flue gas alone could be sufficient for the regeneration of these adsorbents and additional heating using furnace would not be required if we draw some of the raw flue gas before the economiser, which is at a higher temperature (about 180^{o}C). The flow rate of hot flue gas required for regeneration of adsorbents in the prototype unit was about 60kg/hr at 155°C. A cartridge type HEPA particulate filter (CF-01) was placed before the furnace to capture the dust in the flue gas down to less than 1 micron.

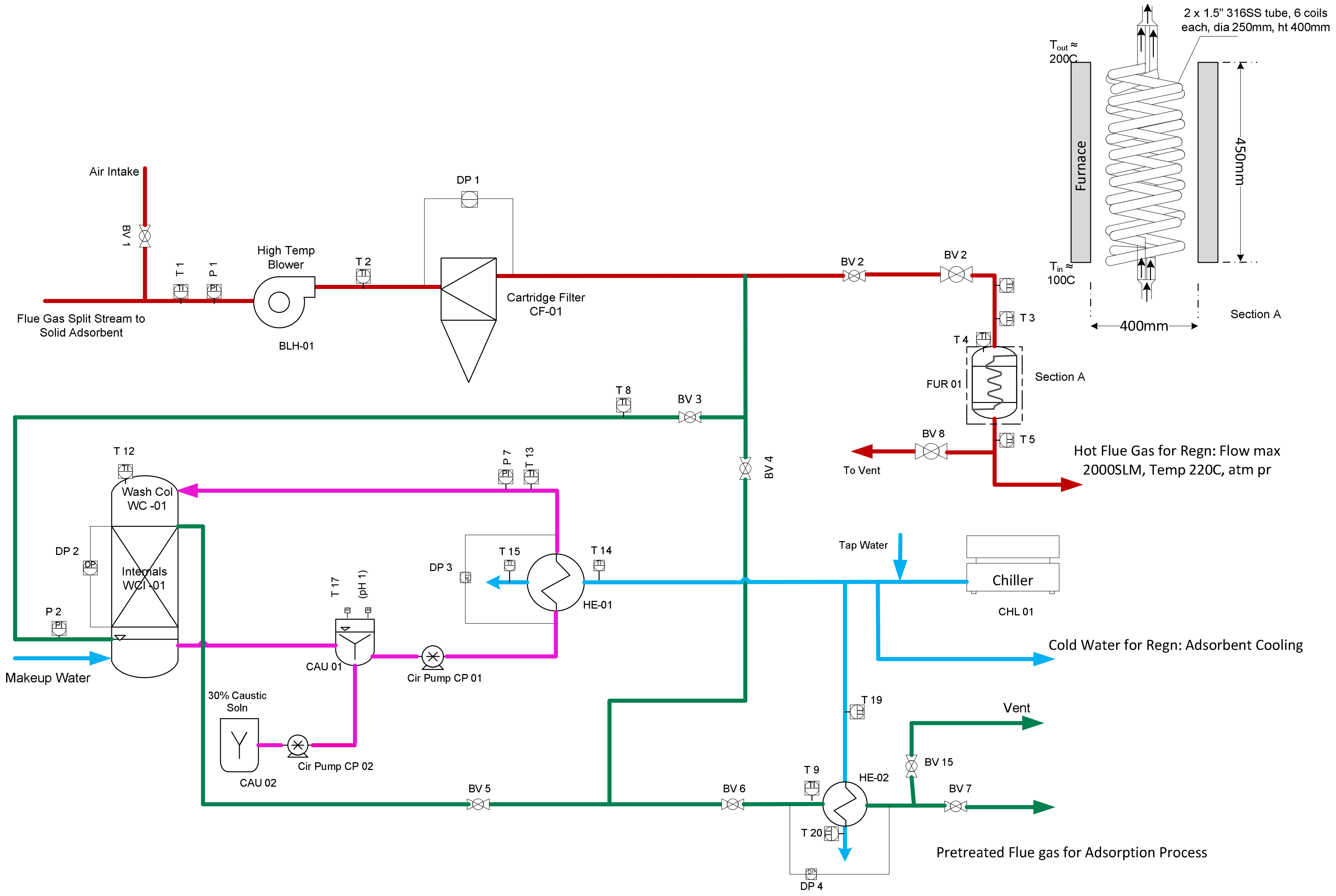


Figure 8: Schematic of the flue gas pre-treatment system for Solid Sorbent CO_2 Capture Prototype Unit

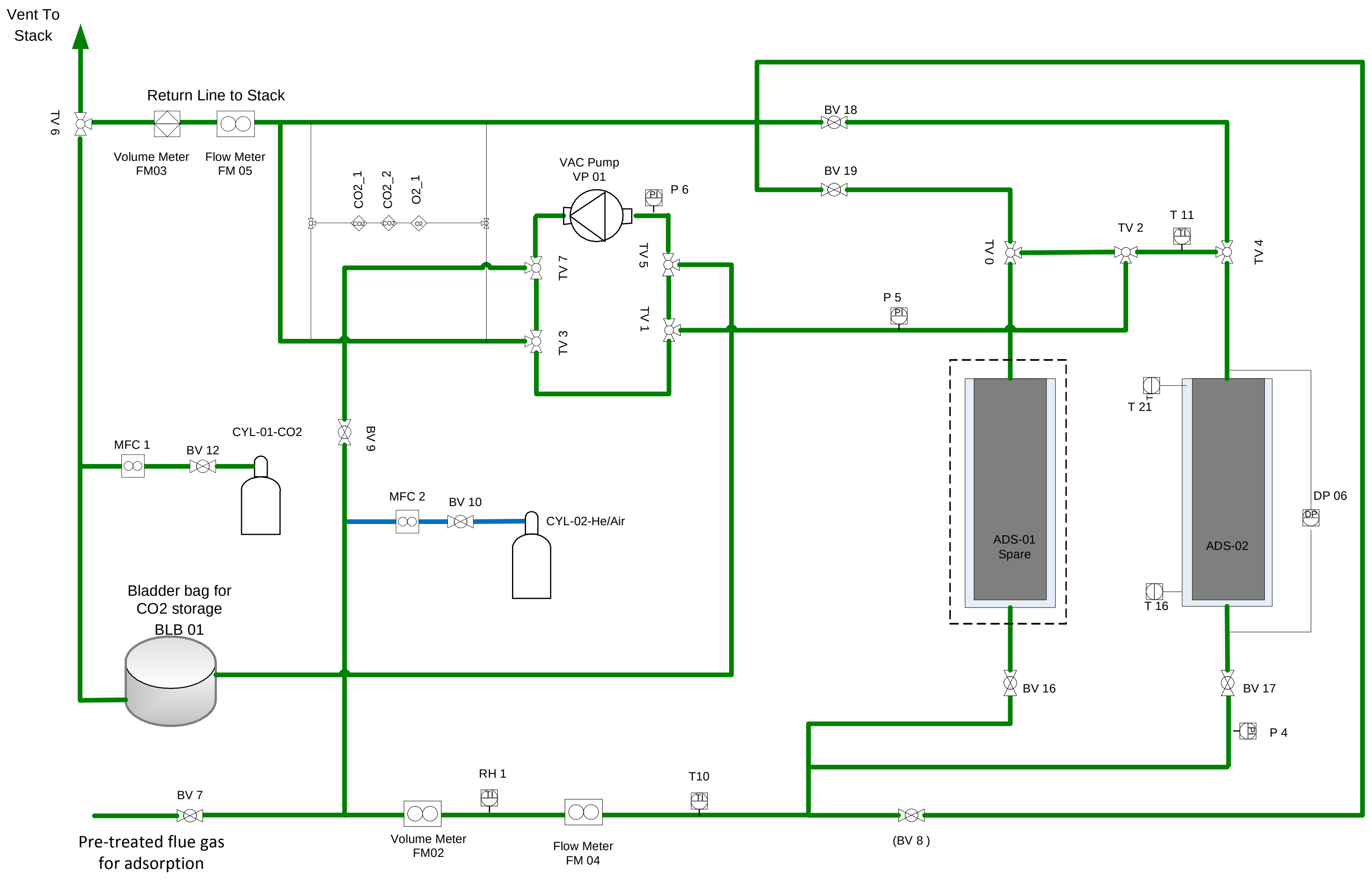


Figure 9: Schematic of capture and discharge circuit for the solid sorbent prototype unit

The other portion of the flue gas stream undergoing pre-treatment before being used for CO_2 adsorption, passes through single stage direct contact cooling (DCC) packed bed wash column (WC-01). The sketch of the designed DCC column is shown in Figure 10. The DCC wash column was used mainly to remove SO_x and some NO_x. The 2m long x 161mm dia (ID) column (316SS) consist of 0.75m pall rings (16mm SS) packing and was operated by circulating a 1% caustic solution (counter current to flue gas) at a pH of ~9.0 to induce good gas-liquid contact surface area. Demisting at the top of the wash column was carried with a stainless steel fibre pad located above the packing. The pre-treated flue gas exited through the top section of the column. Caustic or makeup water was added to the spent wash solution leaving the column from the bottom to maintain the alkalinity of the solution to around pH9. The circulation pump (CP-01) fed the caustic solution to the column. Periodic blow down of the caustic solution from the wash column reduced the build-up of the particulates removed from flue gas, and nitrate and sulphate salts of sodium in the solution. Heat exchanger (HE-01) was used to cool the spent caustic solution coming out from the column before returning to the column for re-use. Cold water from the chiller (CHL-01) was passed through the heat exchanger when required to remove the heat from the spent caustic solution. Representative temperatures of flue gas and wash solutions predicted during the design phase at various locations around the wash column as indicated in Figure 11 for the pre-treatment step are given in Table 5.

The chilled water flow rate of about 6 – 10 L/min through the heat exchanger and the column inlet flue gas flow rate of 200 L/min were used to obtain the representative temperatures given in Table 5. The wash column was designed to treat flue gas up to 350 L/min, although the adsorbent columns are designed for processing up to 200 L/min flue gas, so as to provide an additional buffer capacity for the wash column. A 100L caustic holding tank was also provided in the circuit in addition to the storage sump at the bottom of the wash column to ensure sufficient liquid flow through the system. As the CO_2 adsorption capacity is temperature dependent, the heat exchanger (HE-02) was included for fine adjustments of the feed flue gas temperature to 25^oC (if required) before it entered the adsorption column. A by-pass line to the wash column was provided to evaluate the adsorption capacity of the adsorbents for the flue gas without SO_x and NO_x removal. The wash column was designed to handle flue gas with inlet temperature of 120°C. However, during actual operation, the flue gas temperature was at ambient temperature at the inlet to scrubber column.

Parameters such as temperatures, pH, pressures, differential pressure across the wash column, flow rates of gas and liquid, gas compositions at inlet and outlet of wash column were monitored during the operation. Specifications of the various equipments used for the pre-treatment process are given in Table 6.

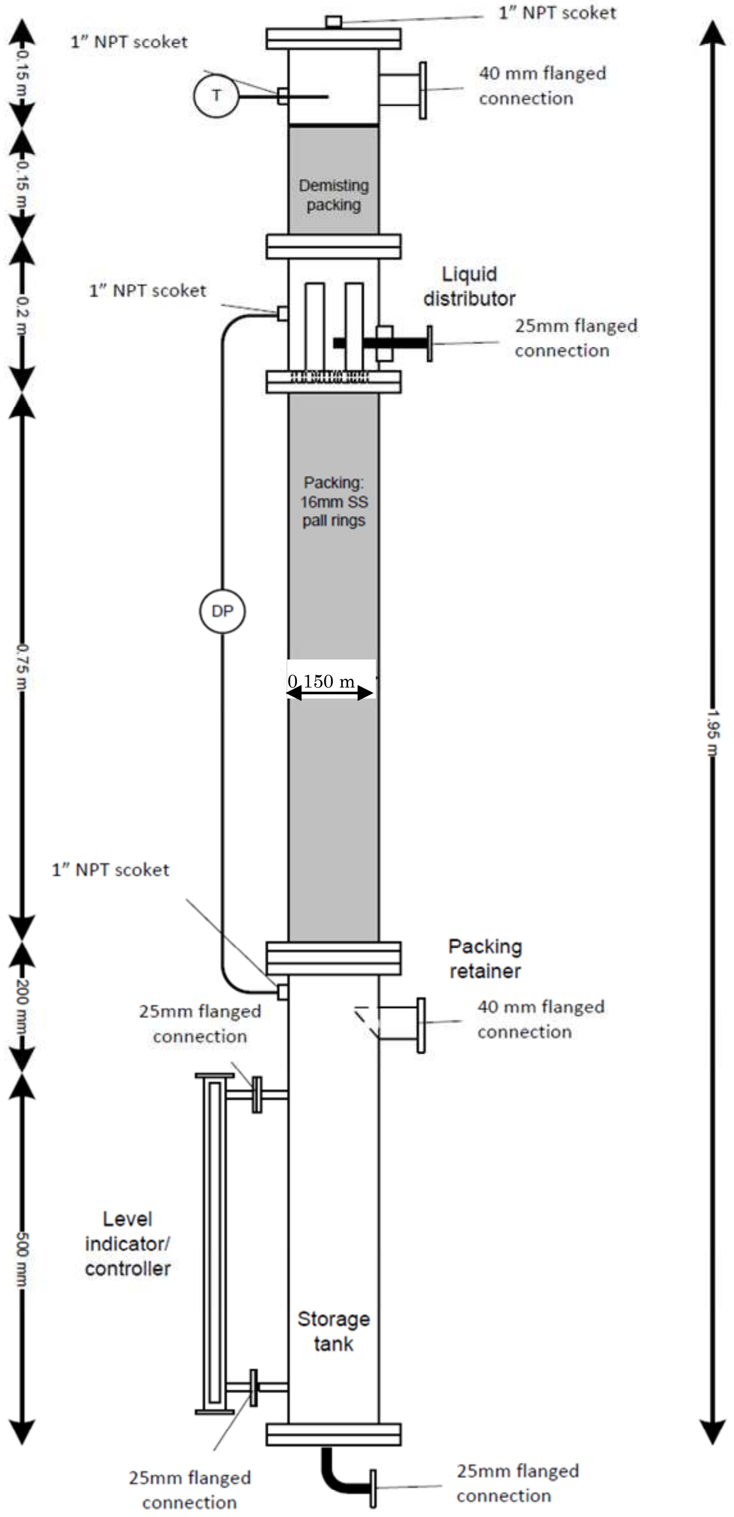


Figure 10: Sketch of single stage direct contact cooling (DCC) packed bed wash column

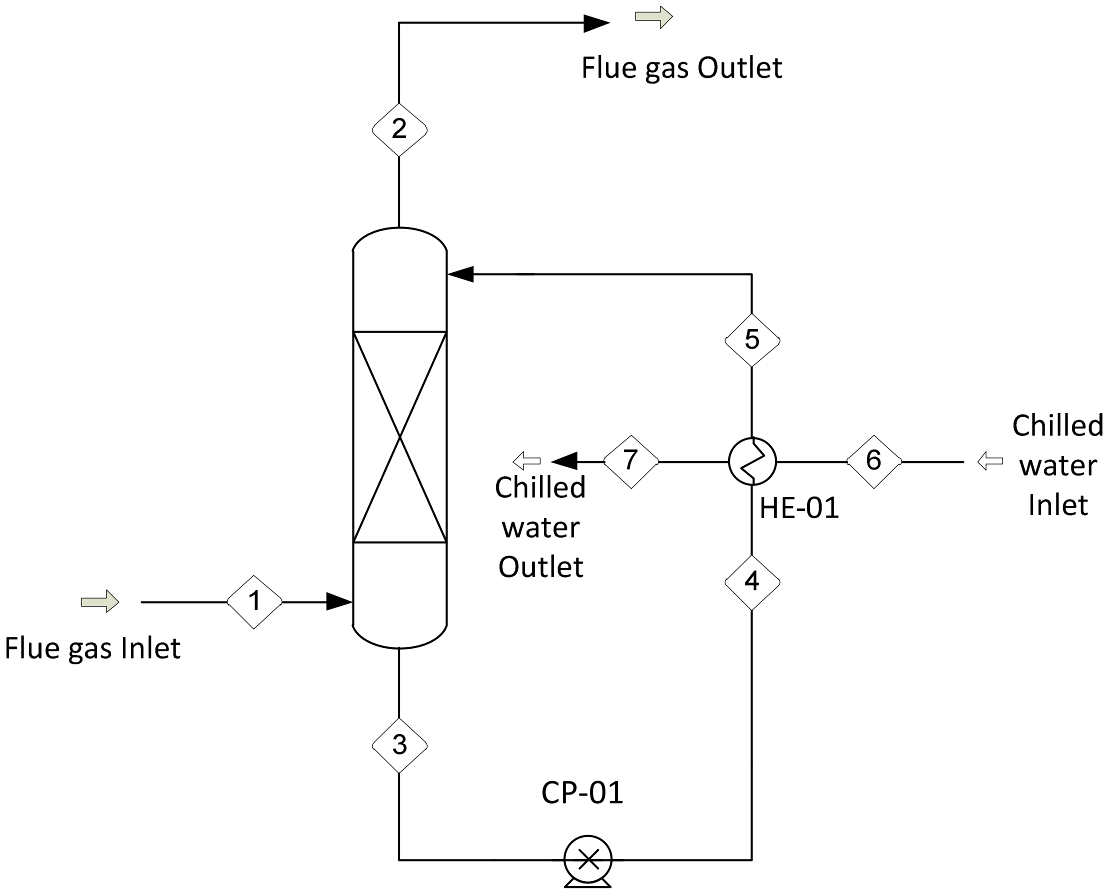


Figure 11: Schematic of the temperature and flow monitoring points around the wash column

Table 5: Predicted temperatures of gas and liquid around the wash column

Locations	1	2	3	4	5	6	7
Temperature, ^{o}C	120	15	18.7	18.7	15	10	13.7

(Note: Ambient temperature during actual operation at Location 1)

Table 6: Specifications of the equipments used in the pre-treatment system

Equipments	Code	Specifications	Pipng Details
High Temperature Blower	BLH-01	Single Stage, Volume throughput 100m^3/hr, Max pressure 6 kpa, operating temperature 180C, fan speed 2900 rpm++	Inlet ID: 150mm, Outlet port: 84x84mm
Cartridge Filter	CF-01	304SS Stainless Steel Housing, HEPA Filter Media, Special gaskets to handle 175^{o}C	38mm BSP
Furnace	FUR-01	1000^{o}C max, fully with control systems	-
Wash Column	WC-01	Design. Size: 150NB Shd 10 x 2.1 m high	-
Wash Column Internals	WCI-01	(1) 16mm Pall Rings with a packed bed depth of 750mm (2) Pan type liquid distributor (3) Random packing support plate (4) Random packing retainer grid (5) Demister pad	-
Heat Exchanger	HE-01	Caustic cooler 316 ss plate heat exchanger	19.05mm BSP
		Flue gas 316 ss plate heat exchanger	31.75mm BSP
Chiller	CHL-01	Supply water temp 5°C	31.75mm BSP
Caustic Circulation Pump	CP-01	Positive displacement pump, rate up to 25L/min	25.4mm BSP

3.3 Modifications to the existing large scale CO_2 test unit

Modification to the existing large scale prototype unit was carried out to suit the added pre-treatment setup. In the earlier design of the adsorption column for the large scale setup, regeneration of adsorbent or CO_2 desorption was carried out by passing the hot gas (or cooling water for cooling) through the hot air channels (13 X 4.76mm SS tubes) through the cylindrical adsorbent (Figure 12). In order to enhance the heat transfer performance in the prototype unit, the size of the hot air channels through the adsorbents were enlarged (13 X 12.7 mm). High temperature viton o-rings were provided around the tubes where it exited the top and bottom flanges, in order to prevent gas leakage from the adsorption column. Aluminium plates with six bolts were introduced on the surface of top and bottom flanges of the column, which held the o-rings in position (Figure 13). The adsorption column was leak tested up to 200 kPa to check the sealing. The modifications to the hot air channels in the adsorbent column and the CO_2 adsorption and desorption pipelines integrating with pre-treatment system were carried out. During the site trials, the use of the o-rings was not a good choice as the o-rings failed to seal the gas leaking after a number of trials, and this issue will be discussed in Chapter 5.3.

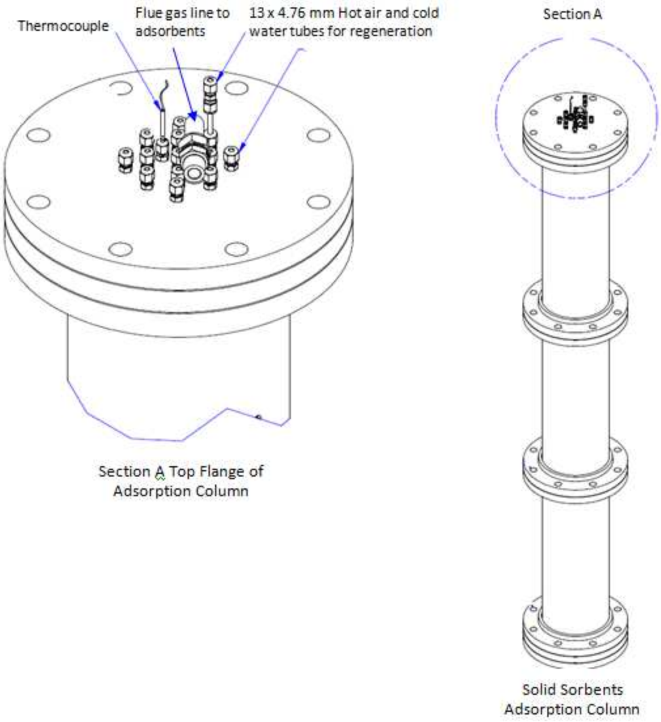
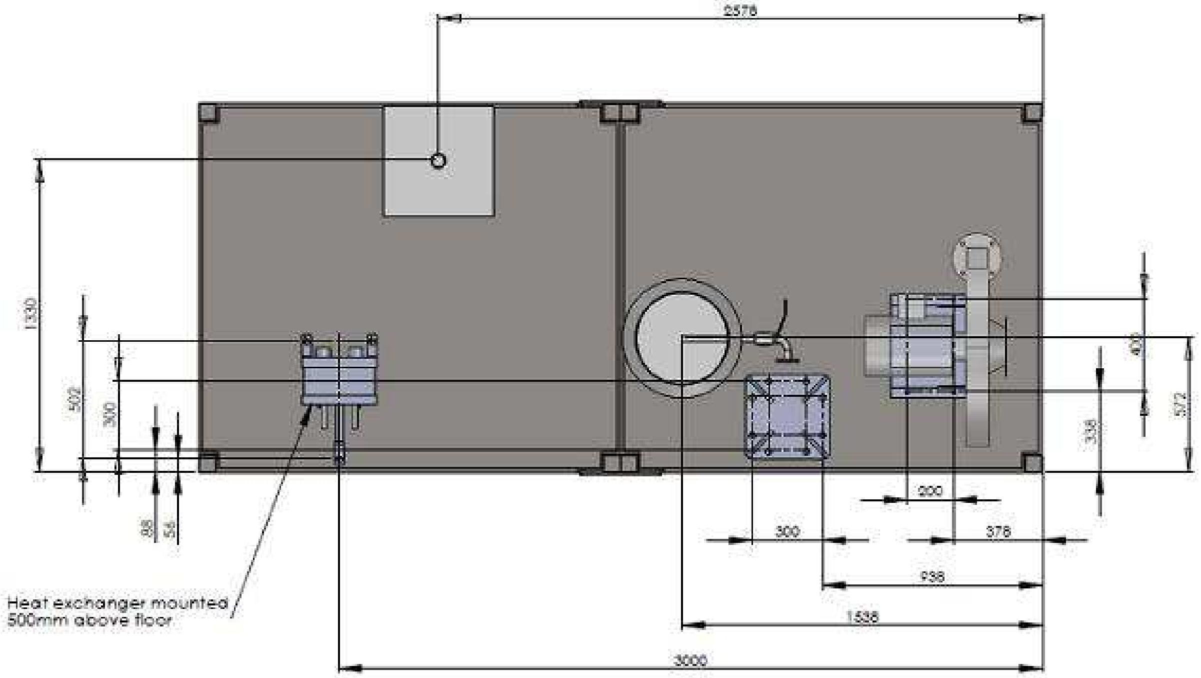


Figure 12: Sketch of the adsorption column with the previous design of regeneration channels (Section A)

Figure 13: Modified regeneration tubes setup for the adsorption column in the prototype test unit

3.4 Design of site trial prototype test unit

Based on the design considerations, the CO_2 capture prototype test unit assembly drawings (both 2D and 3D) were prepared using SolidWorks software. Drawing for the pre-treatment equipment layout (2D) on the frame is shown in Figure 14. Overall test unit assembly drawing (3D) was also prepared as shown in Figure 15. The cylindrical adsorption column will be used for this site trial project. For representation purpose, a rectangular adsorption column that has been investigated separately for better heat transfer through another CSIRO Research Project and is also shown in the unit assembly drawing. Individual pipe work drawings for connecting each one of the equipments were also prepared. These drawings were used for the construction of the test unit assembly.



NOTE: ALL DIMENSIONS APPROXIMATE ONLY

Figure 14: Two dimensional drawing of the positioning of the pre-treatment equipments on the frame

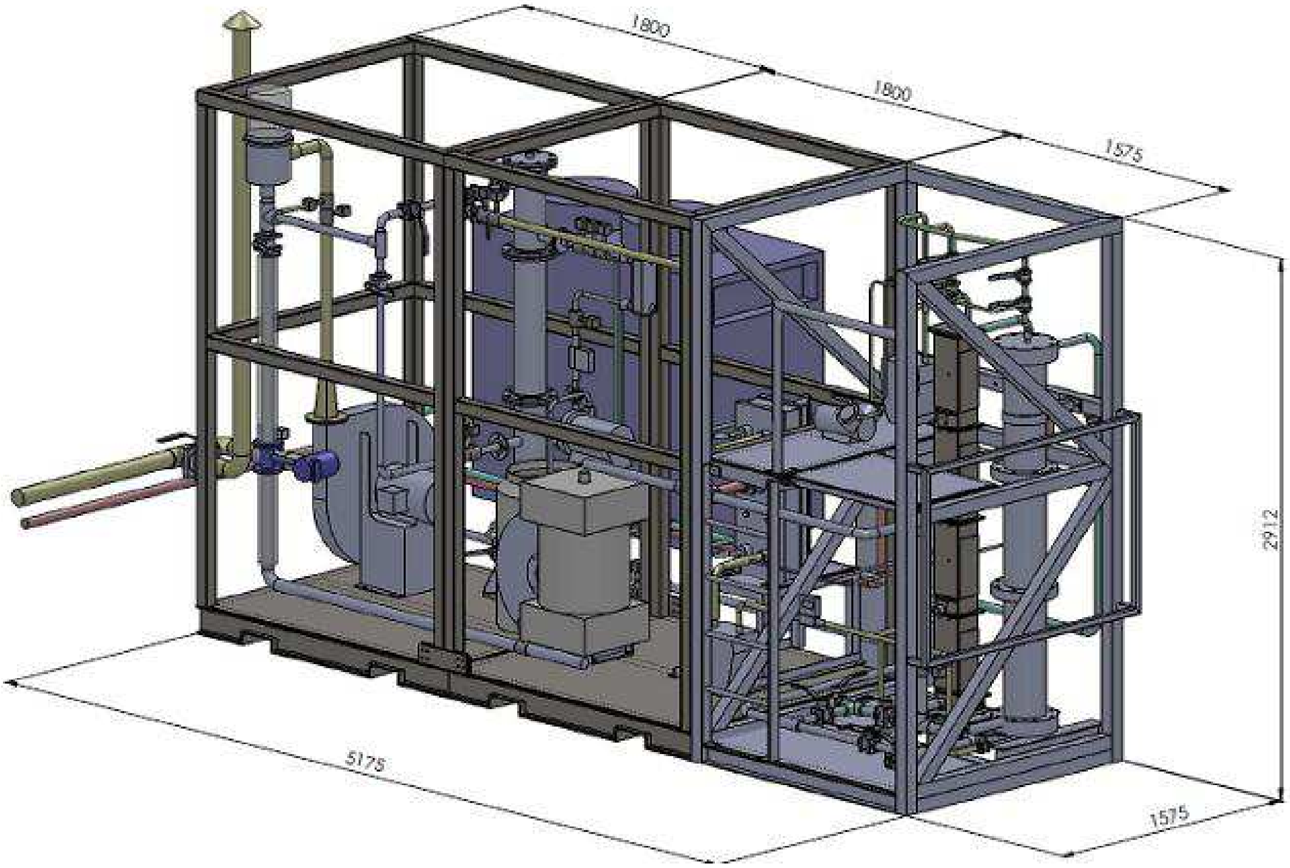
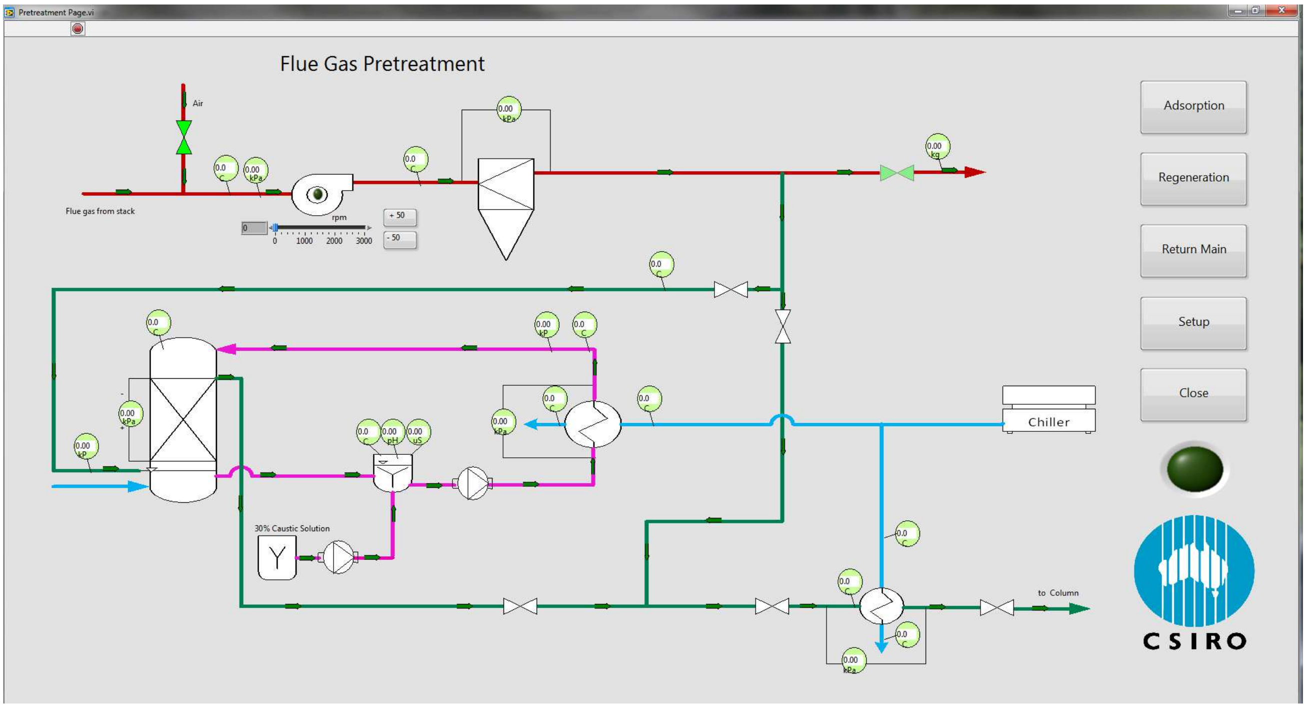


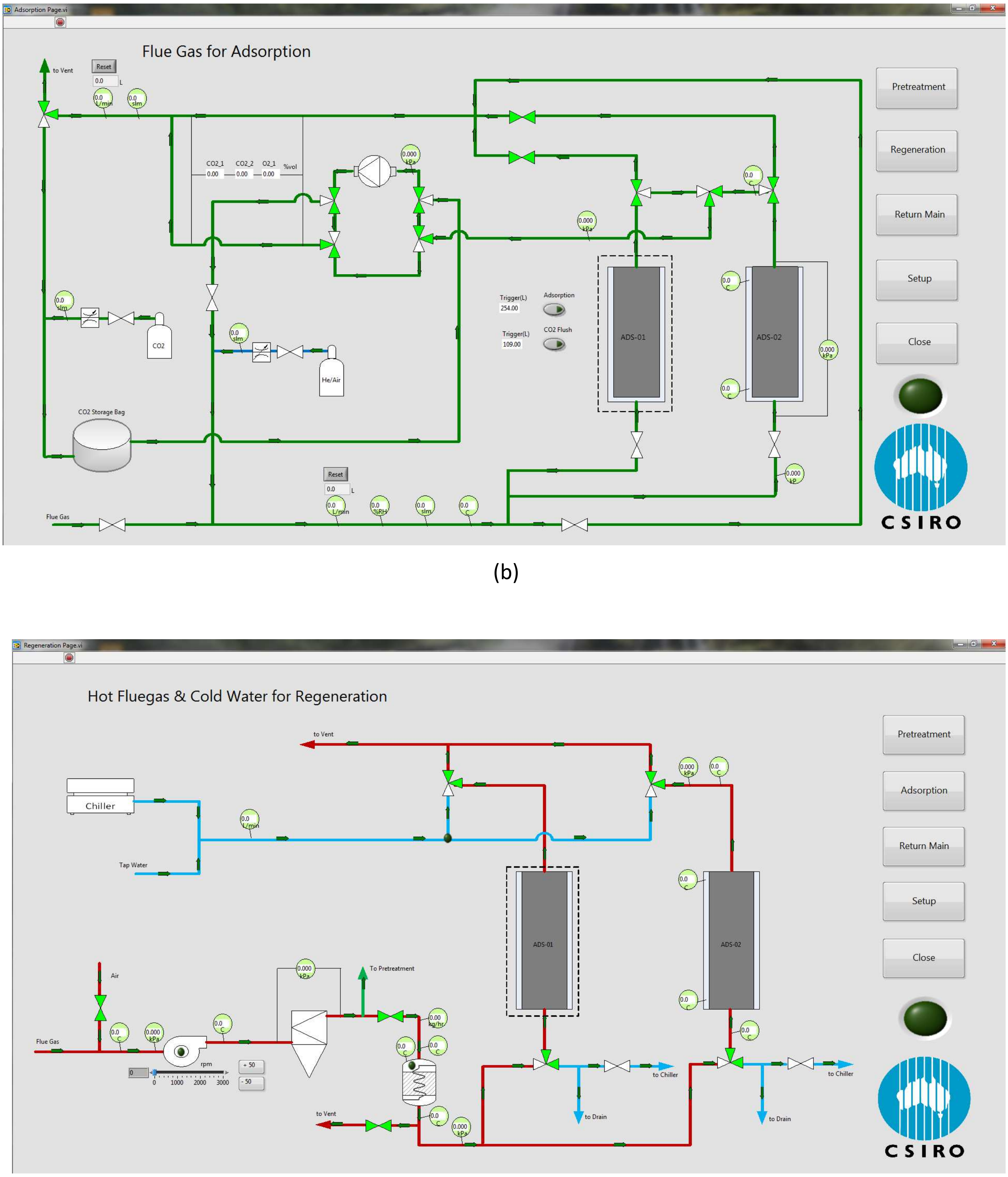
Figure 15: View of the whole assembly of the Solid sorbent CO_2 capture prototype unit

3.5 Control and monitoring system

CO_2 capture and regeneration unit coupled with pre-treatment system was able to be remotely operated from the computer. The operation of equipments such as blower, valves, flow meters etc and continuous data logging of the readings from thermocouple, pressure transducers and gas sensors were carried out through the control and monitoring system developed using LabVIEW interface. The operations of the equipment during the tests were performed via the computer. Safety features such as protection for overshoot of motor speed, temperature etc. were built into the control system. Emergency stop systems were also provided to safely shutdown the system in case of any malfunctions. The screen shot of the control and monitoring system as seen in the computer during operation is shown in Figure 16. As shown, the control monitoring system is divided into three sections, namely, pre-treatment, adsorption and regeneration sections.



(a)



(b)

(c)

Figure 16: Computer screen shots of the control and monitoring system for solid sorbent CO_2 capture prototype unit. (a) Pre-treatment, (b) adsorption, (c) regeneration

3.6 Construction of the CO_2 capture prototype test facility

3.6.1 Assembly of the main body of test facility at CSIRO

Components to be purchased for the site infrastructure construction were determined and suitable suppliers were identified and up to three quotations were obtained wherever possible to match with our required specification at minimum cost. The scrubber wash column was fabricated to our design requirements, to minimise the cost. Some of sensors, flow meters etc. were reutilised from some of our previous test units.

A list of activities and work plan was prepared for the construction of solid sorbent prototype test unit with pre-treatment system, as given in Table 7. At the start of the infrastructure construction work of solid sorbent prototype test unit, CSIRO workshop personnel was assigned to construct the steel frame for the equipments in the site trail prototype test unit and modify the adsorption column previously used in the large scale setup to the required specifications of site trial prototype test unit. The steel frame construction work was completed by a CSIRO mechanical technician.

Table 7: List of activities and working sequence for the solid sorbent test unit construction

Activities and Work Order
1. Construct frames for pre-treatment system according to drawings
2. Prepare existing frame to mount the cylindrical adsorption column
3. Connect flexible tubes to cylindrical column ends for regeneration fluids, install the cylindrical column on the frame, construct and install the two regeneration fluid distribution manifolds which connect to the column through the flexible tubes.
4. Secure various pre-treatment equipments to the frames according to the 2D drawings
5. Check suitable pipes, lengths, valves, fittings etc. to be connected to the equipments according to the drawings. Flanges for the blower and cone sections, furnace coils, flow meter, pipe side flange connection to the scrubber column are to be made.
6. Pipe works leading to the rectangular column must also be laid so that column can be easily included into the system when required.
7. After pipeline installation, weld equipments on to the frame
8. Install thermocouples, sensors etc on the pipelines
9. Carry out pipe insulations
10. Safety rails, platforms, ladders to be mounted on the frames
11. Leak test to be performed for the entire system

Further on, due to unexpected resignation (without prior notification) of the CSIRO contract personnel, the construction work was stopped until a suitable contractor was found to carry out this work. Two external companies were approached and quotations were obtained. With the permission from the Coal Innovation NSW, a contract agreement was prepared and relevant approvals within CSIRO were also obtained, to undertake the infrastructure construction work with the selected external contractor. The assembly unit construction work was then continued through the external contractor in Brisbane. The assembling of various equipments such as blower, heat exchangers, furnace, dust filter, scrubber wash column etc on the frame was carried out (Figure 17), according to the assembly drawings provided by CSIRO.

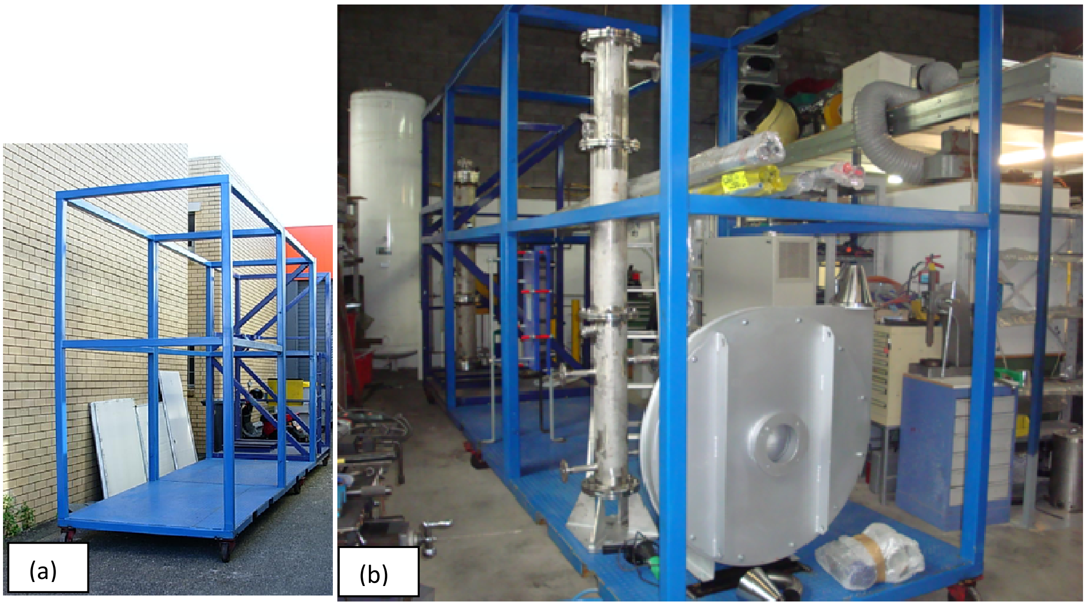


Figure 17: Construction of solid sorbent prototype test unit with pre-treatment system (a) three test unit frames (b) equipments being assembled on the frame.

The construction work on the test unit assembly was carried out according to the list of activities provided to the contractor by CSIRO. CSIRO team regularly visited the contractor's workshop to monitor the progress of work. The assembly work was completed in September 2012. While the prototype test unit was constructed, the work on control and instrumentation for the system was simultaneously carried out by the project team. After completion of test unit assembling, electrical work and control system were installed and the whole unit was ready for transportation to the site. The photo of the fully constructed solid sorbent prototype unit at QCAT, before transportation to the power station site, is shown in Figure 18.

Figure 18: The fully constructed large scale honeycomb carbon fibre composite CO_2 capture prototype test unit at QCAT.

3.6.2 Transportation of constructed solid sorbent prototype unit to site

The unit was pre-tested on some components (like checks on appropriate signals to designated transducers etc) at CSIRO QCAT site before transporting it to the site. After obtaining quotations from two transport companies, one of the transportation companies was chosen for transporting the constructed test unit to the Delta's Point power station site. A travel management plan was prepared and prior consent was obtained from Delta before the transportation of test rig. The fully constructed test unit with control system was transported to the site in October 2012.

3.6.3 On site infrastructure construction

Site infrastructure construction included the following activities:

- Construction of concrete basement on site for housing the Pilot Plant units
- Installation of test unit on-site
- Basic infrastructure connections such as flue gas, electricity and water on site to the test unit
- Installation of control room for test unit operation

3.6.3.1 Construction of concrete basement on-site

At the power station site, the concrete basement to house CSIRO pilot plant test units was constructed in June 2012. The photo of the concrete basement with the allocated location of solid sorbent prototype unit is shown in Figure 19.

Figure 19: Concrete basement with proposed location for solid sorbent prototype test unit at power station

3.6.3.2 Site installation of solid sorbent prototype test unit

The constructed and transported solid sorbent prototype test unit was successfully installed on-site at power station at the designated location near the ammonia pilot plant (Figure 20).

Figure 20: Photo of solid sorbent prototype CO_2 capture test unit installed at the Power Station

3.6.3.3 On-site infrastructure connections to test unit

The operation of solid sorbent CO_2 capture unit required basic infrastructure such as source flue gas for testing, electrical power supply for the operation of instruments, water as part of thermal regeneration of adsorbents and compressed air. Water and electricity connections to the test unit were provided by Delta Electricity. Three phase power supply (60 amps), sufficient to operate all the components of the test unit, was supplied and connected by Delta Electricity. Water chiller was installed near the solid sorbent test unit to supply cold water for adsorbent cooling after thermal regeneration. Compressed air required to operate the valves was obtained using the small compressor installed within the test unit.

The main flue gas inlet and return lines from the flue gas stack to the CSIRO pilot plant units were laid as part of infrastructure construction of ammonia pilot plant unit (Figure 21). A short feed and return flue gas line connecting the test unit and the main flue gas line was then constructed as part of solid sorbent pilot plant unit infrastructure (Figure 22). Double isolation valves on the feed and return lines were installed in the small slip stream line connecting the main source lines with solid sorbent test unit.

Figure 21: Photo of the constructed main flue gas supply and return lines from the flue duct

Figure 22: Photo of the inlet flue gas feed line connected to the solid sorbent test unit

3.6.3.4 Installation of control room for test unit operation

An atco hut (Figure 23) was installed next to the solid sorbent test unit (room facing the test unit) and was used as the control room. This control room was shared by CSIRO personnel working on the ammonia pilot plant unit and solid sorbent prototype unit. Electrical/ control system wirings from the solid sorbent test unit was extended into the control room to facilitate remote operation.

Figure 23: Control room facility on-site located near the solid sorbent prototype test unit

The CO_2 capture prototype unit test facility and the on-site infrastructure for the unit was completed and ready for commissioning in November 2012.

4 Pre-commission of Solid Sorbent Prototype Unit

4.1 Pre-commission safety assessment

Before the commencement of experimentation using real flue gas, the solid sorbent prototype test unit was pre-commissioned using simulated flue gas. A thorough safety assessment of the test unit was carried out before commencing the pre-commissioning tests. Pre-commissioning documentations such as pre-commissioning procedure and check list, OHSE manual, process procedure-flow diagram and control loops were prepared. CSIRO health & Safety risk management plan for the solid sorbent test unit was prepared. All the valve positions were visually examined to check for its default position.

4.2 Preparation for pre-commission

After the safety assessment, the test unit was prepared for the pre-commissioning testing. Bottle gases such as pure CO_2, N_2 and He required for the pre-commissioning tests were purchased. Simulated flue gas for the pre-commissioning step was produced by mixing air and injecting pure CO_2 from cylinder, at the fan inlet. Flexible gas lines were drawn with inline gas regulators and valves to connect the bottled gases to the designated locations in the test unit. The CO_2 analyser (Madur, ANRI Instrument Pty Ltd.) and O_2 (PMA 10, ANRI Instruments Pty Ltd.) were connected inline with the test unit for continuous measurement of gas concentrations. Pre-commissioning test procedure to check the operations of individual units in the test rig was prepared. The analysers were first calibrated using bottled gas. Interface software was connected to the test rig and the control and monitoring system was then commissioned. Valve orientation and positions were checked and labelled. Inlet fan speed was calibrated for air throughput. Furnace operation and ramping rate were monitored. Thermocouples and pressure/differential pressure and relative humidity transducers were checked. Scrubber column pumps were operated and tested using water as liquid medium instead of dilute caustic solution. The pre-commissioning testing using simulated flue gas was commenced in November and early December 2012.

4.3 Pre-commission trials

The experimental plan for the pre-commissioning tests was prepared. The first set of tests for pre-commissioning was carried out in December 2012. Several tests were carried out to study the CO_2 capture and regeneration modes for simulated flue gas with/without pre-treatment through the scrubber column. The preliminary test results were obtained and were analysed. Individual components of the system were found to operate well. Minor issues were identified during the first commission procedure. The CO_2 analyser had to be recalibrated by the supplier and the diaphragm vacuum pump used for regeneration required servicing.

The project team visited the site again in the first week of March 2013 to carry out the second phase of pre-commissioning test with the recalibrated gas sensors and serviced vacuum pump. During this pre-commissioning run, various scenarios of capture and regeneration were evaluated using simulated flue gas, as given below.

- CO_2 adsorption using simulated flue gas
- CO_2 adsorption with cooling water circulation followed by pure CO_2 flush
- CO_2 adsorption without cooling water circulation, with pre-treatment (simulated flue gas through wash water column) followed by pure CO_2 flush
- Thermal regeneration
- Combined thermal and vacuum regeneration.

Simulated flue gas with CO_2 concentration of about 13% was used for this study. Initially the feed gas was bypassed through the column and then the gas was switched into the adsorbent column. It can be seen from the Figure 24 that the CO_2 concentration coming out of the column was almost zero, indicating that almost all the CO_2 in the flue gas has been adsorbed by the adsorbent. During this time no cooling water was circulated through the column and due to the heat of adsorption (especially from CO_2 adsorption), there is about 10°C increase in column temperature. The adsorption run was stopped as soon as a slight increase in CO_2 concentration was noticed in the outlet (breakthrough point). The column was then flushed with pure CO_2 to replace other gases (like N_2 and O_2) that had co-adsorbed, and enrich the column with CO_2. Figure 25 shows the CO_2 adsorption performance tested while cooling water was circulated through the column during the capture process. CO_2 capture with cold water circulation (near isothermal condition of adsorbents) increases the adsorption capacity of adsorbents compared to operation without water circulation. The CO_2 adsorption efficiency was found to be over 98% during flue gas adsorption and CO_2 flush.

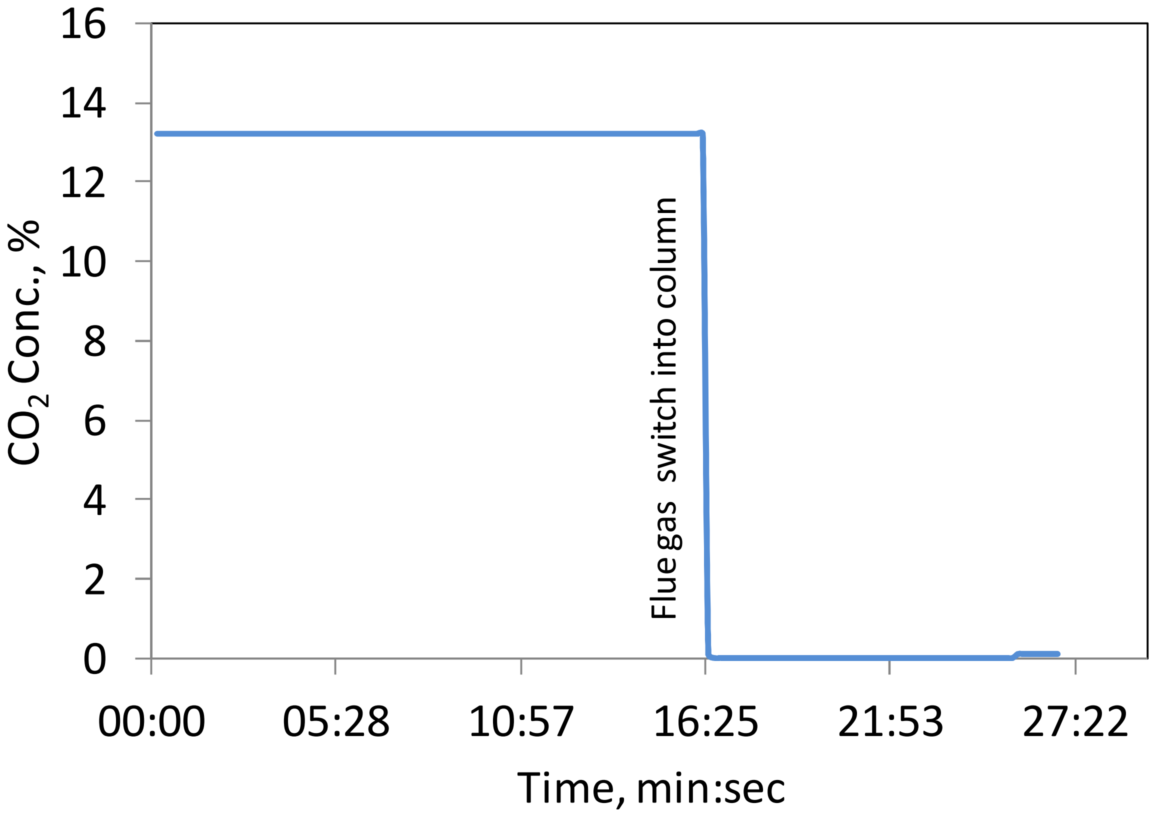


Figure 24: CO_2 capture performance of solid sorbent prototype unit using simulated flue gas

Another scenario tested was CO_2 adsorption using simulated flue gas passed through the scrubber wash column. For the pre-commissioning tests, water was used as the circulating liquid instead of dilute caustic solution. For the pre-commissioning test, after passing through the wash column the simulated flue gas with relative humidity of 86%, enters the solid adsorbent column. It can be seen from the Figure 25, the CSIRO carbon fibre composite solid adsorbents were able to effective capture the CO_2 even with the flue gas containing moisture. The CO_2 adsorption efficiency was over 98% during adsorption and during CO_2 flush.

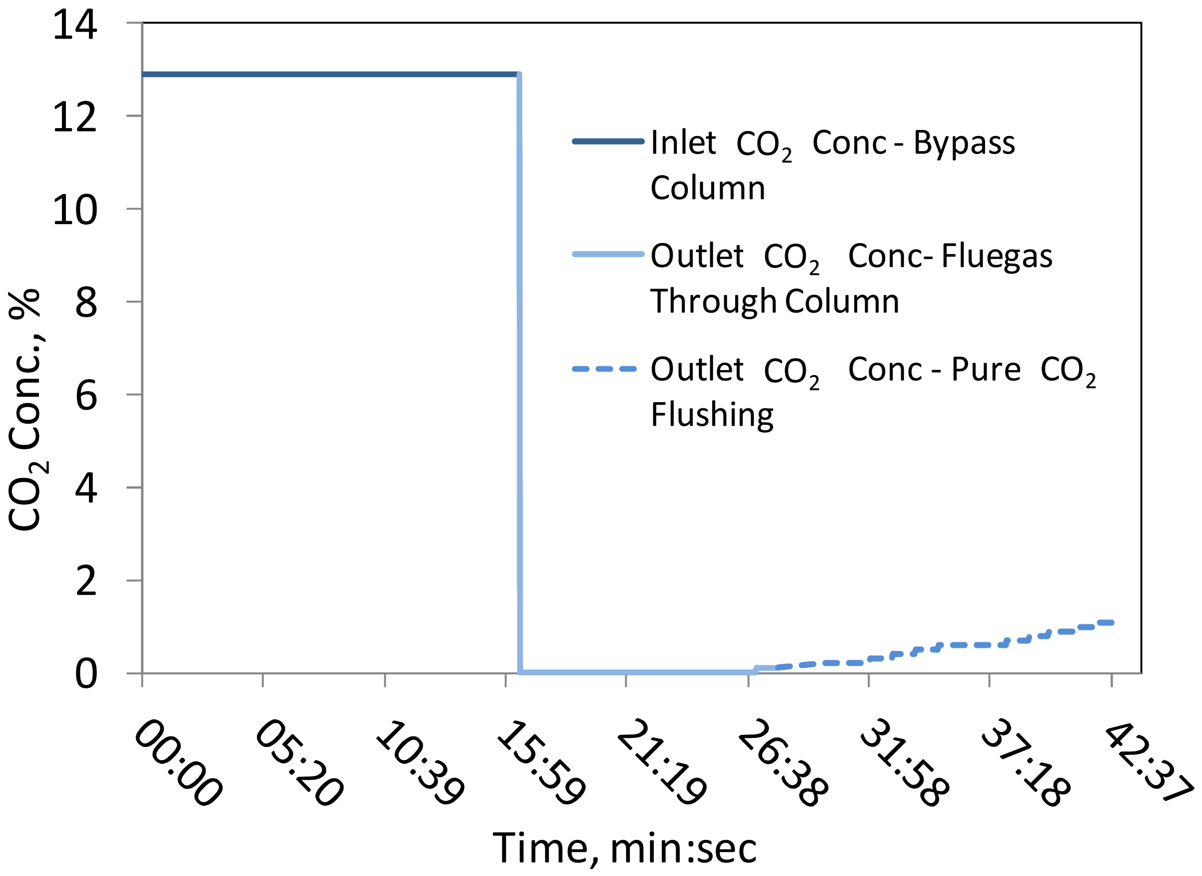


Figure 25: CO_2 capture performance of solid sorbent prototype unit using simulated flue gas during cooling water circulation followed by pure CO_2 flushing

After CO_2 flush, the adsorbents were heated to raise the adsorbent temperature (using air heated in the furnace) to about 120°C to release the captured CO_2 (desorption). The inlet and outlet of the column remained closed during this heating stage. Once the adsorbent temperature reached the required temperature, the outlet of the column was opened and vacuum was applied to extract the desorbed CO_2 from the column. The desorbed CO_2 concentration was found to be almost 100% throughout. It can be seen from Figure 26, the combined thermal and vacuum regeneration was very effective method of desorption to achieve very high CO_2 concentration of up to 100 %. These results are in-line with the data obtained from the studies using large scale unit under laboratory conditions.

The pre-commissioning tests using simulated flue gas was completed in Q1 2013. It was demonstrated through these pre-commissioning tests that the CO_2 capture solid sorbent prototype unit was fully functional at the site and ready for trials with actual flue gas.

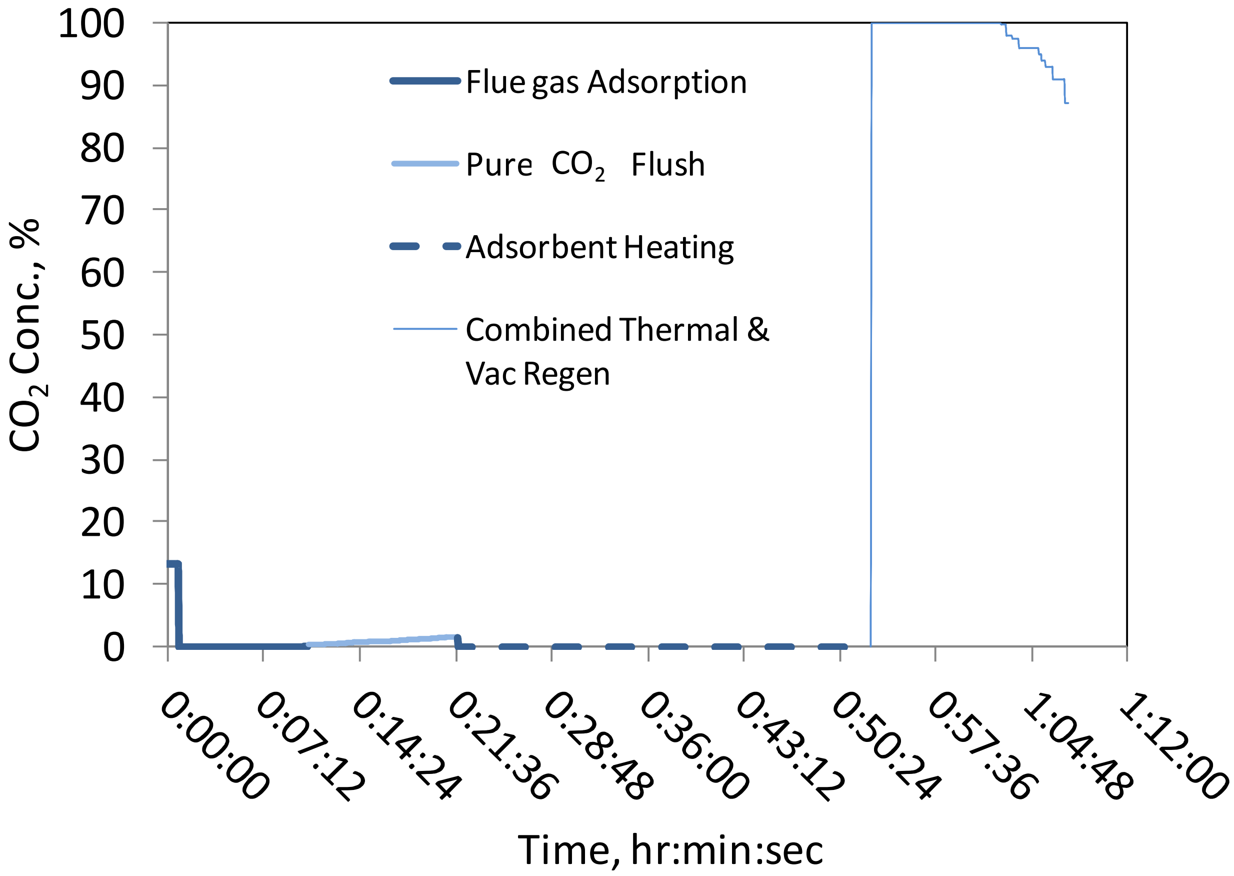


Figure 26: Performance of solid sorbent prototype unit during adsorption, CO_2 flush and combined thermal and vacuum regeneration steps

5 Site Trials and Demonstration with Real Flue Gas

5.1 Safety assessment before access to real flue gas

Extensive pre-preparation was required before the access to real flue gas to the solid sorbent prototype unit. Documents for operational procedure with real flue gas, health & safety risk reviews, waste management procedures were prepared according to Delta's requirements. Measures to be adopted in case of any emergency situations such as, when there is a flue gas leak, when there is a power failure, when there is a leak in the caustic solution etc., were assessed in the risk review document. MSDS and chemical and gas inventory registers were prepared and made available at work area on site for the solid sorbent unit. Isolation procedure of the ammonia pilot unit was evaluated to safely operate the solid sorbent unit with real flue gas, while personnel can continue working on the construction of the ammonia pilot unit. To ensure safety, two additional manual valves (Figure 27) on the pilot plant unit pipelines were also installed. SOx and NOx detectors in ambient air were installed on the solid sorbent test rig (Figure 28) to detect any flue gas leaks from the test unit and were integrated into the control and monitoring system of the test facility.

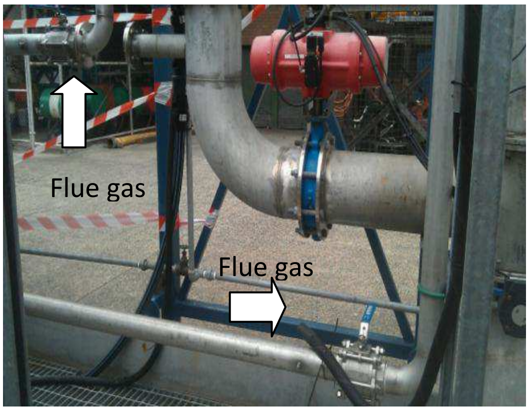


Figure 27: Photo of the additional manual valves on the feed and return flue gas lines in between two CSIRO's CO_2 capture units at the Power Station

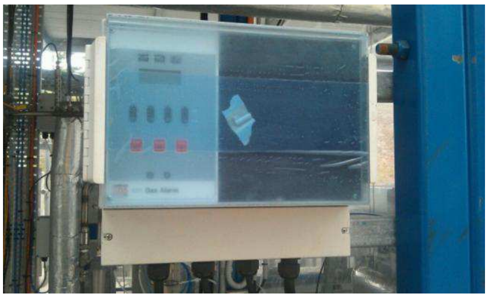


Figure 28: Photo of the four channel hazardous gas detector installed on the solid sorbent test facility

After satisfactorily addressing CSIRO and Delta's requirements in relation to the pre-preparations for the supply of real flue gas to the solid sorbent prototype unit, flue gas to the solid sorbent test unit was provided on the 29th May 2013. Figure 29 shows the photo of Delta personnel releasing the flue gas from the stack to the solid sorbent test unit for the first time.

Figure 29: Opening of inlet flue gas pipeline on-site to provide flue gas to the solid sorbent test unit

5.2 Commission procedure and experimental plan

5.2.1 Commission procedure

Commissioning of the solid sorbent prototype unit with real flue gas followed by site trial demonstration was commenced in June 2013. A step-by-step (comprising of 21 steps) commissioning procedure with real flue gas was prepared. A check list of commissioning activities was prepared. Start up and shut down procedures were prepared. After ensuring the operations of valve, temperature and pressure operations, the chiller water circulation was checked. The furnace heating and ramping procedure was then evaluated. The blower operation was then tested using the variable speed controller. The caustic scrubber unit using circulation pumps was then tested. The adsorption column was heated using hot air/ hot flue gas and cooled using chilled water. Vacuum pump operation was checked. The system was then shut down adopting the shutdown procedure. Commissioning of the prototype test unit system was successfully completed and ready for the site trials and demonstration using real flue gas in June 2013.

5.2.2 Methodology

For the carbon fibre composite adsorbents for CO_2 capture site trial studies, an experimental plan was developed with the consideration of project objectives. The first set of experiments were planned to conduct CO_2 adsorption and desorption tests using pre-treated flue gas. The pre-treatment of flue gas involved particulate removal through the dust filter and passing through the caustic scrubber system to mainly remove SO_2 from the flue gas.

The second set of planned experimental study tested the performance of the carbon composite adsorbents using the flue gas without the caustic scrubber pre-treatment system. However, the flue gas was still passed through the dust filter. The experimental plan on the site trials and demonstration with two scenarios is shown in Table 8.

Table 8: Experimental plan for CO_2 capture site trials with two different scenarios

Experimental Plan
Scenario 1
Adsorption performance studies using real flue gas after pre-treatment with particulate removal and caustic scrubber to remove SO_2.
Adsorption, and then product purge
Thermal and vacuum swing regeneration with raw flue gas/hot air as heat source
Data processing and analysis
Scenario 2
Introduction of flue gas with SOx and NOx and evaluation of performance of solid sorbents
Adsorption, and then product purge
Thermal and vacuum swing regeneration with raw flue gas/hot air as heat source
Data processing and analysis

Experiments were initiated systematically according to the experimental plan since June 2013. The overall capture and regeneration strategy or the testing sequence involved in the solid sorbents testing is given as a flow diagram in Figure 30.

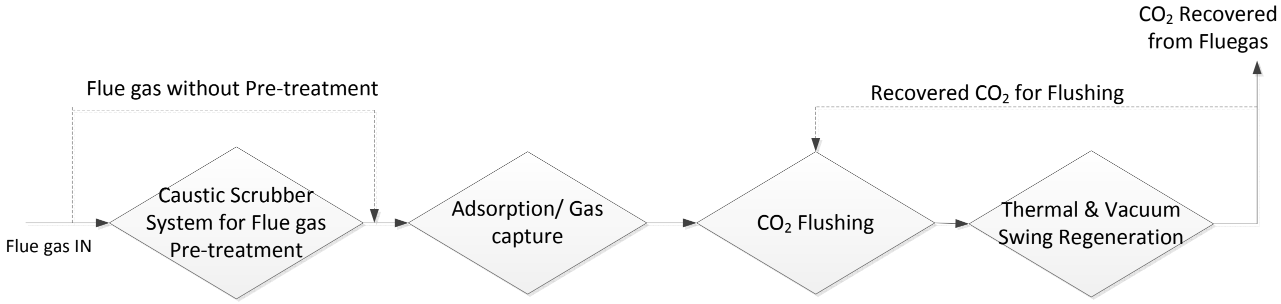


Figure 30: Process sequence procedure for the solid sorbent CO_2 capture and regeneration testing

The raw flue gas from the stack was extracted by the blower and passed through a HEPA cartridge filter (99.9 % efficient at 0.3micron) (Solberg International Pty Ltd) and either passed through the caustic scrubber for SOx and some NOx removal, or bypassed the scrubber column to provide flue gas for the CO_2 capture by solid sorbents. After the CO_2 adsorption step, pure CO_2 was passed into the adsorption column, which helps in enriching the adsorbed CO_2 by removing the N_2 (and O_2) co-adsorbed from the flue gas. The adsorbents were then heated to 110°C with inlet and outlet of the adsorption column closed during heating. The heat releases the CO_2 adsorbed by the sorbent material and once the desired temperature was reached, the adsorption column was opened to recover the adsorbed CO_2. Vacuum was also applied simultaneously to extract the CO_2 from the material. The CO_2 adsorption efficiencies were studied by analysing the raw flue gas composition and at the outlet of the adsorption column. The concentration of CO_2 during regeneration was also continuously monitored. The total amount of CO_2 recovered was evaluated by comparing the amount of CO_2 captured (or passed into the adsorption column) and amount desorbed (extracted out of the column). Gas concentration in the flue gas was measured using the gas sensors. In order to effectively evaluate the CO_2 capture performance and adsorbent stability, we define the following performance parameters.

CO_2 adsorption efficiency

$$\eta_{Cap} = \frac{c}{a} \times 100\% \qquad (1)$$

Where, a is amount of CO_2 in the flue gas entering into the adsorption column during the adsorption stage; c is amount of CO_2 adsorbed by the adsorbent during the adsorption stage; η_{Cap} is the CO_2 adsorption efficiency that is determined based on the adsorption breakthrough profile.

CO_2 desorption efficiency

$$\eta_{Rec} = \frac{d}{a+b} \times 100\% \qquad (2)$$

Where, a is amount of CO_2 entering into the adsorption column during the adsorption stage; b is amount of the product CO_2 used for the purge (CO_2 flushing); d is amount of CO_2 collected during the desorption stage; η_{Rec} is the CO_2 desorption efficiency that is determined based on total CO_2 desorbed from the adsorbent.

5.2.3 Analytic instruments

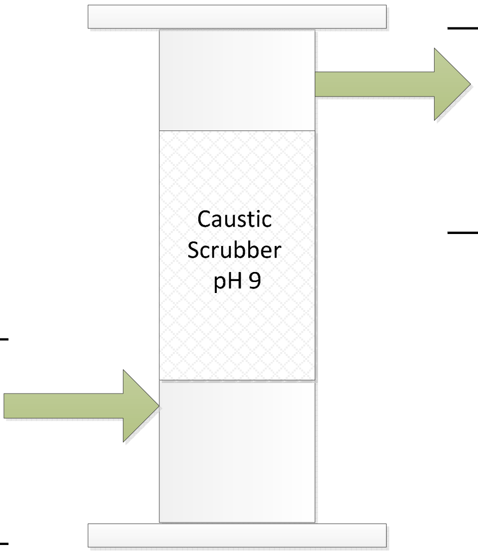
The solid sorbent test unit used CO_2 sensor (Madur, Anri Instruments Pty Ltd), O_2 sensor (PMI 10, Anri Instruments Pty. Ltd.) and a combined sensor for analysis of SO_x, NO_x and CO (and CO_2) (Thermo 60i, non dispersive infrared technique). For initial tests very high peaks of gas concentrations, especially for CO, were noticed from Thermo 60i instrument during the regeneration. The mixture of gas composition with the combination of very low CO_2 concentration (during capture) and very high CO_2 concentration (during regeneration) presented a unique background environment for the analysis equipments. Very high peaks of some gas concentrations, especially for CO, were actually caused due to the analysers response to the change in gas composition background environment. A single analyser to measure various gases present in the flue gas was not an accurate method operation. Therefore, to address this issue, individual sensors to measure SO_2, NOx, CO, O_2 and CO_2 were required to accurately measure the gas concentrations in order to get reliable and consistent data. Individual sensors for SO_2 (Thermo 43i-HL, UV fluorescence), NO_x (Thermo 42i-HL, Chemiluminescence), and CO (Thermo 48i) were obtained (Figure 31) in September 2013 and together with the available O_2 and CO_2 analysers, formed a suite of analyses equipments used in this study.

Figure 31: Individual analysers for measuring SO_2, NOx and CO used for the solid sorbent CO_2 capture site trial

5.3 Results and discussions

5.3.1 Pre-treatment performance

The first series of experimentation were carried out by passing the raw flue gas through the caustic scrubber system (with pre-treatment) before CO_2 capture. Figure 32 shows the concentration of gases in the flue gas before and after caustic scrubber pre-treatment (operated at pH 9). It can be seen that the caustic scrubber removed mainly SO_2 (97.5%), some NO (7.9%) and NO_2 (15.3%) and there was negligible change in CO_2 and CO concentrations. The percentage removal efficiencies of various gases were determined from the difference in concentrations between the inlet and outlet of the scrubber column, expressed as percentage. The caustic solution required periodic replacement or replenishment in order to maintain the performance of the scrubber.



Raw Flue gas at Scrubber Inlet		
CO_2	v%	11.5
SO_2	ppmv	132.6
NO	ppmv	315
NO_2	ppmv	18
CO	ppmv	6.8

Raw Flue gas at Scrubber Outlet		
CO_2	v%	10.9
SO_2	ppmv	3.3
NO	ppmv	290
NO_2	ppmv	15.24
CO	ppmv	6.04

Figure 32: Concentration profile of flue gas at the inlet and outlet of caustic scrubber column

5.3.2 CO_2 capture performance with pre-treatment (Scenario 1)

After the commissioning of test facility with actual flue gas, experiments were carried out with the flue gas pre-treatment. As an example, overall CO_2 concentration profile for one test during the process of CO_2 capture and regeneration with flue gas pre-treatment through scrubber is shown in Figure 33. Extracted raw flue gas with CO_2 concentration of 10-13% was passed through the scrubber column (with caustic solution pH 9). There was very little change in CO_2 concentration at the outlet of scrubber and the flue gas was sent into the adsorption column containing the carbon fibre composite solid sorbents, for CO_2 capture. The CO_2 concentration at the outlet of adsorption column contains very negligible amount of CO_2 (0.01%) as over 98% of CO_2 gets adsorbed by the sorbents. When the concentration at the outlet began to increase (known as the point of breakthrough), the adsorption process was stopped and pure CO_2 was passed into the column. The CO_2 concentration at the outlet of the column remained to be very low (<0.5%) as pure CO_2 was further adsorbed by displacing other gases like nitrogen adsorbed from the flue gas during the capture step. The CO_2 flushing was stopped once the outlet CO_2 concentration starts to increase. The adsorption column was closed and adsorbents were heated by passing hot air through the regeneration tubes (13x12.7mm tubes through the sorbents). Once the adsorbent temperature reached 110°C, the column was opened to extract the gas that has desorbed (regeneration step). Vacuum was also applied to bring out the desorbed gases. The outlet concentration of CO_2 was found to be over 97%. The desorption efficiency as shown in equation (2) for CO_2, was found to be between 90-95%. Figure 34 shows the concentration profiles of SO_2 and NOx for the solid sorbent capture system. It can be seen that the CO_2 as well as the remaining SO_2 and NOx in the flue gas stream were adsorbed by the solid sorbents. The response of the NOx sensor was slower compared to CO_2 and SO_2 sensors and so the drop in NOx concentration at the point of switching the flue gas into the adsorption column is shifted (Figure 34). During thermal regeneration, concentration of NO was noticed in the desorbed gas, but no SO_2. SO_2 is possibly being retained in the adsorbents, or being transformed.

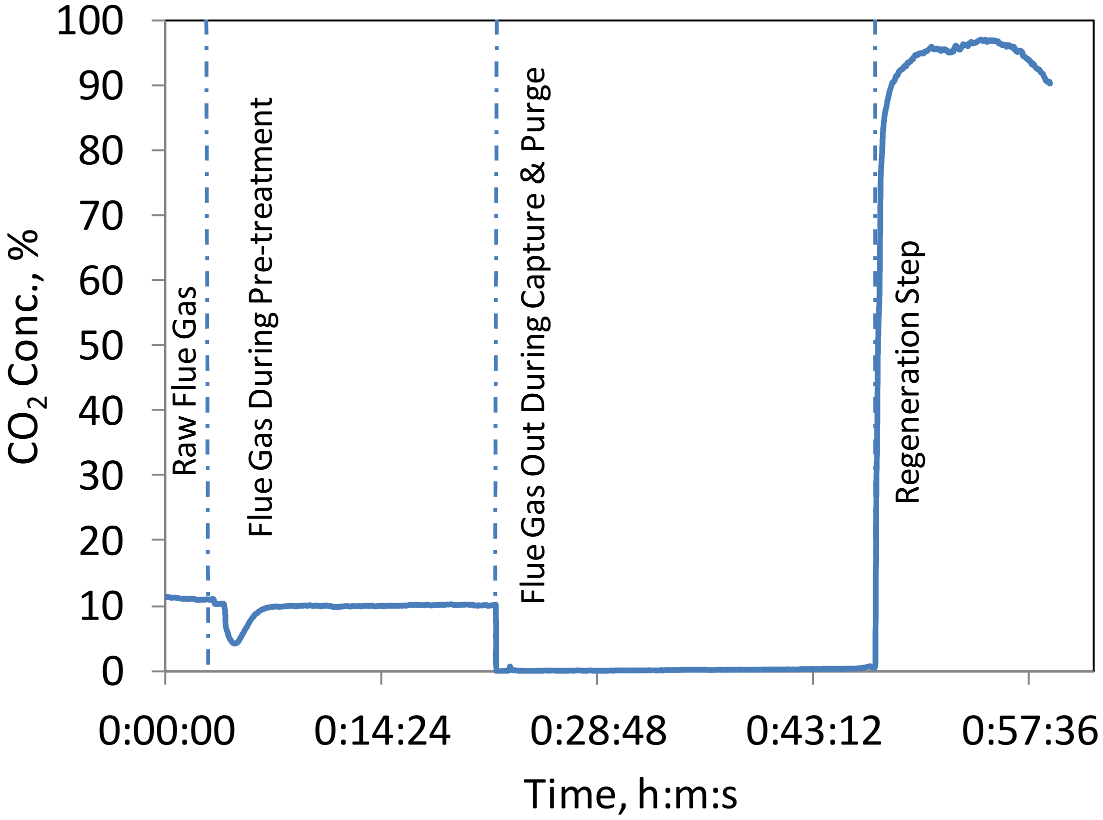


Figure 33: CO_2 concentration profile during capture and regeneration process with flue gas pre-treatment

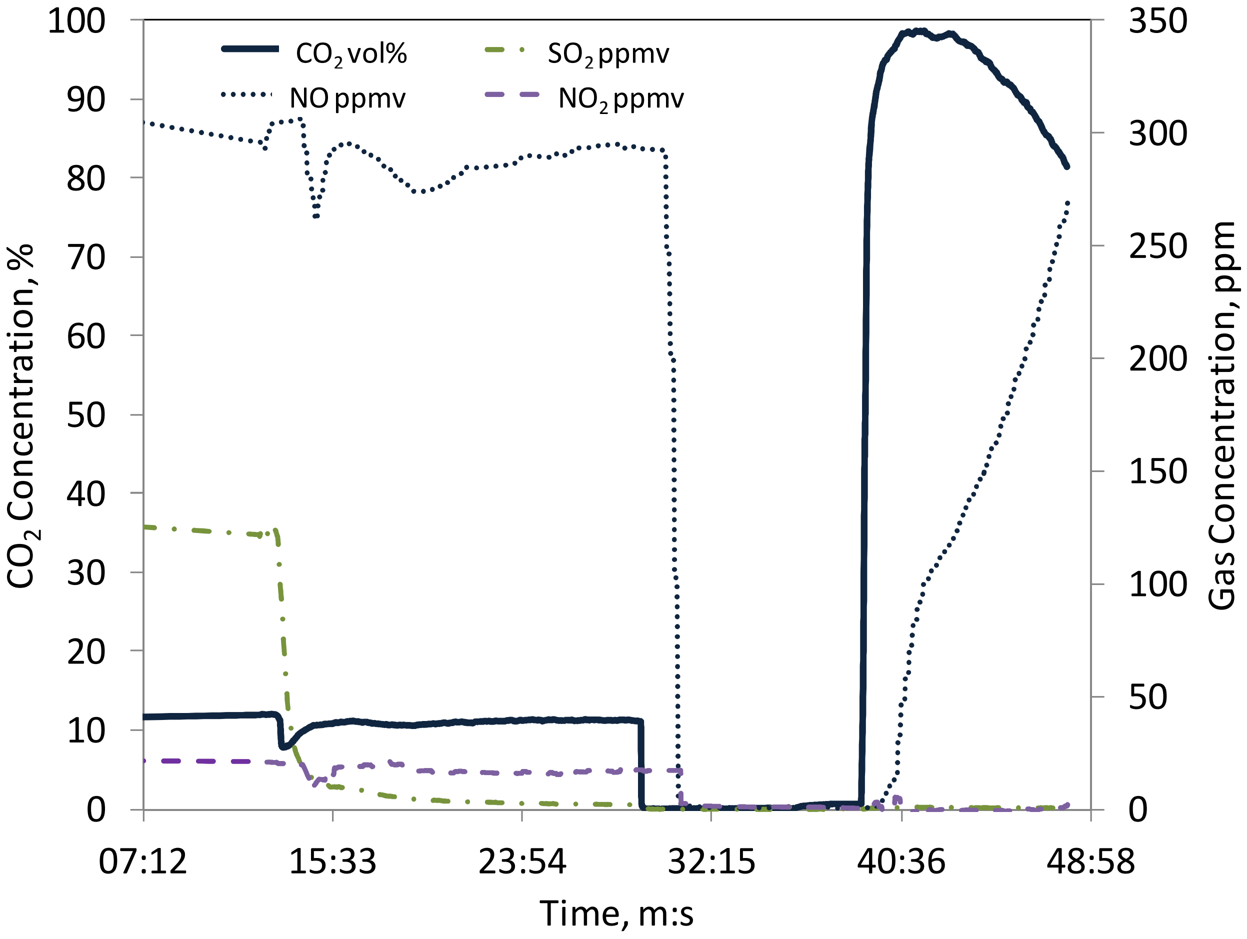


Figure 34: Gas concentration profiles for solid sorbent CO_2 capture and regeneration process with flue gas pre-treatment

5.3.3 CO_2 capture performance without pre-treatment (Scenario 2)

5.3.3.1 CO_2 capture performance

One of the key objectives of the project was to determine the stability of carbon fibre composite adsorbents under actual flue gas conditions. Hence, after the completion of four CO_2 capture tests with the flue gas pre-treatment, we have conducted over 200 tests on the CO_2 capture performance without the pre-treatment of flue gas except the dust filtration by the barrier filter. Figure 35 shows the performance of the solid sorbent for CO_2 capture without flue gas pre-treatment. The CO_2 adsorption efficiency was found to be over 98% even without flue gas pre-treatment and in the presence of SO_2 and NO_x, which were also completely co-adsorbed from the raw flue gas. Regeneration of the sorbents yielded high purity of CO_2 (over 97%). The CO_2 desorption efficiency was between 90-95% even without the caustic pre-treatment of the flue gas. Even after 200 experiments, the CO_2 adsorption performance of the solid sorbents was able to be maintained without any noticeable influence on the CO_2 capture performance due to the presence of SO_2 and NO_x in the flue gas.

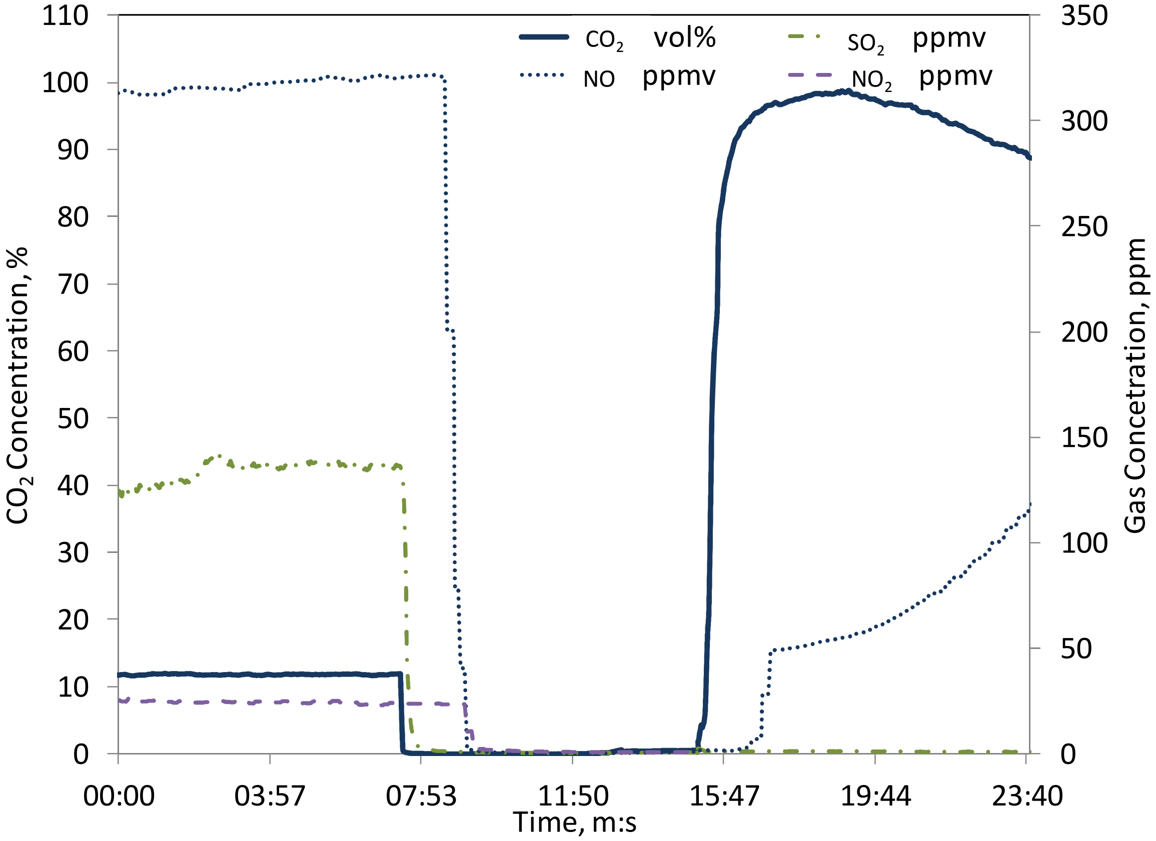


Figure 35: Gas concentration profiles for solid sorbent CO_2 capture and regeneration process with flue gas pre-treatment

5.3.3.2 Repair of column for desorbed gas leakage

After 35 runs, a gas leak from the column was noticed at the top and bottom part of the column during the regeneration as shown in Figure 36. It was identified that this was due to the damage of o-rings in October 2013. Then the leaking was fixed by applying high temperature metal oxide epoxy sealing patty as shown in Figure 37 in November 2013, and then the site trials recommenced.

Figure 36: Photo showing the gas leaking from the adsorption column

About 110 runs were carried out between Nov 2013-Feb 2014 and the project team noticed a recurrence of the leaking problem. Although the sealant applied was able to withstand the applied heat, the repeated heating and cooling made the material to deform (Figure 38). As a result, gas leakage was again noticed at the top and bottom of the adsorbent column. Close observation of the results showed no reduction in the CO_2 adsorption efficiency of the solid sorbents, indicating that the sorbent material performance to adsorb CO_2, was being maintained. During the normal test operation, the adsorbents after CO_2 capture from flue gas were heated to 100°C to desorb the gases from the adsorbent material. During this regeneration step, the inlet and outlet of the adsorption column were sealed to hold the desorbed gas within the column until a certain time till the gases have been desorbed (determined by the pressure transducer monitoring the pressure build up inside the column). Due to the leaking of the desorbed gas from the column, during the regeneration step, the column pressure dropped as it escaped from the column before the column was opened to recover the gas. Due to inadequate sealing of the adsorption column, the CO_2 desorption efficiency (the difference between the CO_2 captured by the adsorbents and the amount of CO_2 extracted out during regeneration), expressed as percentage, dropped to an average of 75% from originally obtained 90-95% at the start of the site trial.

The project team was committed to fix the column leak and demonstrate the performance of the solid sorbent. It was important to carry out the remaining planned tests without gas leak and to ensure that the stability of the solid sorbent was determined correctly. Further attempts to seal the column with more thermal cycle resistant stainless steel based sealants (EK456), which were also not effective as the leaks could not be contained. Clearly, a 'quick-fix' failed to work. Considering the importance to maintain the project milestone timeline, the corrective measure adopted this time, to fix the gas leak from the column was to redesign the regeneration section on the top and bottom of the column. It was decided to remove the existing sealant and weld the thirteen hot air circulation tubes with the flanges, at the points where it exits the top and bottom of the column. Also, the water and hot air distribution manifold was eliminated with a more simple design. Figure 39 shows the sketch of the redesigned regeneration section with a steel cap consisting of ports for flue gas, hot air and cold water circulation through the column.

Figure 37: Photo of column resealing with high temperature epoxy sealant

Figure 38: Photos of deformed adhesive material at the top and bottom of the column

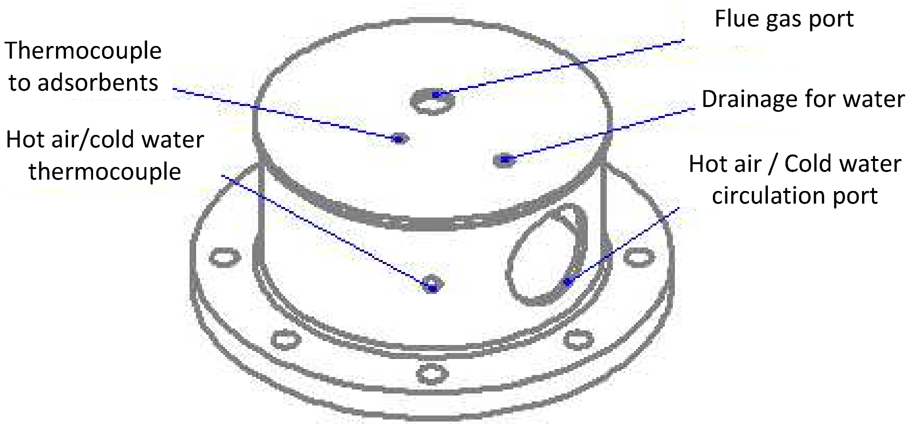


Figure 39: Sketch of redesigned regeneration section of the column

External mechanical contractor carried out the repair work in fixing the column leak, according to design provided. The CINSW was promptly notified about the problem of leak in the column and briefed about the corrective action adopted. It was decided to dismantle the column from the prototype test unit and carry out the repair work at the contractor's workshop. Figure 40 shows the photo of the adsorption column removed from the prototype unit at the power station.

Figure 40: Photo of the dismantled adsorption column from the prototype test unit

The column repair work was commenced during the second week of April 2014. The project team member was present at the workshop while the repair work was carried out at the contractor's workshop, to ensure the work was carefully performed without disturbing or causing any damage to the adsorbents inside the column. Figure 41 shows the repair work on the column being carried out the workshop.

Figure 41: **Photos of the repair work carried out on the adsorption column**

After welding of tubes and sealing the leaks, the column was leak tested. The column was pressurised to 150 kpa and checked if it was able to hold the pressure for 10-15 mins. Then the top and bottom section of the column was immersed in a water container and was checked for any air bubbles from the column. Figure 42 shows the photos of column leak tests carried out at the contractor's workshop.

Figure 42: **Photos of column leak test performed at the workshop**

Once the column was checked for leaks and ensured all the leaks have been completely sealed, the top and bottom steel caps were fixed to the column. After completion of the column repair, it was transported to the power station and installed to the prototype test unit. Figure 43 shows the picture of the redesigned and newly constructed regeneration section of the column.

Figure 43: Photo of the redesigned regeneration set-up with welding of regeneration tubes at the top of the adsorbent column

5.3.4 Adsorbent stability

Final column repair work was completed on 16th April 2014 and the site trial testing was commenced on 17th April 2014. The remaining number of experiments were carried out as planned. Figure 44 shows performance of the solid sorbents with real flue gas during the course of the site trial where more than 200 adsorption and regeneration cycles were conducted to demonstrate the stability of the adsorbents to real flue gas. The CO_2 adsorption efficiency from real flue gas was consistently over 98% (Figure 44) for the solid sorbents, throughout the site trial study period. Even during the column leak period, the CO_2 adsorption efficiency was not affected. The desorption efficiency for CO_2 was found to be between 90-95% and it dropped to an average of 75% during the leaking of desorbed gas. Due to the leaking of desorbed CO_2 from the column during regeneration, the desorption efficiency was found to be low. However, after the column was sealed for the leak it was evident from Figure 44 that the CO_2 desorption efficiency increased back to 90-95%, which was the performance at the start of the site testing. This demonstrated the fact that even after 200 cycles the performance of solid sorbents was able to be maintained indicating the excellent stability of the carbon fibre composite adsorbents towards real flue gas without the pre-cleaning of SO_x and NO_x, particularly in terms of the CO_2 adsorption efficiency. Table 9 summarises the site trials including tests with the gas leaking issue. All the planned tasks set out in this project were successfully accomplished through this study.

Table 9: Statistics of the site trial studies

Experimentation	Number of Tests
Total Number of tests undertaken	207
Tests under Scenario 1 (with flue gas pre-treatment)	18
Tests under Scenario 2 (without flue gas pre-treatment)	189
Tests with the column leaking issue	79
Tests without the column leaking issue	128
Tests under set condition*	93
Tests under other condition	114

* Adsorption temperature 25°C, adsorption flow rate 45-55 L/min, CO_2 purge amount 109-112L, total amount of CO_2 captured 137-141L, combined thermal and vacuum regeneration, desorption column temperature 100-110°C, vacuum pressure 20-25 kPa

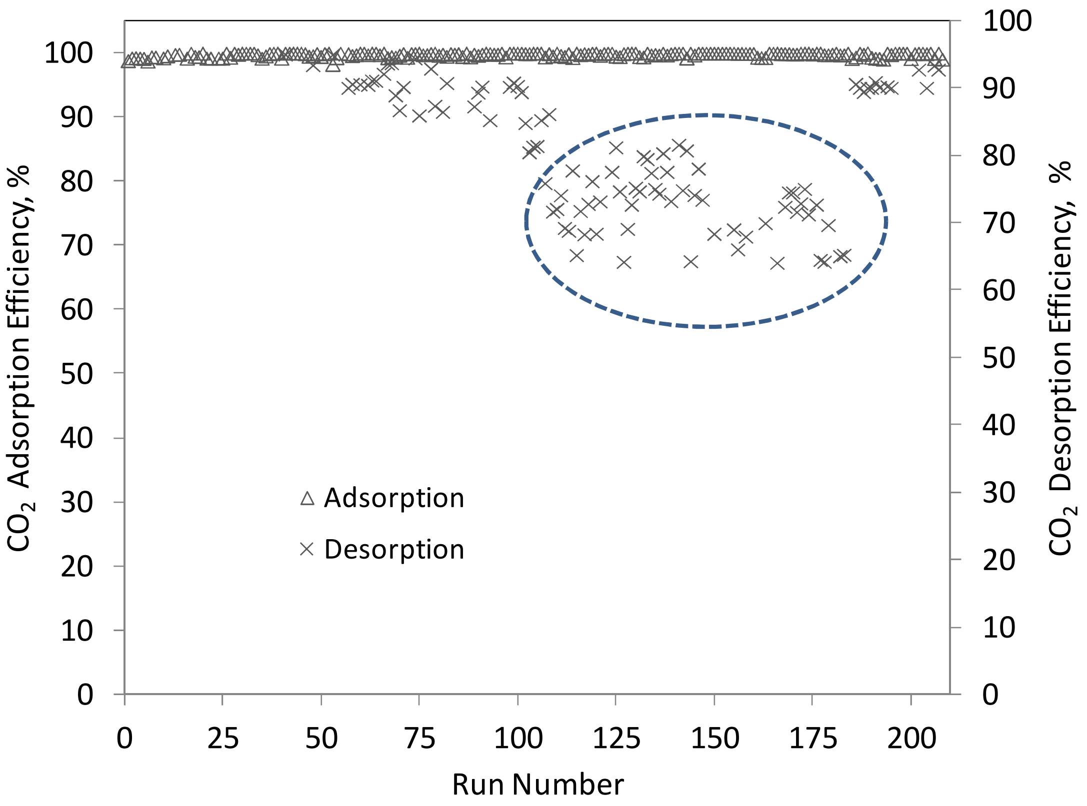


Figure 44: Performance and stability of carbon composite solid sorbents

For most of experimental results presented in Figure 44, the amount of the product CO_2 used for the purge was about four times of the amount of CO_2 from the flue gas adsorbed by the adsorbent. Hence this approach needs to be further evaluated as the increase in purge quantity decreases the CO_2 recovery and also results in energy loss associated with adsorption heat released and increases the desorption energy required [118]. Nevertheless, if this technology is to be pursued for the CO_2 capture with high purity gas product, it is necessary to further investigate better regeneration processes. The effect of small quantities of flue gas impurities like NO on the properties and behaviour of CO_2 in compression and pipeline transportation system is uncertain, and needs to be investigated. However, this is a similar issue faced by oxy-fuel CO_2 capture technology [119].

5.4 Key learning from the site trials

The solid sorbent CO_2 capture site trial and prototype unit demonstration project commenced in Q1 2011 and the site trial was completed in May 2014. Along the study period many challenges were faced and key lessons were learnt. Some of the key learnings from this study are discussed below.

- The original scope of the project was to operate the solid sorbent prototype unit along with ammonia based pilot plant and to obtain pre-treated flue gas to the solid sorbent unit from a slip stream from ammonia based process. It was soon evident that the original plan of extracting pre-treated flue gas from the ammonia pilot plant was not achievable as the timelines of operation for the ammonia pilot plant experienced delays and would not be matched with the project timelines for solid sorbent site trials. This resulted in the development of entire pre-treatment system into the solid sorbent prototype unit to be able to pre-treat the flue gas and operate independently. The pre-treatment system was designed and built. Building an additional infrastructure of a selfcontained pre-treatment system to the solid sorbent prototype test unit, caused some delays in meeting the project milestones on time and substantially increased the project expenditure.

- The project experienced some delays between the completion of infrastructure and installation of prototype unit on-site. Due to the delays in the site access, the construction of concrete basement on-site for pilot plant installation was experienced by ammonia pilot plant, which somehow delayed the on-site installation of prototype unit. Substantial delay in accesses to the real flue gas to the solid sorbent unit was also encountered, and this is because it took unexpected long time to set up major flue gas pipelines connected to the stack, and then to get it ready to supply the real flue gas with a number of safety concerns sorted out. Also, additional safety sensors to detect SOx, NOx in air during an event of flue gas leak were also required to be installed on the solid sorbent test unit. In general, some site research activities and tasks are not easily managed, and a lot of time was spent than earlier planned.
- It was apparent that due to the unique gas compositions and concentrations encountered during CO_2 capture process from actual flue gas, a single analyser to measure various gases was not an accurate method of operation in order to evaluate the performance. An analytical suite with individual sensors for CO_2, O_2, SO_2, NOx and CO were required to precisely measure the gases during testing process.
- During the capture and regeneration operation, the repeated heating and cooling of adsorbent column resulted in the heat related stresses to the joints and o-rings. This led to the wearing of o-rings, sealing the top and bottom of the adsorbent column. This resulted in the leakage of desorbed gases from the column thus affecting the overall recovery of CO_2 during the operation. Application of high temperature sealant to fix the leaks was not successful as the sealants were deformed due to heating and cooling cycle. Welding the regeneration tubes permanently sealed the leaks. Better design of the adsorption column and the regeneration tubes in the first place could have avoided the leaking problem.
- Adsorbent regeneration using hot air through 13 ss tubes was found to be not very effective in heating the adsorbent material as it required significant time (20-30mins) to heat the adsorbent materials (from 30-110°C) and resulted in significant idle time during the operation. However, time for adsorbent cooling using chilled water was substantially shorter. So, it is very important to develop a rapid heating process.

6 Preliminary Process Configuration and Life Cycle Assessment

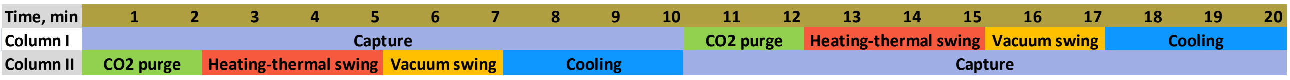
6.1 Preliminary process configuration and energy consumption analysis

6.1.1 Process configuration

A column with a diameter of 7 m and a height of 2 m was selected in the process configuration. Deploying a same column height in the current design as in the large scale test was aimed to adopt the experimental results of pressure drop obtained earlier. The diameter of column chosen is double the column size reported for the process design of packed beds using particulate carbonaceous adsorbents [66].

The following five-stage process includes: the flue gas flows through the adsorbent column for CO_2 adsorption (designated as capture stage); once the breakthrough is reached, the flow of flue gas will be switched to the 2nd column for continuous capture while the 1st column will be purged by flowing product CO_2 which is recycled from captured CO_2 (designated as purge stage). When purge is completed, the 1st column will be heated to 105 °C for thermal regeneration (designated as thermal swing stage) followed by extracting residual adsorbed CO_2 using vacuum (designated as vacuum swing stage), and finally cooled down to 30 °C (designated as cooling stage) ready for next cycle of capture. The above process sequence configuration agrees with the process trialled in the current project. Table 10 shows the sequential description of the solid adsorbent CO_2 capture process involving two columns and five-stage operations. The total duration for four stages of purge, thermal swing, vacuum swing and cooling equals to the time required for the capture stage. A complete cycle requires 20 minutes.

Table 10: Sequential description of one cycle of CO_2 capture process involving two columns and five-stage operations



Time, min	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Column I	Capture										CO2 purge		Heating-thermal swing			Vacuum swing		Cooling		
Column II	CO2 purge		Heating-thermal swing			Vacuum swing		Cooling			Capture									

Due to the low heat capacity of solid adsorbents and the low heat of CO_2 adsorption in our process based on CO_2 physisorption, adsorbents could be regenerated at a relatively low temperature and therefore it is potentially valid for utilising the waste heat from hot flue gas streams for thermal regeneration. It is designed to exchange the flue gas heat to liquid fluids which exchange heat with adsorbents and columns. In this way it is possible to achieve rapid heating as the heat transfer coefficient of liquid is significantly higher than gases. While the pressured water at 120 °C was used in the current process configuration, optimised fluids with a higher boiling point and improved heat transfer properties would be used in the future design.

6.1.2 Process simulation and energy consumption estimation

The HYSYS process simulation was carried out on the current process configuration to estimate the energy consumption based on the process parameters given in Table 11.

Table 11: Parameters used for the HYSYS process simulation

Parameters	Value	Unit
Column diameter	7	m
Column height	2	m
Cycle time	20	min
Capture (breakthrough) time	10	min
CO_2 purge time	2	min
Heating-thermal swing time	3	min
Vacuum swing time	2	min
Cooling time	3	min
Purged CO_2 amount/captured CO_2 amount	2	
Flue gas temperature	180	^oC
Flue gas composition		
CO_2	14	%
N_2	72	%
O_2	6	%
H_2O	8	%
Adsorption temperature	30	^oC
Regeneration/desorption temperature	105	^oC
Temperature of pressurised water for heating	120	^oC
Temperature of water from cooling tower	25	^oC
Height of cooling tower	20	m
Column pressure of vacuum swing	30	kPa
CO_2 capture efficiency	90	%
Efficiency of fans and pumps	75	%

6.2 Preliminary life cycle assessment

6.2.1 Scope and assumptions of life cycle assessment study

Greenhouse gas emission (GHG) of the carbon composite adsorbent based PCC process was studied with life cycle assessment (LCA) methodology which can be used to quantify the environmental impacts of a product or process. LCA seeks to examine all stages of a process's life cycle such as material and energy inputs from the beginning to the end of the process and including consideration of the impacts of materials and energy beyond the boundary of the processing sites. The results of an LCA can be used to identify the key items that contribute to the overall impact and to compare between processes using objective methodology. There is an international standard (ISO 14044, 2006) and there are softwares to undertake LCA studies. SimaPro 7.3.3 software [120] was used to undertake this study. The scope of this study has been identified after the delineation of the boundary. The coal mining, transportation, power production, post combustion capture and compression of processed output CO_2 gas ready liquefaction has been included.

The following main assumptions have been made to undertake this study.

- Reference power-station CO_2 emission factor: 1040 kg CO_2/MWh (SimaPro software for NSW electricity)
- Compression pressure of CO_2 increased before liquefaction: to 90 bar
- Energy of black coal: 27 GJ/t
- Average transport distance by rail from coal mine to power plant: 100 km
- Water use in coal mine: 0.27 t water/t coal (source Australasian unit process within SimaPro)
- Auxiliary heat required for regeneration of carbon adsorbents comes from the steam cycle of the power plant

There are other appropriate and reasonable assumptions made to carry out this LCA study.

Two scenarios were considered in the LCA of the carbon adsorbent based PCC process for the 350 MW unit. In the first scenario (referred to as partial flue gas treatment), the adsorbent PCC process was applied to treat a fraction of the flue gas generated from the 350 MW unit (63 m^3/s) and no additional heat would be required for adsorbent regeneration. The second scenario (complete flue gas treatment) considered treating the complete stream of the flue gas generated from the 350 MW (472 m^3/s), 63 m^3/s of which was treated by the process with the flue gas waste heat as described in Scenario 1 while the remaining 409 m^3/s flue gas was processed by additional heat taken from the steam plant of the power plant.

Life cycle inventory (LCI) data tables have been developed based on HYSYS flowsheet data, mass and energy balances. The LCI data for coal mining and coal transport were taken from a LCA study of the PCC process based on monoethanolamine (MEA) [121]. The LCI estimate for coal mining was based on power station capacity (669.8 MW), efficiency (35.6%) and coal energy value (27 MJ/kg), while 100 km was assumed distance by rail for coal transport. For comparison purpose, the same LCI data for coal mining and coal transport were used in the LCA of all evaluated PCC processes. The contribution of carbon adsorbent material and manufacturing has been estimated based on 20 years life design of the PCC plant.
The captured CO_2 product needs to be compressed for transportation and storage. A final pressure of 110 Bar was adopted here. The total electricity requirement for CO_2 compression from 1.5 to 110 Bar was estimated at 94 kWh/t CO_2 captured [122], and about 88-98 kWh/t CO_2 captured was reported for CO_2 compression to 110 Bar depending on the compression configuration [123]. In this study, we took 100 kWh/t CO_2 captured as the CO_2 compression electricity consumption.

6.2.2 Greenhouse gas emissions

Carbon emission from power plants is a major contribution towards the increase of CO_2 concentration in the atmosphere globally. The GHG emissions have been estimated for both scenarios of carbon composite adsorbent process considering adsorbent materials and energy use for each scenario. The following four parts of CO_2 footprints have been taken into account in the estimation of GHG emissions for carbon adsorbent based PCC process.

1. GHG footprints are from coal mining and coal transport, which were kept the same for different capture processes.
2. The amount of CO_2 that is not captured in PCC plant is accounted as an emission stream to the atmosphere based on the CO_2 capture efficiency of the PCC process.

3. CO_2 footprint is due to materials and fabrication of carbon composite adsorbents.
4. CO_2 footprint is due to energy consumption by the PCC process including all electrical power required by PCC equipments and extra auxiliary heat taken from the steam plant of the power

plant. All these above will draw electrical power from the power plant as shown in LCI data tables. The electricity that is used for the PCC plant will not be delivered from this power plant to the grid and may need to be supplied from the NSW State Electricity grid. This electricity from the grid will have CO_2 emission associated and is accounted here as the CO_2 footprint penalty for replacing lost power from the grid due to PCC-induced efficiency loss at the power plant. The carbon emission from the NSW grid based on coal-fired power generation is found to be 1,040 kg CO_2/MWh [120,124]. It has to be mentioned that the CO_2 intensity of the electricity used for the capture plant will have a sizeable impact on the CO_2-footprint of the capture process. For example, if the electricity is taken from a renewable power generation source, the CO_2 footprint penalty will be significantly reduced, such as the carbon emission of 16.5 kg CO_2/MWh for electricity from wind [125].

LCA studies can include other impacts such as acidification, abiotic depletion, ozone layer depletion, toxicity, land use etc. These numbers can be generated and reported if needed. For this study, CO_2 emission has the main focus since this is the most significant impact from a power plant. If next impact is to be prioritised, acidification and water resource depletion can be selected in further extension of this study. The results can be normalised for Australian population by estimating per capita impact. There is a debate among the LCA practitioners about use of weighting factors for each indicator which may introduce subjectivity with the results. This study has not used any weighting factors.

The GHG emission results per tonne of CO_2 captured for both scenarios of carbon composite adsorbent based PCC process were determined. For comparison, the GHG footprint results of the MEA process which was assessed in a similar LCA methodology [121] were used.

For Scenario 1 of carbon adsorbent process, the total GHG emission will be 295.6 kg CO_2-e per tonne of CO_2 captured if the electricity used for the PCC plant is replaced by coal-fired power generation. The total GHG emission for Scenario 2 is 497.3 kg CO_2-e per tonne of CO_2 captured based on electricity taken from coal-fired power generation. The total GHG emission of Scenario 2 is over 68.2% higher than that of Scenario 1 but about 5.5% lower than that of the MEA process (526.0 kg CO_2-e/t CO_2 captured).

7 Conclusions and Recommendations

7.1 Conclusions

The site trials and demonstration of the carbon fibre composite solid sorbent CO_2 capture prototype unit was successfully carried out at Delta Electricity power station. The solid sorbent prototype unit was successfully designed, constructed, commissioned and tested using real flue gas. Over 200 adsorption and regeneration tests were performed on-site using real flue gas. Various operating parameters were varied during the course of testing to evaluate the performance of the adsorbents, and key performance data and operational experience were obtained. Major technical findings are concluded below.

CO_2 adsorption efficiency, adsorbent stability and product purity

The CO_2 adsorption efficiency for the solid sorbents using real flue gas from coal fired power station was found to be consistently over 98%. The desorption efficiency in terms of CO_2 was found to be between 90-95% and the solid adsorbents were demonstrated to be very stable towards real flue gas without any removal of SO_x and NO_x as the performance of the material was maintained even after more than 200 tests.

Adsorption and then by pure CO_2 flushing enabled the captured product recovered by combined thermal and vacuum regeneration with a high purity of about 99% CO_2. However, this approach needs to be further evaluated as it results in energy loss associated with adsorption heat released and desorption energy required. It would be much better to devise an alternative regeneration process without the need of CO_2 flushing to achieve the better capture efficiency.

Process configuration and LCA

A five-stage CO_2 capture-regeneration process configuration was designed for the honeycomb monolithic carbon composite adsorbent based PCC process. Two scenarios of carbon adsorbent process were investigated in the LCA: Scenario 1 assumed the carbon adsorbent process treated a fraction of flue gas generated only relying on the flue gas waste heat for regeneration, while Scenario 2 considered treating the complete flue gas stream generated with extra auxiliary heat from steam extracted from the power plant.

Preliminary LCA results showed that the GHG emission for carbon adsorbent Scenario 1 is lowest at 295.6 kg CO_2-e/t CO_2 captured if the electricity used for the PCC plant replaced by coal-fired power generation. Scenario 2 has a GHG footprint of 497.3 kg CO_2-e/t CO_2 captured which is over 68.2% higher than Scenario 1 but about 5.5% lower than the MEA process at 526.0 kg CO_2-e/t CO_2 captured.

7.2 Recommendations

For the carbon adsorbents for the post combustion CO_2 capture, so far studies have been carried out only using simulated flue gas and under laboratory conditions. Hence, through this CINSW project the site trials and demonstration of the carbon composite adsorbents for CO_2 at the power station is a pioneering research in the world to study the capture performance and captured gas quality using real flue gas. The important experimental data and site operational experience obtained at the power station form a basis for further development of this carbon composite adsorbent CO_2 capture technology towards its application at fossil fuel fired power stations. Before the development and demonstration of a carbon adsorbent pilot scale plant for CO_2 capture, it is recommended further research needs to be conducted to obtain critical operational parameters and experience for the design of the pilot scale plant.

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