



Reduced cost postcombustion CO₂ capture from coal fired power stations with enzymes

ANLEC Project 3-1110-0099

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Milestone 3 report

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Executive summary

Carbon dioxide, the main by-product of combustion of carbon-rich sources such as coal and oil, is the highest contributor to total greenhouse gas emissions in Australia. Combustion of coal, especially in its use to provide energy for electricity generation, is the single greatest contributor to any of the Australian GHG emissions sectors and has been a major contributor to our increase in emissions over the past two decades. Effective removal of millions of tonne of CO₂ diluted in large volume flue gas streams together with reactive contaminants, followed by gas compression and storage or utilisation, presents a huge challenge.

Economic modelling conducted at CSIRO has identified at least two important hurdles to cost effective CO₂ capture from coal-fired power stations using reactive solvent systems. CO₂ capture based on absorption of CO₂ from power station flue gas via treatment with dilute solutions of amines such as monoethanolamine (MEA) require large capital infrastructure especially the need for long absorption columns of quality stainless steel. Secondly, there is a large requirement for energy to regenerate the CO₂-loaded MEA solvent used for CO₂ capture. While PCC is the most promising technology to reduce GHG emissions from existing power stations, new R&D is required to significantly reduce the capital and energy costs of the process to bring it into a feasible range to ensure coal remains a competitive source for electricity generation.

Enzymes are biological catalysts made of protein that can operate independently of a biological cell to facilitate reactions with high specificity and rapid turnover rates under mild conditions with low energy requirements. Due to rapid rates and genuinely catalytic quantities used, there is potential for enzymes to increase the CO₂ mass transfer rate to solution, reducing the height of the absorber column, and hence reduce overall capital costs of the unit.

Earlier research in this area funded under the APP program focused on the selection of the enzyme, the concept for use of the enzyme in an absorber and the methods for immobilisation of the enzyme and is described briefly to provide background. ANLEC Project 3-1110-0099 *Reduced cost postcombustion CO₂ capture from coal fired power stations with enzymes* aims to demonstrate the utility of enzymes for reducing the capital and/or energy costs of postcombustion capture.

The third Milestone for the project is to provide a report that describes pathways that would lead to either:

- a 30% overall cost reduction of post-combustion CO₂ capture, or
- a 30% overall reduction in the benchmark energy requirements of postcombustion CO₂ capture, and addresses the requirements of cl 1.3 Tasks in the project plan to achieve outcome 1.

The aim of this research was to use appropriate methods to screen enzyme-base solutions for absorption of CO₂ from mixed gas streams for high CO₂ absorption rate, and selecting from a range of bases with emphasis on those with lower vapour pressure, high absorption capacity, lower corrosivity, thermo- and metal ion stability and faster biodegradation, and lower energy of regeneration than monoethanolamine (MEA), our benchmark.

To overcome the issues associated with bubble reactors and the wetted wall apparatus that proved to be unsuitable for our enzyme experiments, a new laboratory-scale gas reactor based on a gentle spray column was trialled with enzyme-base solutions, operated at ambient pressures and with CO₂ concentrations in gas flows similar to those of coal fired power station flue gas. The system has the advantages of a larger surface area than the wetted wall column and it can be used to reliably measure the CO₂ absorption from slow acting solutions such as tertiary alkanolamines. It is also highly suited for experiments containing enzymes. The gas reactor can be used in two modes: Spray mode and Film mode, the latter is where the spray head is removed and absorption occurs through gas contact with the thin film at the bottom surface of the vessel.

Gas mass transfer results from the gas reactor were compared with some obtained from the wetted wall analysis of selected alkanolamines and the flux rates calculated for the two systems were comparable especially allowing for the different conditions they are tested under.

To date the following solutions have been tested in the gas reactor in the presence and absence of enzyme – 3M of the following: AMP, MDEA, MEA, MAE, DMAE, K_2CO_3 , and the following amino acid potassium salts – glycine, alanine and methyl alanine over a range of enzyme concentrations.

The addition of enzyme ($0.16 - 0.32 \text{ mg ml}^{-1}$) to 3 M tertiary alkanolamines can lead to a dramatic improvement in CO_2 capture compared to either component alone. For faster-acting secondary or hindered primary alkanolamines, the addition of enzyme to these was also effective in increasing CO_2 mass transfer although not for all solutions tested. The CO_2 mass transfer calculations for alkanolamines and amino acid salts in the presence and absence of enzymes are given within the commercial-in-confidence Appendix.

Quantitative ^{13}C NMR analysis of the major reacted CO_2 species in 3 M secondary alkanolamine solution showed that the presence of enzyme significantly increased the proportion of bicarbonate species over carbamate species over time in the absorption fluid, and increased the total CO_2 captured. The quantity of reacted CO_2 in 3 M tertiary alkanolamine solutions doubled in the presence of enzyme and this was entirely as the bicarbonate form.

At least two pathways leading to substantial reductions in overall cost or energy reductions of postcombustion capture have been demonstrated by the selective combination of basic solution and the concentration it is used at, with enzyme, and these are detailed in the commercial-in-confidence Appendix.

Further research is planned for the project including the development of enzymes with greater robustness, effective enzyme immobilisation strategies and testing of the basic solutions with enzyme at pilot scale to achieve 30% reduction in either total postcombustion capture cost or 30% reduction in energy requirement.

1 Background

1.1 Australian greenhouse gas releases from coal-fired power plants and approaches to mitigation

1.1.1 AUSTRALIAN GHG EMISSIONS AND THE REQUIREMENT TO PREVENT EMISSIONS

Carbon dioxide, the main by-product of combustion of carbon-rich sources such as coal and oil, is the highest contributor to total greenhouse gas emissions in Australia. Combustion of coal, especially in its use to provide energy for electricity generation, is the single greatest contributor to any of the Australian GHG emissions sectors and has been a major contributor to our increase in emissions over the past two decades. Australia's power sector is approximately 80% coal-fired and emissions are around 170 Mtpa from ~35 existing coal-fired power stations. These facilities have an estimated operational life of 50 years and by 2020, around 38 GW of old pulverised fuel capacity will remain in use. Australia's coal-fired power stations could be substantial stranded assets, and now attract carbon taxes under the current scheme introduced in Australia in July 2012.

1.1.2 GHG EMISSIONS REDUCTION APPROACHES FOR AUSTRALIA

Several leading approaches may be undertaken to reduce Australia's emissions from coal-fired power stations:

- Precombustion, CO₂ separation and storage
- Oxyfiring, CO₂ capture and storage
- Postcombustion capture and storage, where CO₂ is selectively removed from the bulk of the combustion gases, compressed and then stored or utilised.

The most promising technology for reduction in emitted CO₂ is postcombustion capture and storage where CO₂ is selectively removed from the bulk of the combustion gases by reactive gas-liquid absorption, compressed and then stored/utilised. Absorption processes are the only technology that has the demonstrated capacity for removal of CO₂ at atmospheric pressures from large volume gas streams (Feron and Hooper, 2010). CO₂ capture by reactive gas-liquid absorption was developed for natural gas purification many decades ago and the technology has been extended to CO₂ capture from coal-fired power station flue gas. This approach has the advantage of being able to address the existing coal-fired power generating infrastructure and new installations, can be switched off at times of high electricity demand and has potential for continuing reductions in cost and efficiency as the technology advances (Feron and Hooper, 2010).

1.1.3 WHAT ARE THE CHALLENGES FOR PCC?

Typical flue gas from a coal fired power station in Australia has the following components (% vol/vol) – nitrogen (74 %), carbon dioxide (13%), oxygen (5%), water vapour (7%), argon (1 %) and nitrogen oxide species (N₂O, NO₂, NO) at around 300-700 ppmv, and oxides of sulfur (SO₂, SO₃) at 200-600 ppmv for black coals (lower for brown coals). Effective removal of millions of tonne of CO₂ diluted in large volume flue gas streams together with reactive contaminants, followed by gas compression and storage or utilisation, presents a huge challenge.

Economic modelling conducted at CSIRO has identified at least two important hurdles to cost effective CO₂ capture from coal-fired power stations using reactive solvent systems. CO₂ capture based on absorption of CO₂ from power station flue gas via treatment with dilute solutions of amines such as monoethanolamine (MEA) require large capital infrastructure especially the need for long absorption columns of quality stainless steel. Secondly, there is a large requirement for energy to regenerate the CO₂-loaded MEA solvent used for CO₂ capture. CSIRO modelling has estimated that the current cost of electricity generation could double to account for 90% CO₂ capture from the flue gas.

SO_x and NO_x can have a degrading effect on traditional aqueous amines used for CO₂ capture. These contaminants react readily with some amines, and irreversibly; in addition, some of the reaction products can contribute to the corrosivity of the solvents. The consequences include the consumption of amine or other capture chemicals which must be replenished leading to increased operating costs; formation of insoluble materials which need to be removed or cause blockages, and waste removal; and the formation of potentially toxic reaction products such as nitrosamines. The presence of NO_x and SO_x is highly relevant to Australia as, unlike other countries, no flue gas desulphurisation equipment is fitted to our power plants.

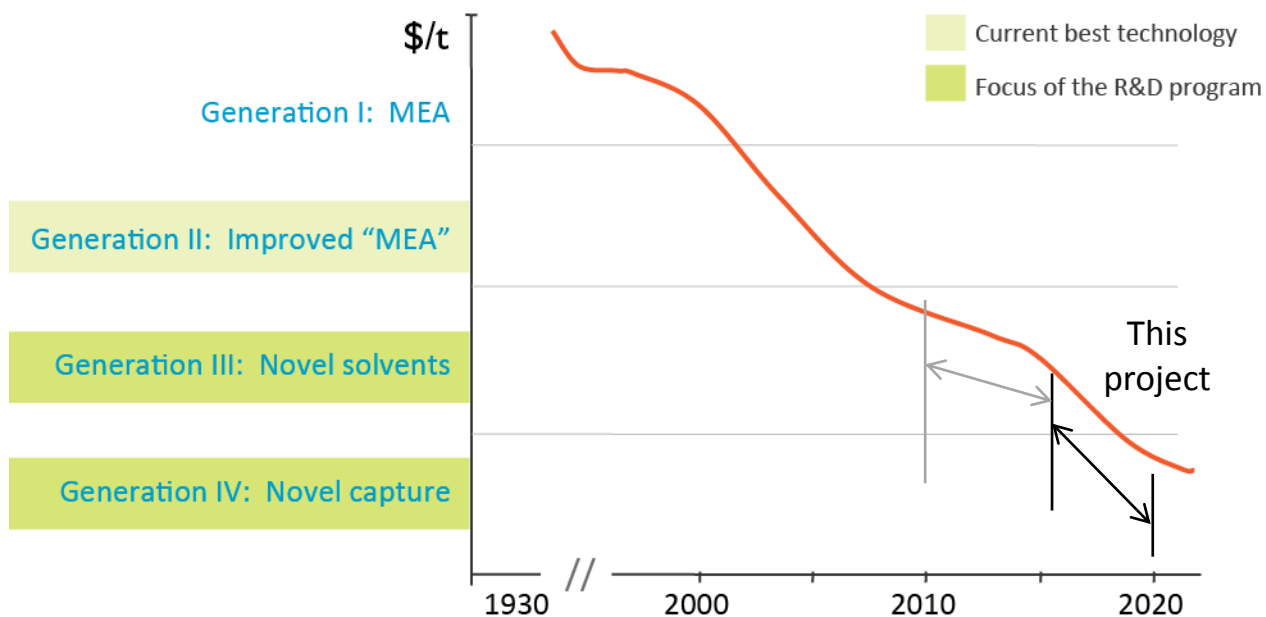
While PCC is the most promising technology to reduce GHG emissions from existing power stations, new R&D is required to significantly reduce the capital and energy costs of the process to bring it into a feasible range to ensure coal remains a competitive source for electricity generation.

1.2 Enzyme use in postcombustion capture

Enzymes are biological catalysts made of protein that can operate independently of a biological cell to facilitate reactions with high specificity and rapid turnover rates under mild conditions and low energy requirements. Due to rapid rates and genuinely catalytic quantities used, there is potential for enzymes to increase the CO₂ mass transfer rate to solution, reducing the height of the absorber column, and hence reduce overall capital costs of the unit.

Enzymes have the advantages of being generally safe and biodegradable, and are non-volatile catalysts of a reaction rather than a component. Enzyme production is a developed but growing industry that uses selected fungi or bacteria as production platforms delivering protein at costs of \$20 - \$200 kg⁻¹ dry weight. Internationally, bulk enzymes such as those used in washing powder and biofuels are currently produced at quantities well in excess of 1000 t per annum.

Where enzyme technologies fit in the postcombustion capture R&D pipeline:



1.2.1 PRIOR RESEARCH UNDERTAKEN TO DEMONSTRATE THE FEASIBILITY OF USING ENZYMES TO FACILITATE THE ABSORPTION OF CO₂ FROM FLUE GAS STREAMS

This research area focused on the selection of the enzyme, the concept for use of the enzyme in an absorber and the methods for immobilisation of the enzyme. The methodologies used were akin to those used for screening of solvents, particularly where it concerned the assessment of the absorption rate for enzyme promoted amine based solvents. Standard biotechnological methods were used throughout the study illustrating that there is an excellent technological basis for use of enzymes in PCC. Methods for increasing the thermal stability of the enzyme were also considered.

- *Selection of enzyme*

Carbonic anhydrase II (CAII) is the main enzyme investigated for CO₂ capture; it catalyses the reversible hydration of CO₂ at rates up to 5-orders of magnitude faster than the background hydrolysis rate [Wolfenden and Snider; 2001]. CAII is a small and relatively robust protein that does not require cofactors for activity and is readily available from cheap natural sources or through biotechnological production. Bovine carbonic anhydrase II has been used throughout our research.

- *Concept for use of enzyme in absorber*

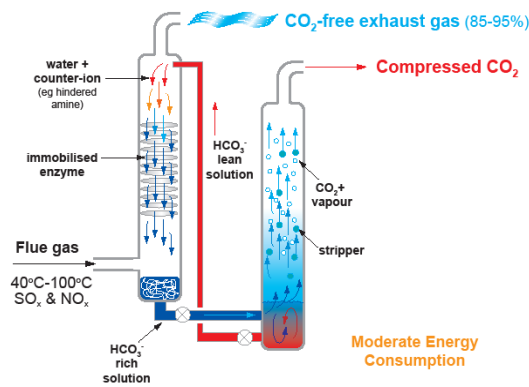


Figure 1: Concept for the use of enzyme for CO₂ capture employing the conventional absorber/stripper configuration.

Post combustion flue gas contains ~13% CO₂ with the remainder mostly composed of N₂, O₂, water vapour, argon and relatively low levels of SO_x and NO_x (in power stations without flue gas desulphurisation equipment fitted). It is envisaged that immobilised enzyme will be arrayed in the flue gas stream of the absorber wetted by an aqueous solution containing counter-ions (Figure 1). The captured CO₂ (as HCO₃⁻) is taken into the base of the absorber with the liquid stream and pumped to the 'stripper' where CO₂ is thermally regenerated and the regenerated counter-ion is recycled into the absorber.

- *Immobilisation*

Industrial enzymes are routinely immobilized, that is, non-destructively bound to inert supports such as silica, resins, nylon and polyurethane for use in reactors. Immobilisation often increases stability of enzymes to pH and temperature and extends their useful life as well as improving the ease of handling, separation and recovery of enzymes [Mateo; 2007].

A review of the literature suggested the best approach for immobilisation in PCC applications would be to form covalent linkages between the enzymes and inert supports, as opposed to less robust ionic or hydrophobic associations, due to the large shear effects of gas flow and circulating solution expected in the absorber. The amino acid residues essential for catalytic activity must not be involved in the covalent linkage to the support, which can be difficult to achieve for some enzymes. After extensive testing of bovine carbonic anhydrase on four different supports: Eupergit C250L, Sepabeads EC-EP, Sepabeads EC-HFA and Nylon (6, and 6,6), two supports performed best overall: Sepabeads EC-EP for the highest protein loading and Eupergit C250L for the highest retained activity (figure 2). Eupergit C250L immobilised CAII has been used successfully in CO₂ uptake experiments in our laboratory-scale capture apparatus.

A

B

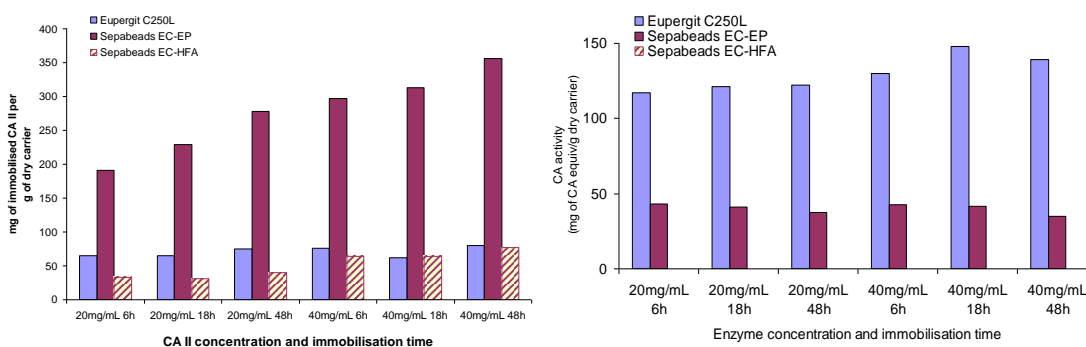


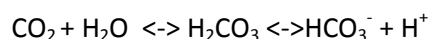
Figure 2: Covalent immobilisation of bovine CAII onto different supports. A. Enzyme loading per g dry weight support (nylon negligible) B. Retained CAII activity per g dry weight support. Activity for CAII immobilised on EC-HFA was undetectable.

Bovine CAII immobilised on Eupergit C250L was assessed for improved thermotolerance and stability in high pH solutions; after treatment at 70°C for 15 min 50% of immobilised CAII was active whereas the free CAII had lost all activity. In addition, immobilised CAII activity was reduced by 25% after incubation at pH 12.4 in 3M dimethylaminoethanolamine (DMAE) for 24 h at 20°C compared with a sample incubated in buffer at pH 8 for the same period which was also equal to a freshly prepared native enzyme. The reduction in CAII activity would also include any loss of enzyme that was not covalently bound to the support, as well as any denatured enzyme.

The results for enzyme loading, retained activity and stability from our work compares very favourably with the range of immobilization strategies that have already been trialled with carbonic anhydrase to date (data not shown), although most of the applications were not intended for, nor are they suited to PCC.

- *Identify enzyme-base solution combinations with improved CO₂ mass transfer potential*

The hydration of CO₂ proceeds with a lowering of solution pH due to the formation of carbonic acid which spontaneously decays, releasing a proton and bicarbonate as shown in the following equation:



The reaction rate is increased by 100,000-fold by the action of carbonic anhydrase II which operates at the limit of CO₂ diffusion. As the solution pH becomes more acidic with hydration of CO₂, carbonic anhydrase becomes less efficient as a catalyst for CO₂ hydrolysis at pH values of 7 or less. Therefore, a counter-ion or base is required to maintain solution pH in the alkaline and operational region for the enzyme to maintain its catalytic rate. We have measured the effectiveness of carbonic anhydrase in capturing CO₂ when combined with one of a range of potential agents to neutralise acidity including bases such as potassium carbonate and hydroxide, alkanolamines, amines and amino acid salts.

The aim of this research was to use appropriate methods to screen enzyme-base solutions for absorption of CO₂ from mixed gas streams for high CO₂ absorption rate, and selecting from a range of bases with emphasis on those with lower vapour pressure, high absorption capacity, lower corrosivity, thermo- and metal ion stability and faster biodegradation, and lower energy of regeneration than monoethanolamine (MEA), our benchmark.

- *Apparatus and results of measuring gas-liquid mass transfer in application to postcombustion CO₂ capture*

We have investigated a range of systems for measurement of CO₂ mass transfer into base solutions in the presence and absence of enzymes as described below, along with the advantages and disadvantages of each system for measuring the CO₂ using enzyme solutions.

Headspace analyser

This was the first system we developed under the APP Postcombustion capture program and used in the laboratory to screen for effective combinations of enzyme and basic solution in terms of CO₂ uptake from a

gas mixture, shown in Figure 3. When combined in solution with bases at 0.1 M, the enzyme catalysed uptake of CO₂ (13%, balance nitrogen) from the headspace was enhanced in all cases, by up to 10-fold in the presence of enzyme in combination with 2-piperidine ethanol (Figure 4). While this system was effective for screening, the major drawback was that the headspace was closed which limited both the amount of CO₂ that could be removed and was not suitable for gas mass transfer measurements. However, it did demonstrate the remarkable potential for increase in uptake of CO₂ from a gas stream by mixing in a small quantity of enzyme, over the CO₂ capture potential of the basic solution itself.

The rate of CO₂ uptake by K₂CO₃ solution (0.1 M) was very effectively enhanced by the addition of enzyme in the headspace system (~10-fold); this was an exciting finding as K₂CO₃ has many desirable characteristics as a capture solution.

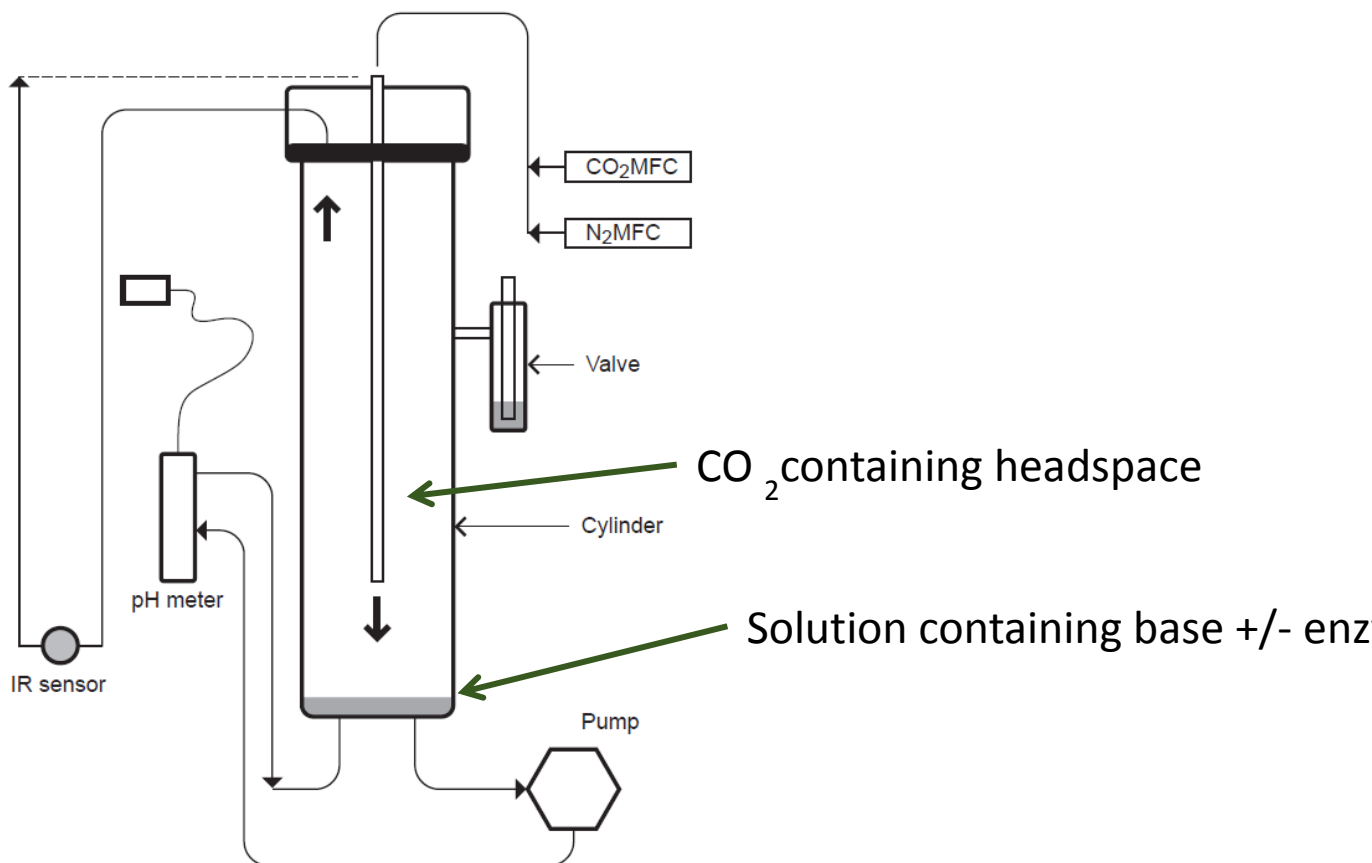


Figure 3. Diagram of the laboratory system for measuring the change in CO₂ concentration from a circulated headspace mixture (13%CO₂, balance N₂) above a solution of base with or without enzyme using an IR sensor.

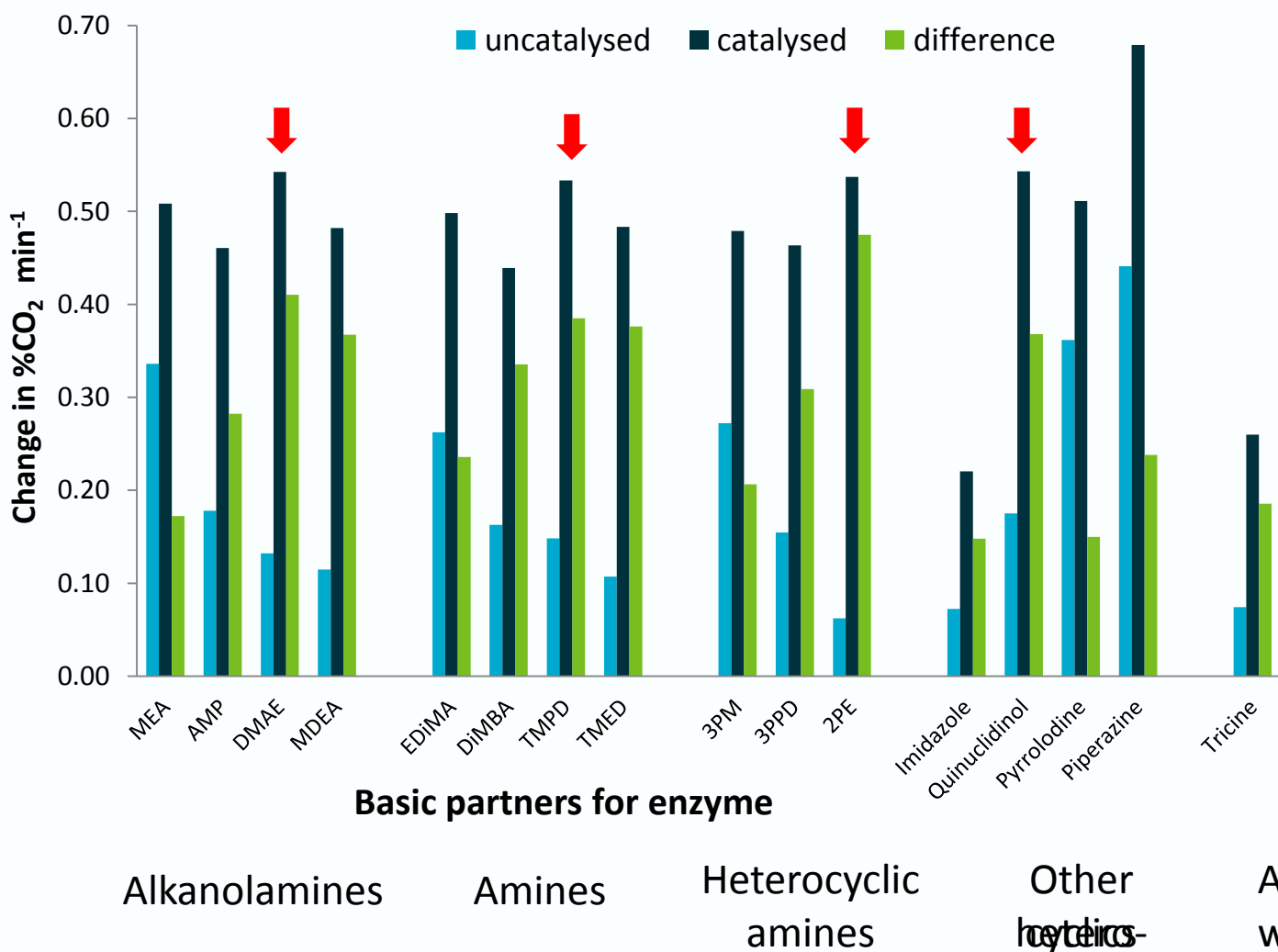


Figure 4: CO₂ absorption from the headspace above solutions containing 0.1 M bases with enzyme at 0.26 mg ml⁻¹ (black bars) or without enzyme (blue bars). The difference in CO₂ uptake rate is shown by green bars and largest differences indicated by red arrows. MEA monoethanolamine; AMP 2-amino-2-methyl-1-propanediol; DMEA N,N-dimethylethanolamine MDEA methyldiethanolamine; 2PE 2-piperidine ethanol; 3PM 3-piperidine methanol; 3PPD Diisopropanolamine; TEA triethylamine; AMPD 2-amino-2-methyl-1,3-propanediol.

Parr stirred cell reactor

Using a Parr stirred cell reactor, CO₂ uptake experiments were conducted within the APP program on 11 alkanolamines and amines at higher concentrations and in combination with enzyme. The amines belong to a range of categories, e.g. primary hindered, secondary hindered, primary, secondary, tertiary, mixtures of alkanolamines and amino acid salts. Standard conditions were 3 M amine solutions, 25°C, stirring rate 900 rpm, and the measurement of CO₂ uptake rate was via the reduction in CO₂ pressure measured from 4 bar (initial pressure 8 bar). Two examples of the CO₂ loss for 3 M alkanolamines are shown in Fig 5 in the presence and absence of enzyme; in both cases addition of enzyme to the base markedly increases the CO₂ loss rates from the headspace.

CO₂ uptake rates were calculated from the linear portions of the CO₂ pressure loss graphs against time from the stirred cell reactor data; uncatalsed rates were compared with enzyme-catalysed and the results are summarised in Table 1. Specifically, linear regression analysis was applied to each graph that recorded the reduction in CO₂ pressure from the headspace of the reactor. For most amines in the presence and absence of enzyme, a linear range was found from 0 to 500 secs, or longer, whereby the correlation coefficient exceeded 0.99 in a graph of CO₂ pressure versus time. In the cases of 2PE and MEA the linear CO₂ loss period was reduced to 0 – 300 secs and maintaining an $r^2 > 0.99$. A ratio of the CO₂ pressure reduction rates

obtained for each condition were directly compared between enzyme-catalysed and uncatalysed solutions to obtain an 'enhancement factor'. There is no obvious trend among the solutions tested with enzyme in the Parr reactor. The rate of CO₂ uptake with tertiary alkanolamine MDEA was enhanced by the most at 1.75-fold, and the rate in MEA was the least enhanced of the amines tested. In all except one case, addition of enzyme improved CO₂ loss rates of the various 3 M basic solutions under high CO₂ pressures.

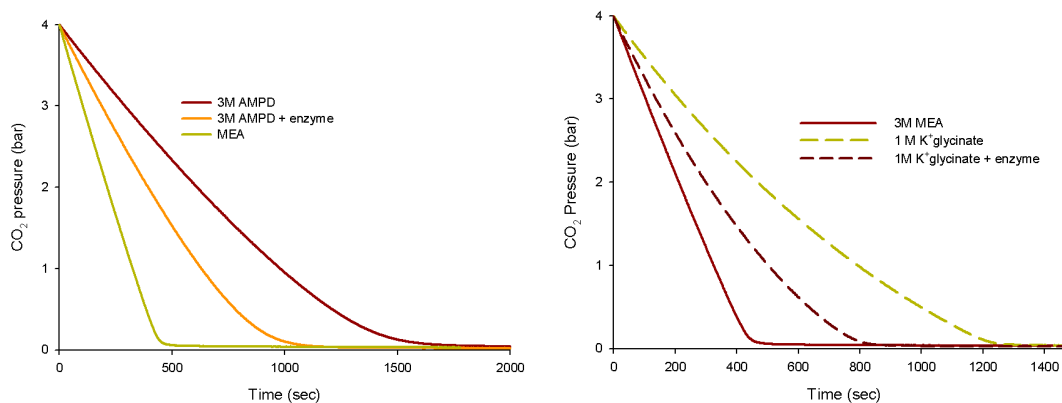


Figure 5: Two examples of enzyme enhancement of CO₂ capture by amine. The left panel compares the CO₂ pressure loss rates for 3M AMPD (2-amino-2-methyl-1,3-propandiol) with and without enzyme (0.26 mg ml⁻¹) and the right panel shows the CO₂ pressure loss in the presence of 1 M potassium glycinate. Both panels also show the uncatalysed 3M MEA CO₂ uptake rate for comparison.

However, there are several factors that present difficulties for extrapolating Parr stirred cell data to the kinetics of capture of CO₂ from flue gas streams. Comparisons of enzyme-catalysed and uncatalysed rates are probably valid for the same amine in this system but there are large uncertainties in comparing the rates of amines (Vaidya and Kenig, 2007) where factors such as viscosity differences between the solutions can have a major influence on CO₂ uptake.

Also, the stirred cell reactor measures the loss of CO₂ from a 100% CO₂ headspace at higher than atmospheric pressure which is somewhat counter to the situation in a flue gas absorber where CO₂ is a minor component of the total stream and is operated at approximately atmospheric pressure. The Parr stirred cell reactor results will tend to increase reaction rates for solutions that are operating under diffusion limited conditions at low CO₂ concentrations by driving CO₂ across the gas-liquid interface. Penders-van Elk et al (2012) have very recently published a study of carbonic anhydrase with MDEA where they conclude the enzyme is very effective at enhancing the rate of this slow acting but very useful alkanolamine using the stirred cell reactor approach.

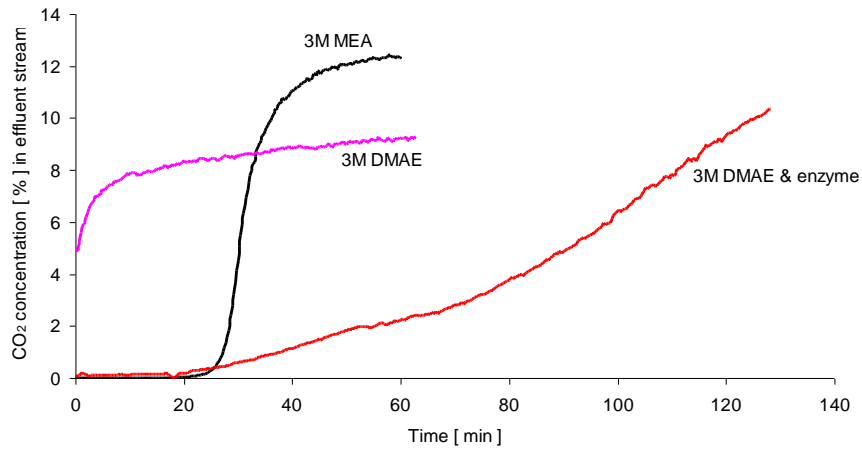


Figure 6. Concentration of CO₂ in the effluent stream (360 ml min⁻¹) over time of a bubble reactor containing 3M alkanolamines with or without immobilised carbonic anhydrase enzyme on Eupergit beads. Enzyme greatly promotes CO₂ absorption of 3M N,N-dimethyl ethanolamine (DMAE) and this combination has an increased capacity to absorb CO₂ than 3M MEA.

Bubble reactor

An initial laboratory investigation under the APP program tested 3M N,N-dimethylethanolamine (DMAE) in the absence and presence of immobilised enzyme (0.4 mg ml^{-1}) in a bubble reactor, constructed from a modified Drechsler bottle. In this configuration, 3 M DMAE plus enzyme appeared to be as effective as 3M MEA in removing all CO_2 from 13% stream in nitrogen yet has greater CO_2 sorption capacity (Fig 6) and the presence of enzyme greatly enhanced CO_2 capture into DMAE solutions.

Table 1. CO_2 uptake rates for 3 M base and effect of combination with enzyme (0.26 mg ml^{-1}) in a Parr stirred reactor with CO_2 (measured from 4 bar) and temperature maintained at 25°C and stirred at 900 rpm. The linear portion of the CO_2 loss curve was used to determine catalysed and uncatalysed rates.

Amine	Uncatalysed rate ($\Delta\text{mbar sec}^{-1}$)	Amine/alkanolamine class	Enzyme CO_2 rate enhancement factor (fold)
MEA	9.28	Primary	1.09
Potassium glycinate	6.08	Primary	1.18
MAE	5.93	Secondary	1.22
2PE	4.95	Hindered secondary	1.45
AMP	4.26	Hindered primary	1.34
2PM	3.66	Hindered secondary	sl reduction
AMPD	3.33	Hindered primary	1.48
Potassium threonate (1M)	3.03	Hindered primary	1.46
MDEA	2.90	Tertiary	1.75
3PM	2.46	Hindered secondary	1.15
DIPA	1.88	Secondary	1.16
Enzyme only	1.41	-	-

MEA monoethanolamine; MAE N-methyl ethanolamine; 3PM 3-piperidine methanol; AMP 2-amino-2-methyl-1-propandiol; AMPD 2-amino-2-methyl-1,3-propandiol; DMEA N,N-dimethylethanolamine; 2PE 2-piperidine ethanol; 2PM 2-piperidine methanol; AMPD 2-amino-2-methyl-1,3-propandiol; AMP 2-amino-2-methyl-1-propandiol; MDEA methyldiethanolamine; 3PM 3-piperidine methanol; DiiPA Diisopropanolamine

2 ANLEC milestone 3 statement and tasks

ANLEC Project 3-1110-0099 *Reduced cost postcombustion CO₂ capture from coal fired power stations with enzymes* aims to demonstrate the utility of enzymes for reducing the capital and/or energy costs of postcombustion capture.

The effective start date for the project was 15th June 2012 and the third milestone report was due five months after the start date (15th Nov 2012). This report addresses the third milestone.

Relevant Project Outcome

1. Pathways that would lead to either: a 30% overall cost reduction of post-combustion CO₂ capture, or 30% overall reduction in the benchmark energy requirements of postcombustion CO₂ capture in the first year.

Third Milestone Statement

Report that describes pathways that would lead to either:

- a 30% overall cost reduction of post-combustion CO₂ capture, or
- a 30% overall reduction in the benchmark energy requirements of postcombustion CO₂ capture, and addresses the requirements of cl 1.3 Tasks to achieve outcome 1

Clause 1.3 Tasks to achieve the relevant Project Outcome 1.

- a. Using bubble reactors, screen up to 7 high concentration ion-immobilised enzyme combinations for CO₂ absorption from mixed gas streams for rates that exceed an MEA benchmark. Ions selected with the following characteristics compared with MEA:
 - i. significantly lower volatility but low molecular weight and
 - ii. Lower corrosivity and
 - iii. Greater thermo- and metal ion stability
 - iv. Faster biodegradation
e.g. potassium salts of glycinate, threonate, alanate and 2-methylalanate; piperazine; imidazole; 2-piperidineethanol.
- b. Test the best 3 candidate ion-enzyme mixtures in a wetted wall apparatus at variable enzyme concentrations to achieve increased CO₂ absorption compared to MEA benchmark at realistic CO₂ loadings.
- c. Using NMR, ion chromatography or FT-IR analysis, determine the species formed in loaded solutions from 3 ion-enzyme mixtures; measure or quote literature sources to show energy requirements for regeneration of the ions.
- d. Prepare report to be assessed by John Burgess (or other nominated specialist) describing enhanced CO₂ absorption rates or lower energy of regeneration that will demonstrate the pathways to capital cost or regeneration energy reductions, using enzymes compared with benchmark.

Experimental data given in this milestone has been drawn from previous research conducted under the APP program, and new research conducted with support of ANLEC R&D Alternatives Program as this provides a broader picture of the application of enzymes and has useful background information. The relevant R&D program is credited in the appropriate area.

3 ANLEC Alternatives and Fundamentals project Milestone 3 report

3.1 Apparatus for measuring gas-liquid mass transfer in application to postcombustion CO₂ capture

To meet Milestone 3 of the ANLEC project plan we planned to screen up to 7 high concentration base-immobilised enzyme combinations in a bubble reactor and determine rates of CO₂ absorption from mixed gas streams, in particular, we were screening for rates greater than that of MEA, our benchmark. The screening work was to be followed by the use of wetted wall apparatus to measure the gas mass transfer kinetics of selected basic solutions with enzymes compared with MEA.

3.1.1 BUBBLE REACTOR

Bubble reactors were used in the initial experiments to measure the CO₂ uptake of 3 M solutions of alkanolamines with and without carbonic anhydrase enzyme (0.26 mg ml⁻¹). The bubble reactor was built from a thick-walled glass vessel and CO₂ (13%) in nitrogen was introduced into the base of the solution through a fine glass frit. The concentration of CO₂ in the gas stream released from the vessel before and after passing through the solution containing bases with and without enzyme was measured by infra-red detector.

Foaming occurred in the 3 M basic solutions both in the presence and absence of enzyme was observed but was of variable quantity for different solutions. In some cases, foam production was exacerbated by the presence of enzymes. Two problems emerged which led us to conclude that this approach was not as useful as expected: basic solution leaked from the gas exit as foam leading to a loss of overall performance and secondly, CO₂ was held up inside the foam which led to an overestimation of the loss of CO₂ from the gas stream. Due to the issues of uncontrollable foam production in the bubble reactor this method was abandoned.

3.1.2 WETTED WALL EXPERIMENTS WITH BASE SOLUTIONS AND ENZYMES

As per the project plan, we attempted to measure the gas mass transfer kinetics of CO₂ into basic solutions containing enzymes using the calibrated wetted wall apparatus at CSIRO Energy Technology in Newcastle. We modified the wetted wall set up to introduce enzyme into the liquid flow and replaced the existing pump with a peristaltic pump. Around 20% of the initial enzyme activity was lost after 60 min circulation via the peristaltic pump.

However, multiple attempts to accurately measure the gas mass transfer of slow reacting amines such as 3 M MDEA (methyldiethanolamine) in the wetted wall apparatus were unsuccessful due to the high variability (>20%) between replicate samples. It was important that we be able to measure gas mass transfer of both slower and faster amines in combination with enzymes so we designed and assessed a new system that would allow for this.

3.1.3 DEVELOPMENT OF A NEW GAS REACTOR

To overcome the issues associated with the measurement approaches in 3.2.2 and 3.2.3, a new laboratory-scale gas reactor based on a gentle spray column was trialled with enzyme-base solutions. The gas reactor was built with a square glass midsection in order to obtain digital images necessary for calculation of

contact surface area of the solvent (Fig 7). At the head of the reactor is a 100 x 100mm 'shower head' with 156 pipette tips (partially shown in Fig 7) to ensure uniformity of droplet size and to prevent streaming of the solvent.

The square moulded end sections were inserted into heated round flanges to which vacuum gas was applied until round shape of the flange was squared off. The ends of the glass flanges were then connected to the square tubing. Both ends of the glass reactor were then ground and secured to machined stainless steel fittings equipped with the groove for a Viton® 'o' ring. To prevent solvent and gas leaks between the reactor and tubing all connections were welded or Swagelok® type fittings used to seal the relevant compartment.

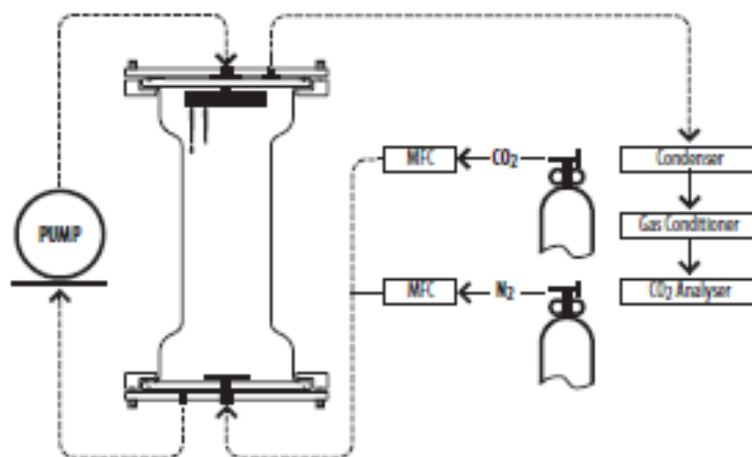


Figure 7. Schematic diagram of the glass gas reactor showing a gas inlet port located in the lower flange and solution circulation via a pump into a 'showerhead' stream delivered from the upper flange.

The gas mixture of 13% CO₂ in 87% N₂ at nominal flow rates at points between 300 – 4000 cm³min⁻¹ were maintained by Brooks® Model 5878 control module with calibrated mass flow controllers 5850E series 0-200 cm³min⁻¹ for CO₂ and 5850TR series 0-500cm³min⁻¹ for N₂. For the higher flow applications, two parallel 5850TR series MFC (0-500ml) were used for CO₂ and two 5850TR series 0-2L for N₂.

Actual flow rate were measured with calibrated Zephyr™ 500HR Digital Gas Flow Meter (Phenomenex, USA) at the point where the gas mixture entered CO₂ analyser.

A flow of 13% CO₂ in N₂ gas mixture at the required (300 to 3150 mL) flow was supplied to the gas reactor by mass flow controllers. The gas mixture entered the bottom of the reactor via a gas diffuser 20 mm above the solution pool and exited the top of reactor. The concentration of CO₂ was measured as it exited the reactor using a Vaisala CARBOCAP® Carbon Dioxide Meter GM70 (Vantaa, Finland) with GMP221 probe and GM70 pump and measuring chamber. Freshly prepared basic solutions (250 cm³) were circulated in the reactor at flow rate of 750 cm³min⁻¹ using a Masterflex® L/S peristaltic pump, drive model 7553-79 and Easy Load II model number 77200-52 pump head.

Digital images were obtained with a Nikon D3x 24.5 Mp camera and the droplet size was measured by ImageJ Processing and Analysis in Java software. A small amount of m-cresol purple dye was added to the solvent to achieve better contrast for droplet size imaging purposes only.



Figure 8. Droplets forming in basic solution pumped through pipette tips attached to the upper flange and falling into the glass gas reactor. High resolution images were used to determine average droplet shape and size.

The system has the advantages of a larger surface area than the wetted wall column and it can be used to reliably measure the CO₂ absorption from slow acting solutions. It is also highly suited for experiments containing enzymes. The gas reactor can be used in two modes:

- Spray mode - where CO₂ absorption occurs both through counter-current contact of gas with droplets and the thin film on the bottom surface of the reactor (Figure 9).
- Film mode – where the spray head is removed and absorption occurs through gas contact with the thin film at the bottom surface. Solution was pumped directly to the pool opposite to solution outlet.

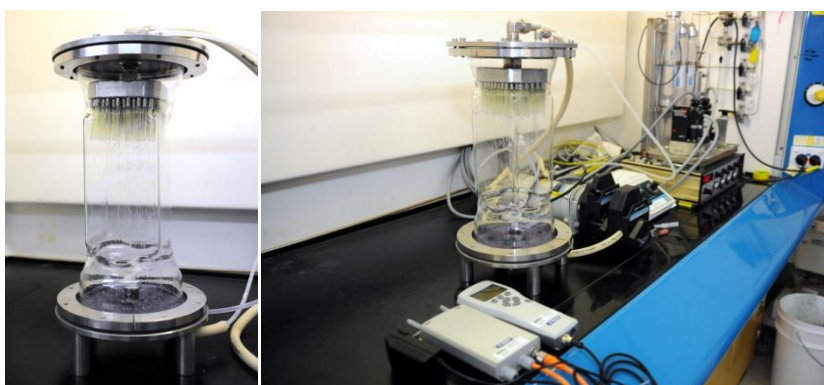


Figure 9: A photograph of the gas reactor (left) in spray mode where droplets fall counter-current to the gas flow (13% CO₂ in N₂) which is introduced at the bottom of the reactor. (Right) Mass flow controllers to control flow and concentration of gases and CO₂ measurement apparatus linked to the gas reactor for detection of CO₂ in the effluent gas stream.

In this system, gas mass transfer can be calculated from the rate of removal of CO₂ having established the droplet average surface area, viscosity and flow rate of droplets for the different solutions, and measured the solution viscosities. To date the following solutions have been tested in the gas reactor with and without enzyme – 3M of the following: AMP, MDEA, MEA, MAE, DMAE, K₂CO₃, and the following amino acid salts – glycine, alanine and methyl alanine over a range of enzyme concentrations.

[MEA - monoethanolamine; K₂CO₃ – potassium carbonate; DMAE - 2-dimethylaminoethanol; MDEA - N-methyldiethanolamine; MAE – 2-(methylamino)ethanol; AMP- 2-amino -2-methyl-1-propanol; BCA II - bovine carbonic anhydrase II.

3.1.4 VISCOSITY MEASUREMENTS

Solution viscosities were measured using a Cambridge Viscosity VISCOLab 4000 piston-style viscometer equipped with accurate temperature sensor; values for both viscosity and temperature are displayed for each measured sample. The instrument was calibrated for three viscosity ranges: 0.5-10 centipose (cP), 5-150 cP and 100-200 cP. Each range has a specific piston calibrated with an upper and lower viscosity range calibration fluids at given temperature range. Typical error was <5% in viscosity range and <0.2°C for temperature.

3.2 CO₂ absorption profiles and gas-liquid mass transfer calculations for bases using the gas reactor

3.2.1 SELECTED BASIC SOLUTIONS

A series of primary, secondary and tertiary alkanolamines (Fig 10) and primary and hindered amino acid salts (Fig 11) were assessed for CO₂ capture in the presence and absence of enzyme. Amino acid salts are generally more biodegradable, have highly stability toward NO_x and SO_x and are more thermostable compared with alkanolamines such as MEA (Eide-Haugmo et al 2011). Due to these attributes we selected amino acid salts as potential basic agents for use in combination with enzymes for CO₂ capture. In addition, potassium carbonate and potassium bicarbonate were also assessed in the system as these basic salts have desirable attributes for CO₂ capture such as tolerance of contaminants and low heat of regeneration, but are also relatively slow acting. The CO₂ absorption profiles and mass transfer rates for the basic solutions are reported in Chapter 3 and the results for solutions containing enzyme with base are given in a separate Commercial-in-Confidence Annex 1 to this report.

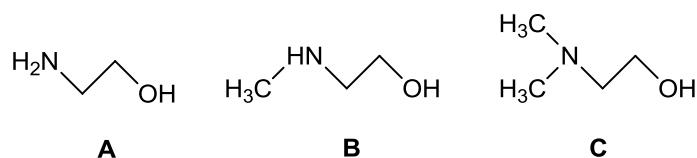


Figure 10. Molecular structures of the alkanolamine series investigated using the gas reactor A. monoethanolamine (MEA) primary and the benchmark solvent for this report B. 2-(methylamino)ethanol (MAE), secondary C. N,N-Dimethylethanolamine (DMAE).

Selected physical characteristics for the alkanolamine series from MEA to DMAE are given in Table 2; of note is the markedly increased vapour pressure of the tertiary alkanolamine.

Table 2. Physical characteristics of selected alkanolamines investigated for CO₂ uptake in the gas reactor.

Abbreviation	Common name	CAS No	BP °C	Vapour pressure (Pa) @ 20°C
MEA	Monoethanolamine	141-43-5	69-70	64
MAE	2-(Methylamino)ethanol	109-83-1	155-157	70
DMAE	2-Dimethylethanolamine	108-01-0	134	816

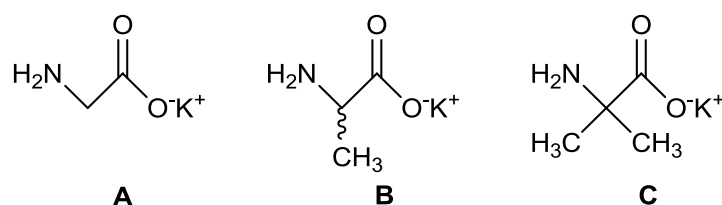


Figure 11. Molecular structures of the amino acid potassium salts series A. glycine - primary B. d/l-alanine – slightly hindered primary and C. 2-methylalanine – hindered primary.

3.2.2 ANTIFOAMING AGENTS

Due to the presence of small to moderate amounts of foam forming on pooled liquid at the bottom of the reactor under high gas flows ($>3100 \text{ mL min}^{-1}$), we investigated the use of anti-foaming agents. As the material would also need to be compatible with enzyme in later studies we sourced an anti-foaming agent used in bioreactors to minimise foaming in our reactor. We selected Antifoam SE-15 (A8582) which is available in a 10% emulsion of active silicone polymer and non-ionic emulsifiers. This antifoam is water-dilutable and effective in both hot and cold systems and used at very low concentrations (200 ppm in our studies).

3.2.3 CO₂ ABSORPTION INTO BASIC SOLUTIONS IN SPRAY REACTOR MODE

The CO₂ uptake from solutions containing slow acting alkanolamines or basic salts such as MDEA and potassium carbonate was observed in the spray reactor operated at relatively low gas flow rates as shown in Figure 12. Potassium bicarbonate solution was tested near the limit of its solubility ($\sim 1 \text{ M}$) and found to have almost no CO₂ absorption activity or capacity. These were useful baseline conditions with which to compare the ability of carbonic anhydrase enzyme to increase the rate of CO₂ capture as shown in Appendix 1.

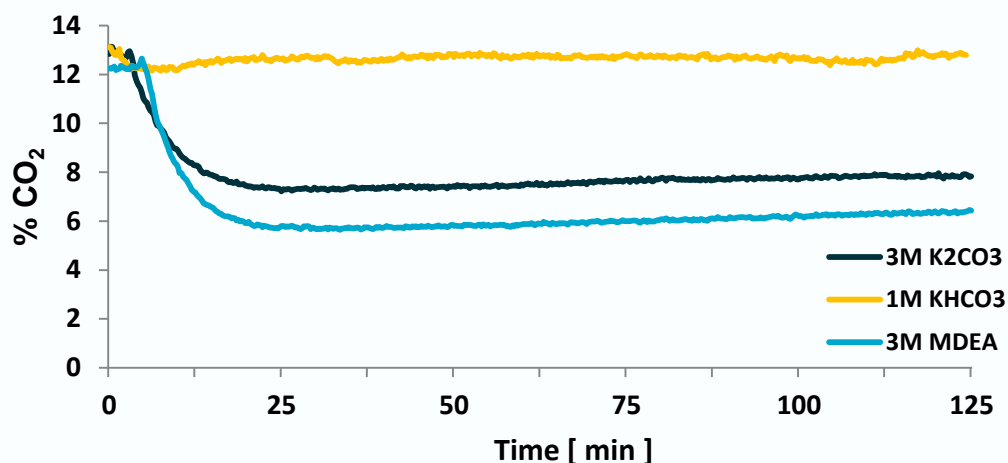


Figure 12. Absorption of CO₂ by slow reacting basic solutions in glass reactor over time operated in spray mode. Inlet gas 13% CO₂ in N₂ at 300ml/min; solution volume 250 ml.

The relationship between gas flow rate and CO₂ flux rate into 3 M AMP using the reactor in the spray mode (Fig 13) suggested that CO₂ flux rate became independent of flow rates at 3.1 L or greater per min. Faster-acting alkanolamines or amino acid salts were also tested in the spray reactor but at much higher gas flow rates as the consumption of CO₂ was much more rapid (Fig 14). Glycine amino acid salt and MAE were rapid acting but their capacity to absorb CO₂ was limited.

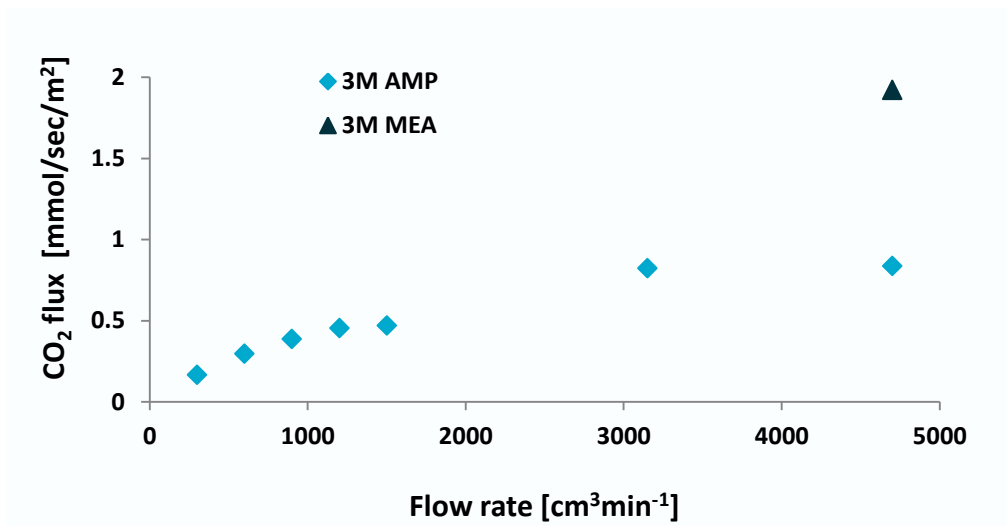


Figure 13. Flux rate of CO₂ into alkanolamine solutions the glass reactor operated in spray mode calculated for a range of gas flow rates. Inlet gas 13% CO₂ in N₂ at 300ml/min; solution volume 250 ml.

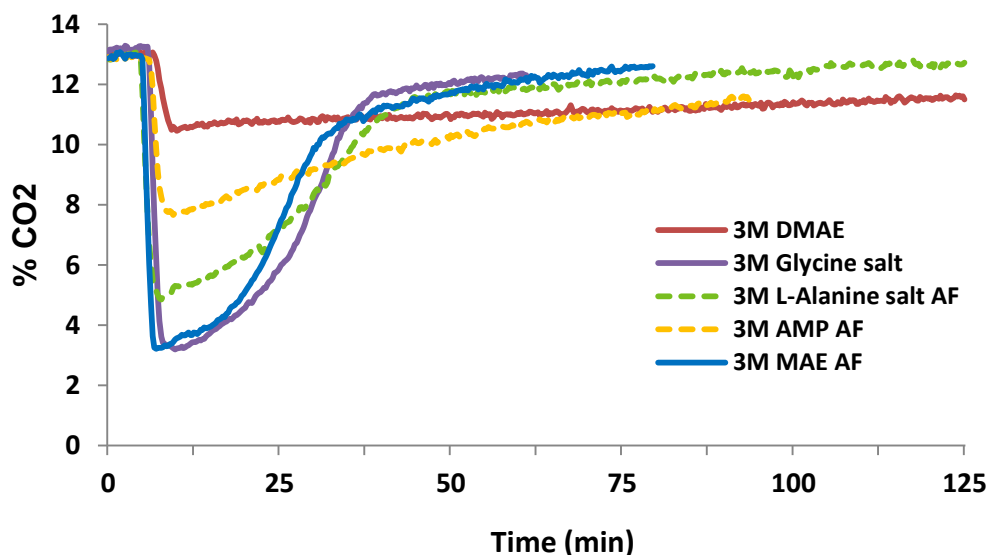


Figure 14. Absorption of CO₂ by moderate to fast acting basic solutions in the glass reactor over time operated in spray mode. Inlet gas 13% CO₂ in N₂ at 3100ml/min; solution volume 250 ml.) AF= anti-foaming agent added.

3.2.4 CO₂ ABSORPTION INTO BASIC SOLUTIONS IN FILM REACTOR MODE

The fast acting alkanolamines and amino acid salts operated in spray mode removed a considerable amount of the CO₂ from the gas mixture under high gas flow conditions as shown in Fig 14. However for the calculation of CO₂ mass transfer rates experiments were conducted at flow-independent gas flows without the use of spray and in the presence of antifoaming agent (200 ppm). The absorption profiles for a range of 3M alkanolamines and amino acid salts at high flow rate without spray are shown in Figure 15.

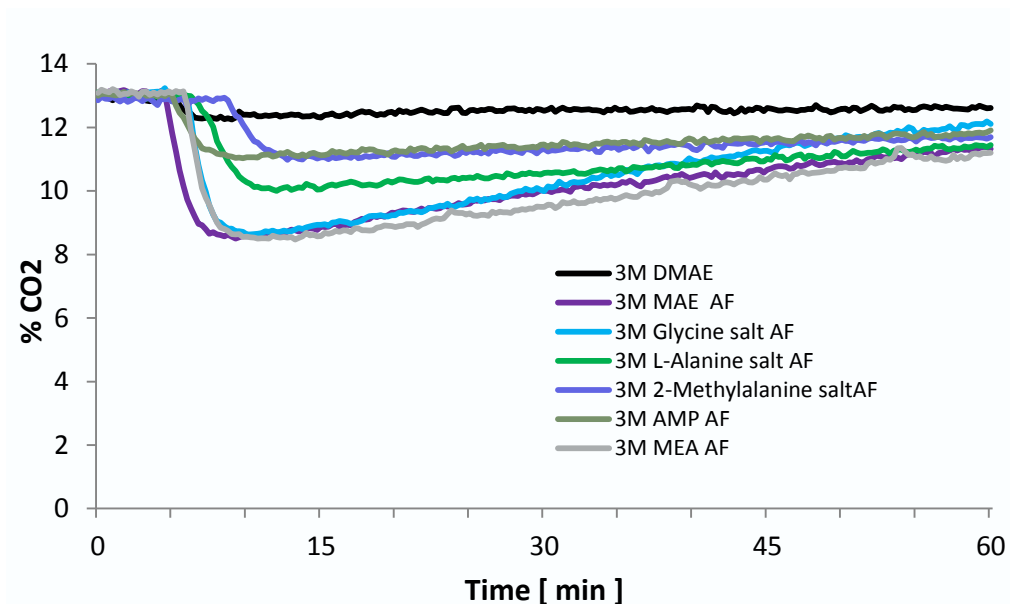


Figure 15. CO₂ absorption profiles of 3 M alkanolamine or amino acid salt solutions in the gas reactor operate in film mode (no spray). Inlet gas 13% CO₂ in N₂ at 3100ml/min; solution volume 250 ml.) AF= anti-foaming agent added.

3.2.5 GAS MASS TRANSFER CALCULATIONS FOR SOLUTIONS IN THE GAS REACTOR

The solution in the reactor was circulated two different ways, via the Spray Mode that provided droplets or Film Mode when solution was pumped directly to the pool opposite to solution outlet. The contact area between the gas and liquid was calculated accordingly. The surface area for the Film Mode was calculated to be 197.26 cm². When the Spray Mode was used the contact area was calculated by adding surface area of the droplets, calculated by digital imaging and ImageJ Processing and Analysis in Java software, typically 315 cm², to the film surface area.

As the CO₂ concentration was measured at the inlet and outlet point of the reactor over the period of time and the absorption of CO₂ (mmol) was known as was the film contact area with gas (m²), therefore the mol CO₂ absorbed by m² of the solvent contact area per unit time (sec) was calculated. The mass transfer coefficient (k_c) is a diffusion rate constant that relates to the mass transfer rate, mass transfer area, and concentration gradient as driving force.

$$k_c = n_A / A \Delta C_A$$

k_c is the mass transfer coefficient [mol/(s·m²)/(mol/m³), or m/s]

n_A is the mass transfer rate [mol/s]

A is the effective mass transfer area [m²]

ΔC_A is the driving force concentration difference [mol/m³].

3.2.6 COMPARISON OF MASS TRANSFER RATES BETWEEN THE GAS REACTOR AND WETTED WALL

As mentioned previously there are few measurements from the wetted wall apparatus of slow reacting alkanolamines and bases particularly for 3 M solutions. However, we were able to compare mass transfer measurements obtained in the gas reactor in Film Mode under flow-independent conditions with some wetted wall measurements from the CSIRO Energy Technology laboratories in Newcastle, and these are shown in Table 3.

The flux rates calculated for the two systems are comparable especially allowing for the different conditions they are tested under, but overall the fluxes from our gas reactor are consistently lower by

about a factor of 2. A probable cause may be the gas-liquid contact area; used in the Film Mode the gas contact area of the reactor is 197.26 cm² and 32.4 cm² for the wetted-wall. The larger surface area means much more CO₂ is absorbed into the solution in a shorter time leading to CO₂ accumulation and a drop in the flux.

Table 3. Comparison of mass transfer rates measured for alkanolamines using the Film Mode of the gas reactor (in the presence of 200 ppm antifoaming agent) with wetted wall apparatus (supplied by G Puxty).

Alkanolamine	Mass transfer Film Mode (mmol m ⁻² sec ⁻¹)	Conditions	Mass transfer Wetted wall (mmol m ⁻² sec ⁻¹)	Conditions
MEA	5.51	3 M, 13 kPa CO ₂	14.4	5 M, 7 kPa CO ₂
DMAE	0.91	3 M, 13 kPa CO ₂	1.3	5 M, 10.9 kPa CO ₂
AMP	2.46	3 M, 13 kPa CO ₂	5.6	3 M, 10.3 kPa CO ₂

4 Future Directions and Planned Research

4.1.1 MEASURED LIFETIMES FOR ENZYMES IN PCC ABSORBERS AND ESTIMATED ENZYME OPERATING COSTS FOR POWER STATION CO₂ CAPTURE

Native bovine carbonic anhydrase has been used to examine the potential enhancement of CO₂ capture from gas streams and while it is a relatively stable and hardy protein, the environment of CO₂ capture from coal fired power station flue gas may involve elevated temperatures, SO_x and NO_x in the gas stream and shear forces as a result of large gas flows. Similarly, enzymes may be combined with amine solvents under very high pH conditions to improve the rate of CO₂ capture. Harsh conditions can denature enzymes; this results in frequent replacement and increases operating costs. However, enzymes with improved robustness for these conditions but maintaining the same high catalytic rate will be a valuable addition to post combustion CO₂ capture.

Our project plan will undertake measured lifetimes for enzyme in PCC absorbers and estimated enzyme operating costs for power station CO₂ capture.

- At time intervals measure activity of immobilised enzymes (native and engineered) constantly exposed to:
 - elevated temperatures (50 - 90°C)
 - aqueous salts from flue gas constituents, especially SO_x and NO_x, chloride
 - concentrated ion solution e.g. 3-5M selected from leading candidates in 1. above
- Calculate effective lifetime of enzyme exposed to expected PCC conditions of temperature, ion and flue gas constituents and extrapolate enzyme operating cost to power station-scale absorber. Prepare report for ANLEC.

4.1.2 DEMONSTRATE LOW CAPITAL COST OR LOW ENERGY CO₂ CAPTURE SYSTEM WITH ENZYMES USING A LABORATORY OR SMALL PILOT-SCALE SYSTEM

- Determine optimal enzyme immobilisation configuration to fit with laboratory/small pilot requirements with respect to existing packed column arrangement and operating pressures.
- Combine immobilised enzyme, concentrated ion solution in a conventional absorber-stripper arrangement and establish:
 - i. rates of CO₂ capture from a mixed gas stream equivalent to that of MEA but using reduced column height, or
 - ii. significantly reduced overall energy requirement which takes into account the regeneration of capture solution (sensible, enthalpy, stripping energy), pumping requirements etc.

4.1.3 ATTRACT A COMMERCIAL PARTNER TO INVEST IN THE FURTHER DEVELOPMENT OF THE TECHNOLOGY WITHIN PROJECT TIMEFRAME

- Leverage industry contacts and interested parties that have expressed an interest in enzyme technology to date for potential investment in expanded laboratory or pilot scale research program
- Prepare prospectus of the technology and intellectual property for examination by potential commercial partners.

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