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Harnessing energy with CO_2 utilisation – a feasibility study

Draft Final Report [Project Number RDE493-29]

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Executive Summary

Carbon capture and utilisation (CCU) is considered as a key technology option in the quest to reduce near term carbon dioxide (CO_2) emissions from a range of major industrial processes including fossil fuel use in power generation. Currently many of the CO_2 reduction and utilisation technologies suffer from high energy requirement. An energy favourable route that can utilise captured CO_2 and produce value added product is of importance. In this project, a feasibility study was carried out on a novel electrochemical CO_2 utilisation method to simultaneously harvest electrical energy and produce a saleable product, bicarbonate soda. Two electrochemical processes were studied. The first process involves electrical energy harvesting by cyclic mixing of CO_2 rich and lean electrolyte solutions in an electrochemical capacitive cell, using porous carbon composite electrodes. In the second method electrical energy is generated through the CO_2 utilisation reaction process. These electrochemical processes utilised industrial wastes such as CO_2, sodium-ion (Na^+) rich mine wastewater brine and alkaline flyash as feedstocks, enabling their use in a circular way.

The specific objectives of this feasibility project were;

- To develop a life cycle assessment (LCA) to provide an estimate of CO_2 emission reduction for the novel electrochemical CO_2 utilisation
- To carry out a techno-economic assessment to evaluate the economic viability of this technology
- To develop a path to commercialisation indicating the stages involved in the development and evaluation of the potential market

This project commenced in January 2019 and has been successfully completed in June 2020 within the allocated project budget. This study involved the initial feasibility assessment for an electrochemical CO_2 utilisation process to simultaneously harvest electrical energy and produce a value-added sodium bicarbonate product. A review of relevant literature in the areas of electrochemical processes, CO_2 utilisation with bicarbonate production and electricity harvesting was carried out. Available information was collected to conduct this feasibility study and no experimental work was involved in this study. Two electrochemical CO_2 utilisation mechanisms, cyclic mixing capacitive cell process and CO_2 utilisation reaction cell process, have been considered in this study. The capacitive cell consists of a pair of porous capacitive carbon composite electrodes covered by ion selective membranes. The CO_2 rich and lean solutions are alternatively passed between the capacitive electrodes. The process is operated cyclically in ionic charge and discharge modes at ambient temperature and pressure to produce electricity and bicarbonate. The electrochemical reaction cell process consists of a pair of platinum catalyst carbon electrodes representing an anode and cathode with distribution plate and current collectors. The electrodes are separated by selective ion transfer membranes. The electrical energy harvest and bicarbonate production mechanism in this process involves chemical reaction and the pH difference established by the amine-CO_2, sodium salt brine and the $Ca(OH)_2$ solutions between the electrodes. In presence of H_2 this pH difference is transformed into a potential difference thereby generating electricity. Process configuration and mass balance were developed, and chemical reactions and activity models were further applied for the capacitive cell and reaction cell CO_2 utilisation to determine the sodium bicarbonate production and energy harvesting potential. Preliminary life cycle assessment and economic evaluation were carried out to assess the feasibility of

these processes. The sodium bicarbonate market and the path to commercialisation for this technology was also assessed.

A theoretical prediction using chemical reactions and activity models applied to the CO_2 electrochemical reaction cell process for two different amines, MEA and AMP/PZ scenarios, showed a sodium bicarbonate yield of 0.11 kmol/s and 0.3 kmol/s respectively and an electricity generation of 2.57 MW and 6.25 MW respectively. For the capacitive cell CO_2 utilisation electrochemical process with carbon composite porous electrodes based on MEA as electrolyte, the sodium bicarbonate yield was 0.11 kmol/s. The maximum theoretical electrical energy harvest with 54% process efficiency was found to be 19.4 MW. The chemical reaction and activity model was not applicable to determine the energy harvest from the capacitive cell process and was determined based on the information from available literature for MEA.[1] To our best knowledge, no information was available in the literature for the capacitive cell process using AMP/PZ.

The electrochemical processes were integrated with post combustion amine based CO_2 capture in a 660 MW coal-fired power station to carry out a preliminary LCA study. From the reference case a CO_2 footprint of 522.91 kg CO_2/t CO_2 processed was calculated for the power station coupled with CO_2 capture. Integration of the electrochemical reaction cell process showed a reduction in the CO_2 footprint of about 6.4 % (489.27 kg CO_2/t CO_2 processed) for the MEA system, and by about 17.8% (429.92 kg CO_2/t CO_2 processed) for the AMP/PZ system. Similarly, integration of the capacitive cell process based on MEA, showed a reduction in CO_2 footprint of about 7.4% with 484.29 kg CO_2/t CO_2 processed. This CO_2 footprint reduction is attributed to the combined effects of electricity recovery from the electrochemical process, CO_2 fixing through its utilisation via sodium bicarbonate formation, and the reduction of capture process regeneration energy duty resulting from the decreased amount of CO_2 for desorption because part of the CO_2 is used for $NaHCO_3$ production. With further modification to the CO_2 rich amine electrolyte composition, for example, changing the ratio of AMP/PZ, the bicarbonate yield and the electricity generation would be further increased, that could have additional scope for further reduction in the overall CO_2 footprint.

Based on the obtained theoretical performance, a preliminary economic evaluation was carried out for the two electrochemical CO_2 utilisation processes, thus revealing their impact on the PCC process integrated with the power plant. The capital cost of the electrochemical capacitance cell was estimated to be AUD 100.1 M and the reaction cell was AUD 91.9 M and AUD 236.8 M for the MEA and AMP/PZ systems respectively. Considering periodic replacement of electrochemical cell components every 6 years, the capital investment for the 30 year period was found to be AUD 149.1 M for the capacitance cell MEA system, and AUD 132.9 M and AUD 340.4 M for the reaction cell MEA and AMP/PZ systems respectively. Among the three cases, the reaction cell using PZ/AMP had the highest capital cost due to its larger sodium bicarbonate throughput and the associated equipment and component costs such as increased catalyst requirements. The electrochemical processes require additional capital investment, fixed and variable operating and maintenance costs, chemical consumption, and other costs. Based on the study conditions used, the revenue from the power production, and more notably from produced sodium bicarbonate was able to compensate for these costs and enable a net positive revenue over the project, with an estimated payback period of 2-3 years.

The levelised cost of electricity and the CO_2 avoided cost from the overall integrated system of the electrochemical cell and the power station with amine-based PCC were calculated. It showed that the

PZ/AMP based CO_2 utilisation reaction cell process was most economically favourable followed by the capacitive cell process as given below:

Parameter	Power plant+ amine-based PCC		Power plant+ MEA-based PCC and capacitive cell process	Power plant+ amine-based PCC and reaction cell process	
	MEA	AMP/PZ		MEA	AMP/PZ
Levelised cost of electricity, AUD/MWh	183.9	174.7	163.4	175.8	150.5
CO_2 avoided cost, AUD/tonne CO_2	109.1	98.5	85.1	99.8	70.8

Due to lack of theoretical models or experimental data to analyse the capacitive cell process, only MEA was considered for this case and at this stage sufficient information is not available to determine if AMP-capacitive cell system would be better than the MEA-capacitive cell system.

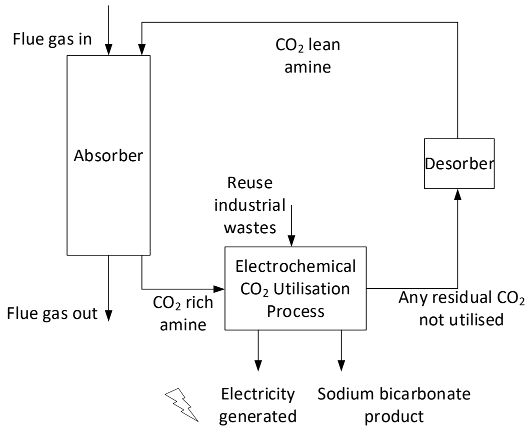
In Australia, the mining industry with suitable partnerships with coal fired power station and CO_2 capture facility could be one of implementation pathway for this electrochemical CO_2 utilisation technology. It is also potentially beneficial as it would also encourage sustainable development of the industry by addressing greenhouse gas mitigation and waste management. Carbon pricing would provide an additional incentive for the industry uptake.

In summary, theoretical analysis and feasibility study found the electrochemical CO_2 utilisation processes, when integrated in a power station with CO_2 capture, to improve CO_2 emission reduction and lower CO_2 mitigation costs when compared to a system without the processes. The sensitivity analysis identified that the capital investment of the electrochemical CO_2 utilisation unit and the sale revenue of $NaHCO_3$ were the two most significant factors influencing the economic performance of the system.

Despite the potential attractiveness of the electrochemical CO_2 utilisation system as estimated through this initial feasibility study, it has been based on the assumption that all bicarbonate (HCO_3) in the rich absorbent reacts to form sodium bicarbonate ($NaHCO_3$). Such key assumptions must be verified through the experimental studies. The technical viability of the capacitive and reaction cell electrochemical processes must be proven through comprehensive lab scale experimentation, as the next step to further develop this technology.

Lay Summary

Carbon capture and utilisation (CCU) is considered as a key technology option in reducing near term CO_2 emissions from a range of major industrial processes including fossil fuel use in power generation. CO_2 utilisation technologies that recycle carbon dioxide as a resource is attracting increasing interest globally. Processes involving synergies of CO_2 utilisation and other industrial wastes as raw material substitutes can produce positive results in CO_2 sequestration, cost effectiveness and environmental benefits. This project introduced a novel low temperature electrochemical method of simultaneously utilising CO_2 with wastewater brine rejects from coal mines to produce a value-added sodium bicarbonate product and harvest electrical energy. Capacitive cell and reaction cell processes were the two electrochemical CO_2 utilisation methods studied. The fundamental principle behind harvesting electrical energy from the two electrochemical processes studied are: in harnessing the mixing energy of two aqueous electrolytes (CO_2 rich and lean amine solutions) through porous carbon composite electrodes, and utilising the CO_2 mineralisation reaction energy in the production of electricity. The capacitive cell consists of a pair of porous capacitive carbon composite electrodes covered by ion selective membranes. The CO_2 rich and lean solutions are alternatively passed between the capacitive electrodes. The process is operated cyclically in ionic charge and discharge modes at ambient temperature and pressure to produce electricity and bicarbonate. The electrochemical reaction cell process consists of a pair of platinum catalyst carbon electrodes representing an anode and cathode with distribution plate and current collectors. The electrodes are separated by selective ion transfer membranes. The electrical energy harvest and bicarbonate production mechanism in this process involves chemical reaction and the pH difference established by the amine-CO_2 and other industrial waste products (sodium salt brine and calcium hydroxide solutions) between the electrodes. In presence of hydrogen this pH difference is transformed into a potential difference thereby generating electricity. CO_2 containing aqueous electrolytes for the electrochemical process are obtained by combining the system with the post-combustion amine-based CO_2 capture unit. As a first step in screening the benefits of this electrochemical CO_2 utilisation option, a feasibility study was carried out to determine if there is an overall net reduction in CO_2 emissions and energy intensity of this process through a preliminary life cycle assessment and techno-economic evaluation. Theoretical analysis found a reduction in overall CO_2 emissions and cost of CO_2 mitigation when the electrochemical CO_2 utilisation units were integrated in a coal-fired power plant with CO_2 capture, compared to an equivalent system without the electrochemical process. The technical viability of electrochemical processes in sodium bicarbonate and electricity production must be proven through further comprehensive lab scale experimentation, as the next step of the technology development.



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Abbreviations	
ACCE	Aspen Capital Cost Estimator®
AEM	Anion exchange membrane
BEC	Bare erected cost
Capex	Capital expenditure
CEM	Cation exchange membrane
CEPCI	Chemical Engineering Plant Cost Index
CCS	Carbon Capture and Storage
CCU	Carbon capture and utilisation
CCUS	Carbon Capture Utilisation and Storage
EPC	Engineering procurement construction
GHG	Greenhouse gas
IEM	Ion exchange membrane
LCA	Life cycle assessment
LCI	Life cycle inventory
LCOE	Levelised cost of electricity
O&M	Operation and maintenance
Opex	Operating expenditure
PCC	Post combustion capture
PPE	Polyphenylene ether
TDC	Total direct cost
TIC	Total investment cost
tpa	tonnes per annum
TPC	Total plant cost
USC	Ultra supercritical coal fired power plant

1 Introduction

1.1 Background

Global energy-related CO_2 emissions amount to about 33.1 Gt CO_2/yr,[2] with fossil fuel use being the primary source of CO_2. Simultaneously, the average annual global energy demand growth rate approximately doubled between 2010-2018. Although the share of coal in primary energy demand and electricity generation is slowly decreasing,[3, 4] coal-fired power stations make up around one third of total energy-related emissions globally.[2]

It is becoming more apparent for the need for substantial emission reduction to mitigate climate change,[5, 6] and several targets and scenarios have been set for critical thresholds of CO_2 in the atmosphere.[7-10] Carbon dioxide capture, utilisation and storage (CCUS) is an essential part of the technology mix to help reduce emissions towards meeting climate targets and the transition to diverse low carbon energy sources.[11] The current total CO_2 capture capacity of the major CCS facilities combined is about 40 MtCO_2/yr.[12] Post combustion capture technologies can be retrofitted to existing fossil fuel power stations without major modifications to the combustion process and have the greatest potential for the reduction of CO_2 emissions in the near term.[13] Capture of CO_2 from power plant flue gas and other industrial processes using absorbent solvents such as monoethanolamine (MEA) are by far the most mature and commonly employed post combustion carbon capture strategies.[14, 15] Similarly, piperazine (PZ) blended with 2-amino-2-methyl-1-propanol (PZ/AMP) has been shown to have advantages such as faster reaction rate, higher CO_2 absorption capacity, and resistance to oxidation and thermal degradation.[16, 17]

Utilisation of CO_2 can also play a significant role in mitigating CO_2 emissions and is being considered as an important option in the context of climate change mitigation.[2, 6, 18, 19] Further, alternate options for the management of captured CO_2 is required due to uncertainties on CO_2 storage as there are significant economies of scale associated with capture and transport of CO_2.[20] Globally about 230 Mt/y of CO_2 is used commercially, largely in the fertiliser industry for urea production and in the oil and gas industry for enhanced oil recovery. At present most commercial applications generally involve direct use of CO_2 without conversion or as physical solvent as a supercritical fluid.[2] CO_2 is a recognised carbon feedstock and another commercialisation pathway is the transformation of CO_2 to chemicals and fuels using chemical and biological conversion processes.[21-26] It is broadly classified into two categories, high energy intensive reaction processes[27] and less energy intensive pathways including reacting CO_2 with minerals or waste streams to form carbonates.[2]

1.2 Literature review

While efforts are directed towards utilising recovered CO_2, technologies that display additional environmental benefits by making use of other industrial waste materials in the CO_2 utilisation process may derive more advantage and contribute to a circular economy. For example, coal-fired power generation and other industrial processes globally generate about two billion tonnes of alkaline residues such as flyash and slag,[28] which can be applied for CO_2 mineralisation and utilisation.[29, 30] CO_2 sequestration potential is studied by substituting carbonated slag or flyash as a cement additive in concrete.[31-33] In a gas-liquid reaction, when CO_2 gas is bubbled through slag or fly ash slurry, the divalent ions such as calcium ions (Ca2+) are leached from the alkaline waste and react with dissolved CO_2 to form calcium carbonate. This further reacts with certain fractions in the concrete forming calcium carboaluminate hydrate, which increases the strength of the cement mortar. Another example is the use of gypsum from the flue gas desulfurisation process in a power plant and CO_2 utilisation to produce marketable products such as calcium carbonate and ammonium sulphate fertiliser.[34, 35] Similarly, global desalination of water produces approximately 140 million m^3/day of waste brine.[36] There are currently very little economical and environmentally safe disposal options for the waste brines produced from the desalination of brackish water, especially for inland locations of greater than 50km from the nearest coastline, which accounts to a smaller yet significant proportion of the volume of approximately 22 million m^3/day brine produced.[36-38] In Australia, over the last 10 years, desalination of extracted brackish water from coal seam gas operations, produced an estimated 9.5 million m^3 of brine waste.[39] Most coal mine operations in Australia are also located inland and do not have the option of ocean disposal, and thus require alternate methods to handle the brine.[40] Recent studies have investigated using waste brine simultaneously with CO_2 utilisation.[41, 42] Inorganic cations in the brine react with CO_2 to produce value-added products like sodium, calcium and magnesium carbonates. While sequestering CO_2, the sodium carbonate (soda ash) obtained from reject brine serves as an important raw material for various industrial applications.[43] Typically, the conventional Solvay process is used to produce sodium bicarbonate and sodium carbonate using ammonia as a catalyst to aid the reaction of CO_2 with sodium chloride, with the ammonia then recovered using lime.[44] This process poses several drawbacks when applied to power plants including, high CO_2 emissions, energy intensiveness, and dealing with volatile ammonia at the temperatures of conventional CO_2 capture processes.[45] A modified Solvay process has recently been applied, replacing volatile ammonia, sodium chloride and limestone, with amines, lime from steel slag, waste desalination brines and utilising CO_2 to produce sodium bicarbonates.[46-49] Such processes involving synergies of CO_2 utilisation and reuse of industrial wastes as raw material substitutes can produce positive results in CO_2 sequestration, costs and for the environment.

The influence of process configurations involving raw materials (such as amine, CO_2, alkaline waste and brine) on the final bicarbonate product formation have been reported in earlier studies.[46, 48] Amines have different absorption capacities of CO_2 and show different bicarbonate yield. Sterically hindered amine and tertiary amines (for example, AMP) have higher affinity towards CO_2 and have shown higher bicarbonate formation than with monoethanolamine (MEA).[50-53] The dominant reaction product of CO_2 with aqueous AMP has found to be bicarbonate. Suggested mechanisms include decomposition of zwitterion to bicarbonate and alkaline hydrolysis of carbamate to bicarbonates, in which hydroxide ions also play an important role. The relative contributions of these pathways and the reaction kinetics will vary depending on the actual experimental process conditions, for example, temperature, pH etc. and the raw material concentrations including the concentration of CO_2. In presence of sodium chloride, the main constituent in the brine, the reaction product is sodium bicarbonate and a lower operating temperature is preferred to increase the precipitation of product with higher purity.[54, 55] Also, pH is a key parameter in this process and an elevated pH increases the solubility of CO_2, saturation of salt and yield of sodium bicarbonate precipitate.[54, 56] Addition of alkaline waste (flyash) to brine solution forms calcium hydroxide ($Ca(OH)_2$), and in presence of amine solution provides a strong basic environment and maintains the pH level to maximise the formation of sodium bicarbonate. Addition of a buffer solution to flyash brine solutions to maintain elevated pH levels increases CO_2 sequestration efficiency and maximises the mineral carbonate precipitate yield.[57]

Studies on harvesting electrical energy through an electrochemical cell with CO_2 mineralisation have been limited. Of particular interest to this study has been applying mechanisms for the extraction of mixing energy from two solutions with different ionic concentrations using a capacitive electrode cell[1, 58, 59] and the conversion of CO_2 mineralisation reaction energy into electricity.[60-62] Carbon dioxide reacting with an aqueous solution of calcium hydroxide and sodium chloride in an electrochemical cell, realised an energy output.[62] The solutions established a pH difference between the cathode and anode when hydrogen (H_2) was introduced, and this difference was transferred into potential difference between two electrodes. The role of H_2 was to promote the electron transfer and there was no stoichiometric net production or consumption of hydrogen in the reaction.[62] In addition to the electricity generation, sodium bicarbonate of 99.4% purity was also produced. Xie et al.[60] used sodium sulphate instead of sodium chloride with improved mass transfer due to its higher chemical potential and showed an increased energy output. On the other hand, Hamelers et al.[1] studied the generation of electricity from the mixing energy of two electrolyte solutions with different CO_2 concentrations, through a pair of porous carbon capacitive electrodes. Porous carbon electrodes with their high surface area have the ability to accumulate ionic charge in the diffuse layer and within their micro porous structure because of the formation of electrical double layers (EDLs).[59] The porous carbon was essential to achieve higher electrochemical performance.[63] When a set of anion- and cation-exchange membranes is placed between the porous carbon electrodes, electrical energy can be produced from the spontaneous ionic current induced by the membrane potential, when solutions of different ionic composition are passed through the cell.[59] The absorption of CO_2 in solution can be increased by using amines as the electrolyte. The higher CO_2 absorption leads to an increase in the concentration of the dissociated ions (protons H^+ and bicarbonate ions HCO_3^-)[64] resulting in the difference in the ion concentrations between the rich and lean solutions, which is harvested as electrical energy. Recently, a similar electrochemical energy harvesting technique, integrating with an ammonia-based CO_2 capture process has been applied, providing overall energy saving in the CO_2 capture process.[65]

1.3 Novel low temperature electrochemical CO_2 utilisation technology

This project introduces a novel low temperature electrochemical CO_2 utilisation process. the process uses amine electrolyte, coal mine water desalination brine rejects and alkaline flyash wastes to simultaneously harvest electrical energy and produce marketable sodium bicarbonate. The raw material components such as CO_2, Na cations and hydroxide are obtained from the waste streams of flue gas, brines and flyash respectively. In the process, amine is used as a CO_2 carrier and not consumed in the reaction. Another approach also utilises the mixing energy of the two solutions along with CO_2 through the porous carbon composite electrodes with very high surface area. In this study, the electrode used for the electrochemical process adopted CSIRO developed carbon composites.[66] These carbon fibre composites have been used earlier as adsorbents for CO_2 capture from flue gas.[66] Given the structural stability, electrical properties and other inherent characteristics of these composites,[67] they can be used as novel capacitive electrodes. The novelty of this electrochemical CO_2 utilisation process lies in the simultaneous sodium bicarbonate production as well as electricity generation utilising CO_2 and other waste streams as raw materials.

As a first step in identifying the benefits of this electrochemical CO_2 utilisation option, a feasibility study was conducted to determine if there is an overall net reduction in CO_2 emissions and the energy intensiveness of this process through a preliminary life cycle assessment and techno-economic evaluation.

1.4 Project description

The aim of this project was to carry out a feasibility study on a novel method of simultaneously utilising CO_2 with wastewater brine rejects from coal mines, while harvesting electrical energy and producing saleable bicarbonate soda. The fundamental principle behind this technology is harnessing the mixing energy of two aqueous electrolytes through porous carbon composite electrodes, as well as utilising the CO_2 mineralisation process to produce a useful carbonate salt. CSIRO developed carbon composites are applied as electrodes in the capacitive cell electrochemical process. Electrical energy is produced when flowing aqueous electrolytes, such as wastewater brine and amine solution flushed with CO_2 (for example, from combustion flue gas), through an ion selective porous carbon electrode through the electrochemical reaction cell process. Mixing amine-CO_2 solution and sodium salt brine (for example, from coal mining wastewater and reverse osmosis brine wastes) also results in the formation of bicarbonate soda that is a usable product. The precipitate by-product formed is settled and filtered and solid bicarbonate obtained under ambient conditions. The conversion of bicarbonate into carbonate is avoided, which occurs at temperature above 50°C.

This feasibility study aims to conduct a LCA system analysis, evaluate the economic viability of the technology and assess its commercialisation pathway. The specific objectives of this project are to:

- Develop a greenhouse gas LCA to provide an estimate of CO_2 emission reduction through this novel electrochemical energy harvesting method of CO_2 utilisation in combination with sodium bicarbonate production
- Conduct a techno-economic assessment to evaluate the economic viability of the technology
- Develop a path to commercialisation indicating the stages involved in the development, and evaluation of the potential market

1.5 Milestone progress

This project had four key project milestones as shown in the Table 1. The main milestones were to determine the LCA for the electrochemical processes with CO_2 utilisation, carryout an economic assessment, develop a path to commercialisation and preparation of the project final report.

Technology review on electrochemical processes and CO_2 utilisation with bicarbonate production has been carried out through available literature. Electrochemical process configurations and the reaction mechanisms for CO_2 utilisation, energy harvesting, and bicarbonate production have been identified. We determined the CO_2 utilisation and bicarbonate production from the stoichiometric reaction and calculated the theoretical electrical energy harvested from the Standard Gibbs energy for the reaction. A further analysis of this electrochemical CO_2 utilisation process was carried out by applying the chemical reactions and activity model. Once the electricity production and bicarbonate production amounts were determined, electrochemical reactor size was calculated.

Preliminary LCA evaluation was carried out after defining the boundary for the electrochemical processes. Life cycle inventory (LCI) data tables have been developed based on the flowsheet data, mass and energy balances. The preliminary Greenhouse Gas (GHG) footprint per tonne of CO_2 utilised for the electrochemical processes have been evaluated. Cost estimation and potential commercialisation pathway was introduced. Table 1 provides a summary of the project status.

Table 1 Summary of project status

Milestone ID	Milestone Title	Status	Relevance to project and achievement	
1	Life cycle assessment (LCA)	100%	Carried out a greenhouse gas life cycle assessment (LCA) for the electrochemical process with CO_2 utilisation.	This milestone estimated of CO_2 emission reduction through this novel electrochemical energy harvesting method of CO_2 utilisation. The electrochemical process showed a reduction in the CO_2 footprint of about 6.4-7.4% for MEA absorbent and about 17.8% for the AMP/PZ system, when integrated with a power station coupled with CO_2 capture. This CO_2 footprint reduction is attributed to the combined effects of electricity recovery from the electrochemical process, CO_2 fixing through its utilisation with the sodium bicarbonate formation, and the reduction of capture process regeneration energy duty resulting from the decreased amount of CO_2 for desorption because part of the CO_2 is used for sodium bicarbonate production.
2	Economic evaluation	100%	Economic assessment of this technology carried out	This milestone carried out a preliminary techno-economic assessment to evaluate the economic viability of this technology. The economic performance of the power station and amine-based capture plant integrated with electrochemical cell with CO_2 utilisation showed a significant reduction in CO_2 avoided cost compared to the power station and capture plant without the electrochemical utilisation system. The cost was decreased from AU$ 109.1 to AU$ 85.1 /tonne CO_2 for the capacitive cell, and from AU$ 98.5 to AU$ 70.8 /tonne CO_2 for the electrochemical reaction cell when using PZ/AMP. This cost reduction is attributed to the electrochemical CO_2 utilisation process that produces power and turns the CO_2 into a valuable product. Of the three electrochemical systems, the PZ/AMP based reaction cell is more favourable for electrochemical CO_2 utilisation, resulting from its high content of bicarbonate species and high sale revenue from the sodium bicarbonate product. The levelised cost of electricity and the CO_2 avoided cost from the overall integrated system of the electrochemical cell and the power station with amine-based PCC

			showed that the PZ/AMP based CO_2 utilisation reaction cell process was most economically favourable followed by the capacitive cell process.
3	Path to commercialisation	100%	Market size of bicarbonate product and path to commercialisation investigated. End user application areas for this product and the market producers in Australia and overseas were studied, showing a growing market demand for sodium bicarbonate. Technology development stages were described. An early business case would involve both energy and mining industries to play an important role for the development of this novel electrochemical CO_2 utilisation technology. Some of the key challenges for the development of this technology were also analysed.
4	Management and reporting	100%	Five quarterly reports prepared and submitted to CINSW. Final report completed and submitted

2 Technology Description

Two process configurations for the electrochemical CO_2 utilisation and energy harvesting, namely the capacitive cell and the reaction cell (Figure 1 and Figure 2 respectively), are evaluated in this study.

2.1 Capacitive cell process

Energy harvesting from the capacitive cell mode is due to the cyclic flow of solutions of different ionic composition (CO_2 rich solution and water or amine solution) between a set of porous carbon electrodes with anion- and cation-exchange membranes. The capacitive cell consists of a pair of capacitive carbon composite electrodes with high pore surface area of about 1061–1312 m^2/g.[66, 67] The anode and cathode electrodes are covered by anion-exchange and cation exchange membranes (AEM/CEM) respectively. A sketch of the electrochemical capacitive cell configuration is shown in Figure 1.

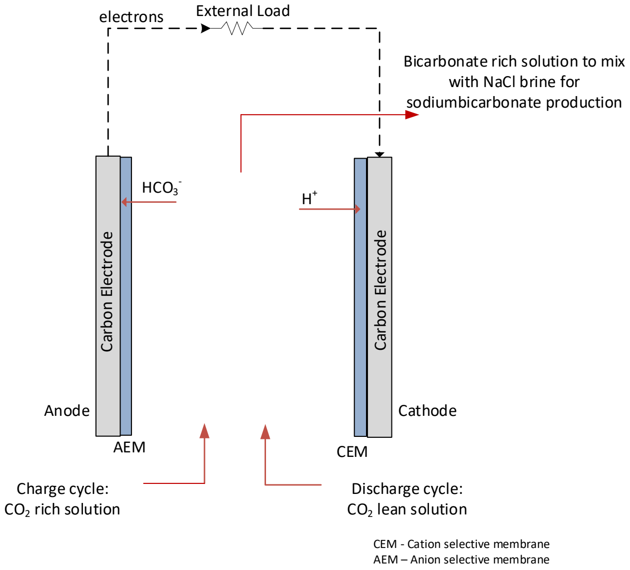


Figure 1 Schematic of capacitive cell for energy harvesting and CO_2 utilisation

The CO_2 rich and lean solutions are alternated between the two ion-exchange membranes. These two steps together constitute one cycle. The capacitive process operates at ambient temperature and pressure. Stowe et al.[50] indicate that bicarbonate formation would be kinetically more favorable than the carbamate formation for sterically hindered amines such as amino methyl propanol (AMP) compared to primary amine like MEA.

The porous carbon electrodes acting as capacitive electrodes accumulate ionic charge within their porous structure forming an electrical double layer.[59] The cell is operated cyclically in charging and discharging operation, alternating respectively with CO_2 rich amine/water solution and CO_2 lean water/amine solution. For a CO_2 rich solution, the predomiant ions formed are bicarbonate and protons. These ions accumulate onto the anode and cathode electrodes respectively resulting in potential which is able to produce electricity by connecting the two elctrodes. As the electrodes keep accumulating the ionic charge, the electrical potential in the cell gradually decreases after a certain period. When the current has diminished, the system is switched to the discharging step where the CO_2 lean solution is fed to the system and the ionic flux and membrane potential is now reversed with the porous electrodes releasing the accumulated ions. Electron tranfer direction is now reversed and the electrical current is again produced. The charging and discharging cycles are alternated. Herein, the charging and discharging cycles are used to refer to the operation of the cell using CO_2 concentrated or CO_2 diluted solutions respectively.

In the capacitive cell configuration, the bicarbonate ions precipitation is carried out in a separate reactor after the electrochemical energy harvesting process. The aqueous solution with bicarbonate ions discharged from the cell is reacted with the sodium chloride brine to form sodium bicarbonate brine, which is precipitated and then filtered using a filter press.

2.2 Reaction cell process

The second electrochemical operation mode involves the reaction cell where the energy harvest mechanism is from the pH difference established by the solutions between the cathode and anode. In presence of H_2 this pH difference is transformed into a potential difference thereby generating electricity (equation 1).[62] The pH difference can be manipulated by changing concentrations of the raw materials, including CO_2 concentration in the amine, resulting in different pH values in the cathode side. This implies that the higher the concentration of the CO_2, the higher the power density that could be achieved.[62]

$$E_{cell} = 0.0591(pH_{anode} - pH_{cathode}) \qquad (1)$$

The electrochemical reaction cell constitutes a pair of platinum catalyst carbon electrodes representing an anode and cathode with distribution plate and current collectors. The electrodes are separated by selective ion transfer membranes AEM and CEM. The schematics of the electrochemical process configurations is shown in Figure 2.

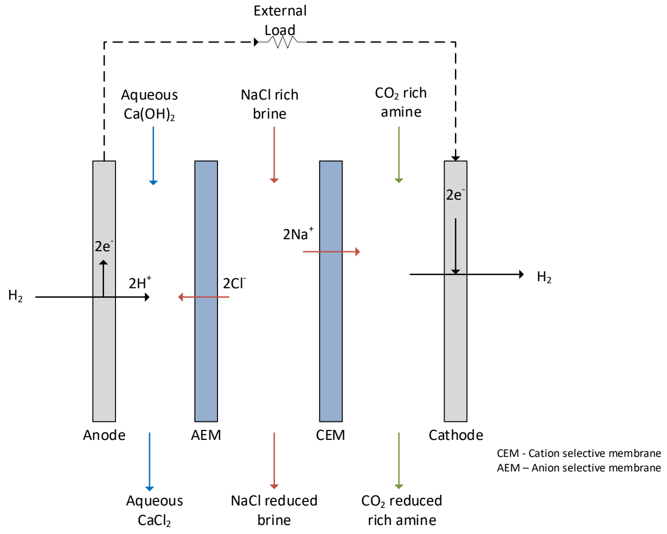


Figure 2 Schematic of electrochemical reaction cell for energy harvesting and CO_2 utilisation

CO_2 rich amine is passed on the cathode side and Na^+ containing brine flows between the AEM and CEM. The aqueous CO_2 partially dissociates into HCO_3^- and H^+. Then, two electrons are accepted by two H^+ to evolve H_2 at the cathode and HCO_3^- combines with Na^+ permeating through the CEM. Waste salt brine from coal mines, rich in NaCl or Na_2SO_4, can be utilised. The reaction at the cathode is given in equation 2.

Cathode reaction

$$2R_3NH^+ + 2HCO_3^- + 2Na^+ + 2e \rightarrow 2R_3N + 2NaHCO_3 + H_2 \qquad (2)$$

Where R_3N represents the amine, and R_3NH^+ the protonated amine. The H_2 produced in the cathode is recirculated to the anode side, where, hydrogen loses two electrons and H^+ is formed, which react with $Ca(OH)_2$ to produce H_2O, and Ca^{2+}. The anode side reaction can be written as in equation 3.

Anode reaction

$$H_2 + Ca(OH)_2 + 2Cl^- \rightarrow CaCl_2 + 2H_2O + 2e \qquad (3)$$

The Cl^- or SO_4^{2-} permeating through the AEM combines with Ca^{2+} to form calcium chloride or calcium sulphate. By electrically connecting the cathode and anode, an electrical current is produced in the cell and the overall reaction can be written as follows (equation 4):

Overall reaction

$$2NaCl + Ca(OH)_2 + 2R_3NH^+ + 2HCO_3^- \rightarrow CaCl_2 + 2R_3N + 2NaHCO_3 + 2H_2O \qquad (4)$$

The amine-CO_2, brine and the $Ca(OH)_2$ solutions establish a pH difference between the cathode and anode and, in presence of H_2, this pH difference is transformed into a potential difference generating electricity. The role of H_2 is to promote electron transfer and it is not consumed in the process.[62] The pH difference can also be manipulated by changing CO_2 concentration in the amine resulting in different pH values in the cathode side. The electrochemical reaction on both electrodes requires catalysts to proceed. The bicarbonate formed can be precipitated separately from the electrochemical cell in the settling tank and filtered using a filter press to recover the value-added bicarbonate. This electrochemical reaction pathway allows stable generation of electricity and formation of sodium bicarbonate.[61, 62]

2.3 Process configurations

Two different amine solutions, MEA and sterically hindered AMP, are considered for the electrochemical processes. Sterically hindered amine, AMP, provides higher CO_2 absorption capacity and higher bicarbonate precipitate yield compared to primary amines such as MEA.[48, 52, 68] This is because tertiary and hindered amines form a greater proportion of bicarbonate (HCO_3^-) on absorption of CO_2 compared to primary and secondary amines. Hindered and tertiary amines have much lower CO_2 mass transfer coefficients, which results in large absorbers being required in a CO_2 capture plant. Adding rate promoters (for example, PZ) to hindered and tertiary amines is often proposed as a result. An AMP/PZ mix is found to have kinetics comparable to an MEA based process, but lower regeneration energy requirements.[68]

The CO_2 capture plant conditions were taken from a process simulated for a 660 MW ultra-supercritical coal fired power plant (USC).[68-70] As a first estimation, the bicarbonate present in the rich amine solutions is assumed to fully react with Na^+ ions provided by the brine solution. This assumption must be verified through experimentation. Similarly, the reaction rate must also be experimentally verified. If the reaction of bicarbonate with Na+ is too low or has a slow reaction rate, it would affect the process economics. The input conditions used for the CO_2 rich stream from the absorber of the CO_2 capture plant are provided in Appendix 1. A typical CO_2 absorption plant with MEA solution (90% capture) and AMP/PZ solutions were considered to compare the bicarbonate production.

The electrochemical capacitive cell configuration can be operated as a standalone unit utilising the high concentration CO_2, for example from a carbon capture plant or integrated with the amine- based CO_2 capture plant (Figure 3). Another potential location for integration of the capacitive cell process with the CO_2 capture plant is to utilise the CO_2 saturated stripping column condensate (Appendix 1). The condensate return stream from the stripping column is saturated with CO_2 content and can be used as CO_2 rich solution during the charging process. However, this scenario is not modelled in this study.

For the electrochemical reaction cell configuration, the CO_2-rich amine stream from the absorber can be used as the catholyte in the electrochemical process (Figure 3). The condensate returning from the stripping column that is rich in CO_2 content can also be used as the catholyte solution.

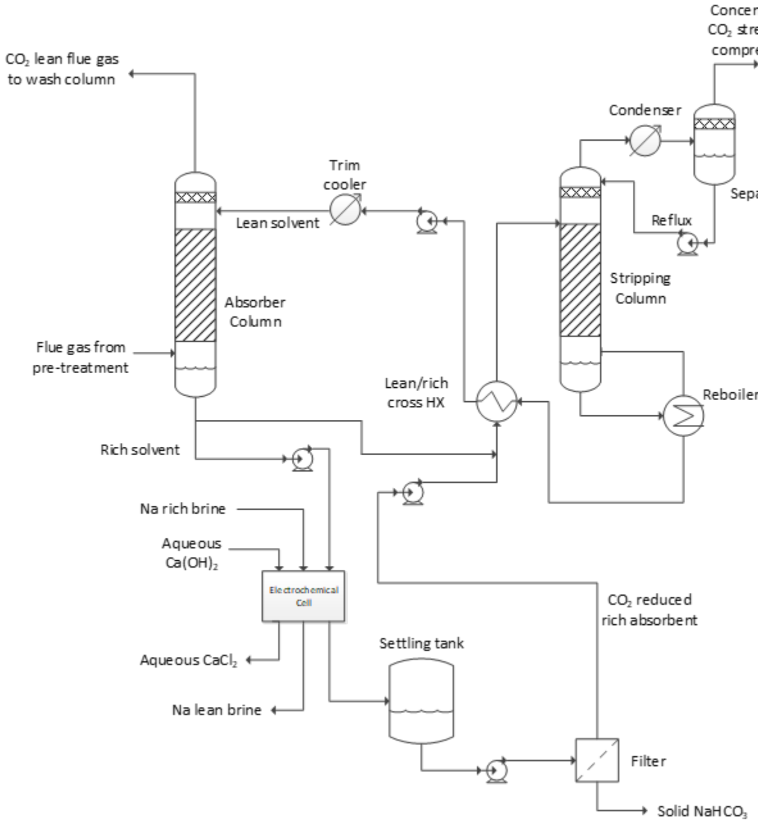


Figure 3 Schematic of CO_2 capture and regeneration with the electrochemical cell applied to CO_2 rich stream

A mass balance was carried out for the process integrating the electrochemical reaction cell into the CO_2 capture plant using both MEA and AMP/PZ as the CO_2 capture absorbents and is given in Appendix 1. The initial mass balance estimation using ProTreat model gave the sodium bicarbonate production for MEA and AMP/PZ processes to be 0.08 (24.2 tonnes/h) and 0.14 kmol/s (42.3 tonnes/h) respectively. The sodium bicarbonate production with the hindered amine AMP/PZ solvent was higher compared to the primary amine MEA solution due to the higher HCO_3^- available to react in the hindered amine absorbent. Then a chemical reaction and activity model was further applied to verify the bicarbonate production and electricity harvest in the electrochemical reaction cell process.

2.4 Chemical reactions and activity model

The electrochemical CO_2 utilisation reaction cell process was further evaluated using the chemical reactions and activity model applied to CO_2-amine-water mixes as described by Puxty and Maeder.[71] For the given CO_2 loading and amine concentration, the variation in solution pH, bicarbonate production and cell voltage were determined for two different amine solutions, MEA and PZ/AMP, during their reaction in the electrochemical cell.

As indicated in Figure 2, $Ca(OH)_2$ is introduced into the anode compartment for neutralising the proton reduced from H_2. $Ca(OH)_2$ has a solubility of 1.4 g/L (0.019 mol/L) in water at 40°C, leading to a constant pH of 12.58 in saturated $Ca(OH)_2$ solution during the anodic process. With respect to cathode compartment, amine solution after CO_2 absorption is introduced where the solution pH is determined by the concentration of amine and CO_2.

2.4.1 MEA system

Table 2 shows the process chemistry of MEA-based CO_2 capture and their equilibrium constants at approximately 40°C where the CO_2 absorption takes place.

Table 2 Chemical reactions in MEA-CO_2-H_2O system together with the equilibrium constants at 40°C

Reaction types	Reactions	Equilibrium constants, $\log_{10}K$	Reference
CO_2-H_2O interaction	$H^+ + OH^- \Leftrightarrow H_2O$	13.53	Edwards et al.[72]
	$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-$	10.22	
	$HCO_3^- + H^+ \Leftrightarrow CO_2 + H_2O$	6.3	
Amine protonation	$MEA + H^+ \Leftrightarrow MEAH^+$	9.03	Puxty and Maeder[71]
Carbamate formation	$MEA + HCO_3^- \Leftrightarrow MEACOO^- + H_2O$	1.7	
Carbamic acid formation	$MEACOO^- + H^+ \Leftrightarrow + MEACOOH$	6.7	

The equilibrium constants of each reaction were determined by equation 5;

$$K_i = \frac{\prod c_{P,i}\gamma_{P,i}}{\prod c_{R,i}\gamma_{R,i}} = K_i^0 \frac{\prod \gamma_{P,i}}{\prod \gamma_{R,i}} \tag{5}$$

where K_i and $K_i^0$are the activity-based and concentration-based equilibrium constants for reaction i; $c_{P,i}$ and $c_{R,i}$ are the concentrations of product species and reactant species involved in the reaction i; $\gamma_{P,i}$ and $\gamma_{R,i}$ represent the activity coefficients of product species and reactant species, respectively, which can be calculated using modified Debye-Hückel activity model (equation 6).

$$lg_{10}\gamma_i = \frac{-z_i^2 A\sqrt{I}}{1+1.5\rho^{-1/2}\sqrt{I}} \tag{6}$$

where z_i is the charge of species $i;$ I is the ionic strength (mol/L); ρ is the density of water (kg/dm^{-3}); A = (1.8248 × 10^6)/(eT)$^{3/2}$ is the Debye–Hückel law slope.

Calculation of these chemical equations was accomplished by the use of chemical model software[73] with the principal of charge balance and mass balance of the MEA-CO_2-H_2O system, including CO_2 balance (equation 7), MEA balance (equation 8), and proton balance (equation 9).

$$[CO_2]_T = [CO_2]_{molecule} + [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] + [MEACOO^-] \tag{7}$$

$$[MEA]_T = [MEA]_{free} + [MEAH^+] + [MEACOO^-] \tag{8}$$

$$[H]_T = [H^+] + [HCO_3^-] + 2[H_2CO_3] + [MEAH^+] - [OH^-] \tag{9}$$

Incorporating the charge balance, the concentration and activity of each species can be determined given the total concentration of MEA and CO_2 loading. Our previous investigation revealed that this chemical model can adequately represent the behaviour and characteristics of MEA-CO_2-H_2O system as demonstrated by the excellent agreement between experimental and calculated data, such as vapour-liquid equilibrium and solution species.[74]

Figure 4 shows the pH change as a function of CO_2 loading with the results derived from the chemical model. ProTreat modelling indicated that 30wt% MEA under coal-fired flue gas condition resulted in a rich CO_2 loading of ~0.48 mol CO_2/mol MEA, leading to a solution pH of 8.43. It should be noted that while the pH of anolyte is assumed to be constant (12.58) due to the saturated $Ca(OH)_2$ solution, the catholyte pH would undergo an increase due to the proton consumption during H_2 evolution. The proton consumption is determined by the concentration of HCO_3^- for $NaHCO_3$ production. Based on charge balance, the amount of proton consumed equals the amount of Na^+ transported into the catholyte. As the electrochemical process utilises CO_2 in the format of sodium bicarbonate, the redox reaction stops when the amount of Na^+ matches the HCO_3^- concentration for a maximised $NaHCO_3$ production. According to the chemical model, 30% MEA solution at 0.48 CO_2 loading has HCO_3^- concentration of 0.12 mol/L, resulting in $NaHCO_3$ production rate of 0.11 kmol/s.

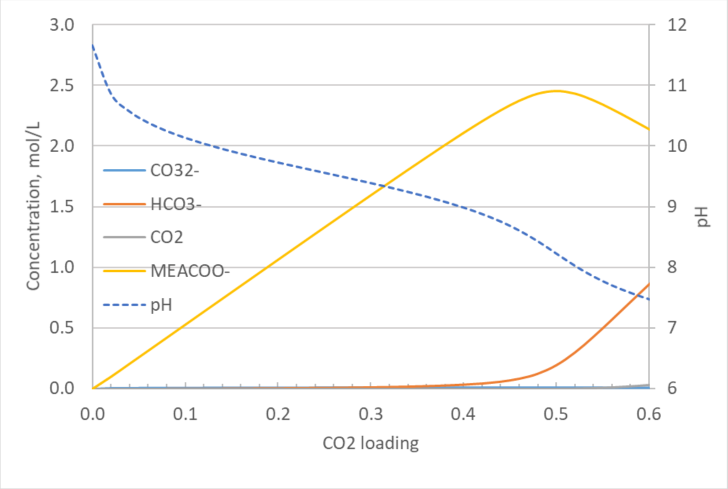


Figure 4 Species concentration and solution pH profile as a function of CO_2 loading in MEA-CO_2-H_2O system

Figure 5 shows the pH profile of anolyte and catholyte during the redox reaction process. Due to the pH buffer property of MEA/$MEAH^+$, the catholyte pH changes marginally from 8.43 to 8.53 during the H_2 evolution process. Coupling with the anolyte pH (12.58), the open-circuit voltage of electrochemical cell is calculated in the range of 0.240-0.245 V according to the equation 1.

The theoretical maximum energy generation was then calculated by (equation 10)

$$\Delta G = -ZFE \qquad (10)$$

Where Z is the number of electrons, 0.11 kmol/s determined by the HCO_3^- concentration; F is the Faraday constant, 96485 C/mol; E is the open circuit potential difference during the cell reaction. Assuming an average cell voltage of 0.242 V, this leads to the power output of 2.57 MW in the electrochemical CO_2 utilisation. In this study, all the bicarbonate present in the rich amine solutions is assumed to react with Na+ ions provided by the brine solution. This assumption must be verified through experimentation. If less bicarbonate is reacting, Z will be lower, leading to less electrical output.

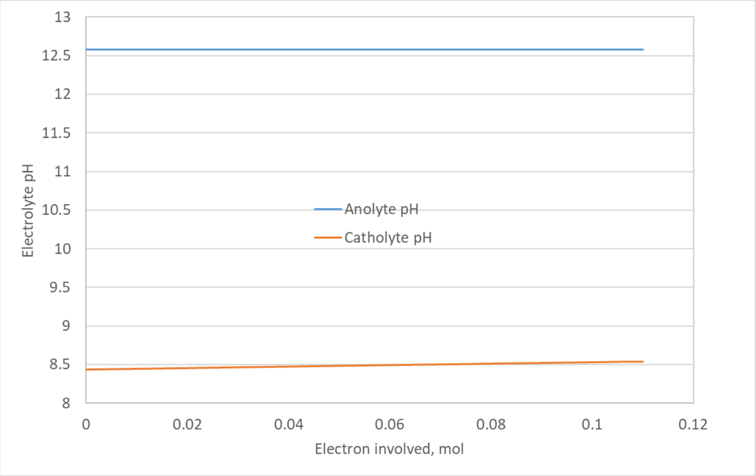


Figure 5 Solution pH profile of anolyte and catholyte as a function of electron involved in the redox process

2.4.2 PZ/AMP system

Similarly, the cell voltage was calculated by determining the pH of PZ/AMP solution after CO_2 absorption. ProTreat modelling indicated that 1.5M PZ/3M AMP has a CO_2 loading of 0.61 mol CO_2/mol amine and a subsequent pH value of 8.87 (Figure 6) after CO_2 absorption under flue gas conditions from coal-fired power station. Taking into account the H_2 evolution and $NaHCO_3$ production, the average pH of catholyte in the battery discharge process is 9.0 based on the chemical model of PZ-AMP-CO_2-H_2O (reaction chemistry in Table 3) with the results shown in Figure 7. Coupling with the anode, this leads to cell voltage of 0.213 V and a subsequent energy output of 6.25 MW with a $NaHCO_3$ production rate of 0.3 kmol/s.

Table 3 Chemical reactions in PZ-AMP-CO_2-H_2O system together with the equilibrium constants at 40°C

Reaction types	Reactions	Equilibrium constants, $\log_{10}K$	Reference
CO_2-H_2O interaction	$H^+ + OH^- \Leftrightarrow H_2O$	13.53	Edwards et al. [72]
	$CO_3^{2-} + H^+ \Leftrightarrow HCO_3^-$	10.22	
	$HCO_3^- + H^+ \Leftrightarrow CO_2 + H_2O$	6.3	
Amine protonation	$AMP + H^+ \Leftrightarrow AMPH^+$	9.28	Puxty and Maeder [71]
	$PZ + H^+ \Leftrightarrow PZH^+$	9.3	
	$PZCOO^- + H^+ \Leftrightarrow H^+PZCOO^-$	9.2	
Carbamate formation	$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$	1.26	
	$PZCOO^- + HCO_3^- \Leftrightarrow PZ(COO^-)_2{}^- + H_2O$	0.25	

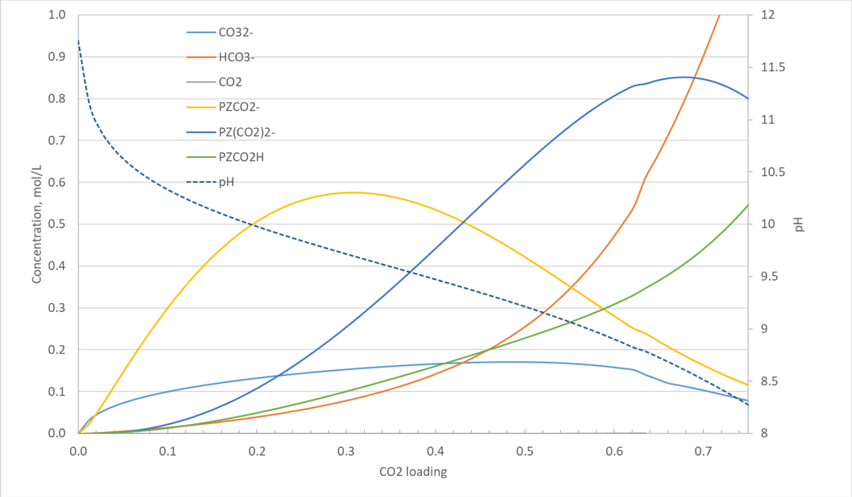


Figure 6 Species concentration and solution pH profile as a function of CO_2 loading in PZ-AMP-CO_2-H_2O system

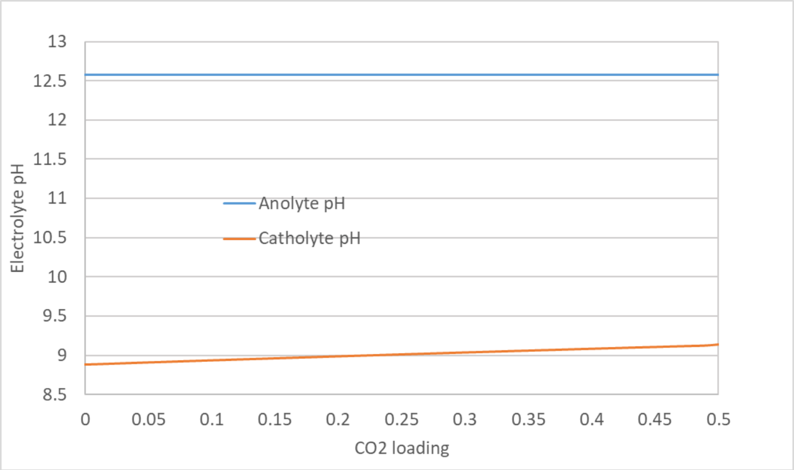


Figure 7 Solution pH profile of anolyte and catholyte as a function of electron involved in the redox process

The re-calculated bicarbonate production rate and the electricity production obtained for electrochemical reaction cell process using MEA and AMP/PZ are given in Table 4.

Table 4 Theoretical electricity production for different amines in the electrochemical reaction cell

Amine type	CO_2 utilisation rate, kmol/s	$NaHCO_3$ production rate, kmol/s (tonnes/h)	Electricity production, MW
MEA	0.11	0.11 (33.27)	2.57
AMP/PZ	0.3	0.3 (90.73)	6.25

For the capacitive cell electrochemical process, cyclic operation of CO_2 rich and lean solutions creates an open circuit potential. The theoretical maximum energy harvest for such a system was reported to be 330 kJ per mol of CO_2 at 20˚C.[1] From this reported estimate, for our given amounts of CO_2 utilisation and sodium bicarbonate production rates of 0.11 kmol/s, the maximum theoretical energy harvest for the carbon composite electrode capacitive cell process with MEA was found to be 19.4 MW. The capacitive cell process efficiency was assumed to be 54%. The capacitive process efficiency of 44% of theoretically expected was reported by Hamelers et al.[1] With the application of carbon composite electrodes instead of using a conventional activated carbon electrode, a further 10% increase in efficiency is assumed. This assumption requires experimental verification. The morphology of the carbon composites has shown to have a structured fibre bonding and greater electrosorption properties. [75]

The electrochemical processes were integrated with the coal-fired power station to carry out a preliminary life cycle assessment (LCA).

3 Life Cycle Assessment of Electrochemical CO_2 Utilisation Process

CO_2 emissions of the electrochemical CO_2 utilisation processes were studied with a LCA methodology to quantify the environmental impacts of the processes based on material and energy inputs and outputs. SimaPro 7.3.3 software[76] was used to undertake this preliminary LCA study.

3.1 System boundary of LCA

The whole life cycle for the proposed process includes coal mining and transportation, a coal fired power station for power generation, amine-based post-combustion CO_2 capture (PCC), electrochemical CO_2 utilisation and CO_2 compression for geological storage. The system boundary for the LCA is shown in Figure 8.

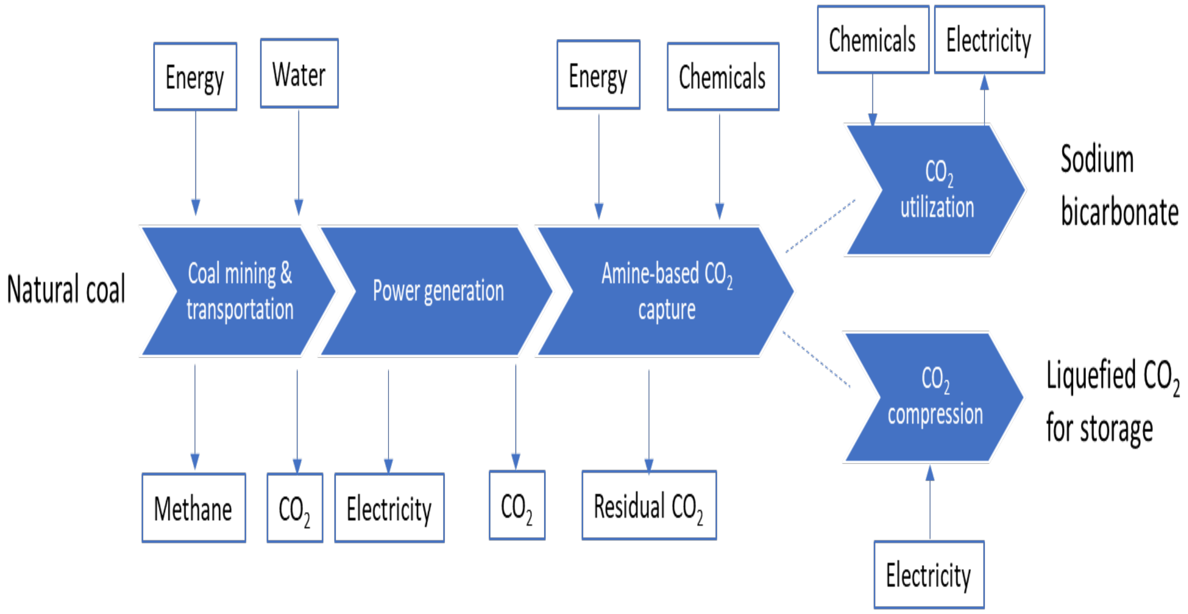


Figure 8 Cradle-to-gate system boundary for the LCA study

The amine-based CO_2 capture is based on a conventional process configuration consisting of a pre-treatment unit, CO_2 absorber and CO_2 desorber. The schematic process flow sheet of amine-based CO_2 capture process is shown in Figure 9. The operating conditions assumed as in previous publication.[77] In this study, only a proportion of the captured CO_2 is being utilised in the electrochemical process for the production of electricity and sodium bicarbonate, and a desorber would still be required. The type of amine used and the process chemistry, influence the CO_2 utilisation and amount of bicarbonate formation. Ability to form bicarbonate for tertiary and hindered amines are greater than the primary and secondary amines, where the tendency to form carbamate is higher.[48, 50] Methods for increasing bicarbonate formation must be studied further through experimentation. This would reduce the dependence on the use of the desorber. Earlier studies have reported the use amine blends, use of promotors or catalysts as some of the approaches to increase CO_2 utilisation and bicarbonate formation.[78, 79]

As such, the system boundary for the proposed LCA study starts from the natural resource – raw coal, and ends with the sodium bicarbonate and liquefied CO_2. Note that the present study does not consider the CO_2 transport and storage after CO_2 compression, this study is therefore considered to be a cradle-to-gate study, although part of the CO_2 produces sodium bicarbonate which will be used later on and release CO_2 again. The present does not consider the subsequent CO_2 emission associated with CO_2 transport and storage and the use of sodium bicarbonate.

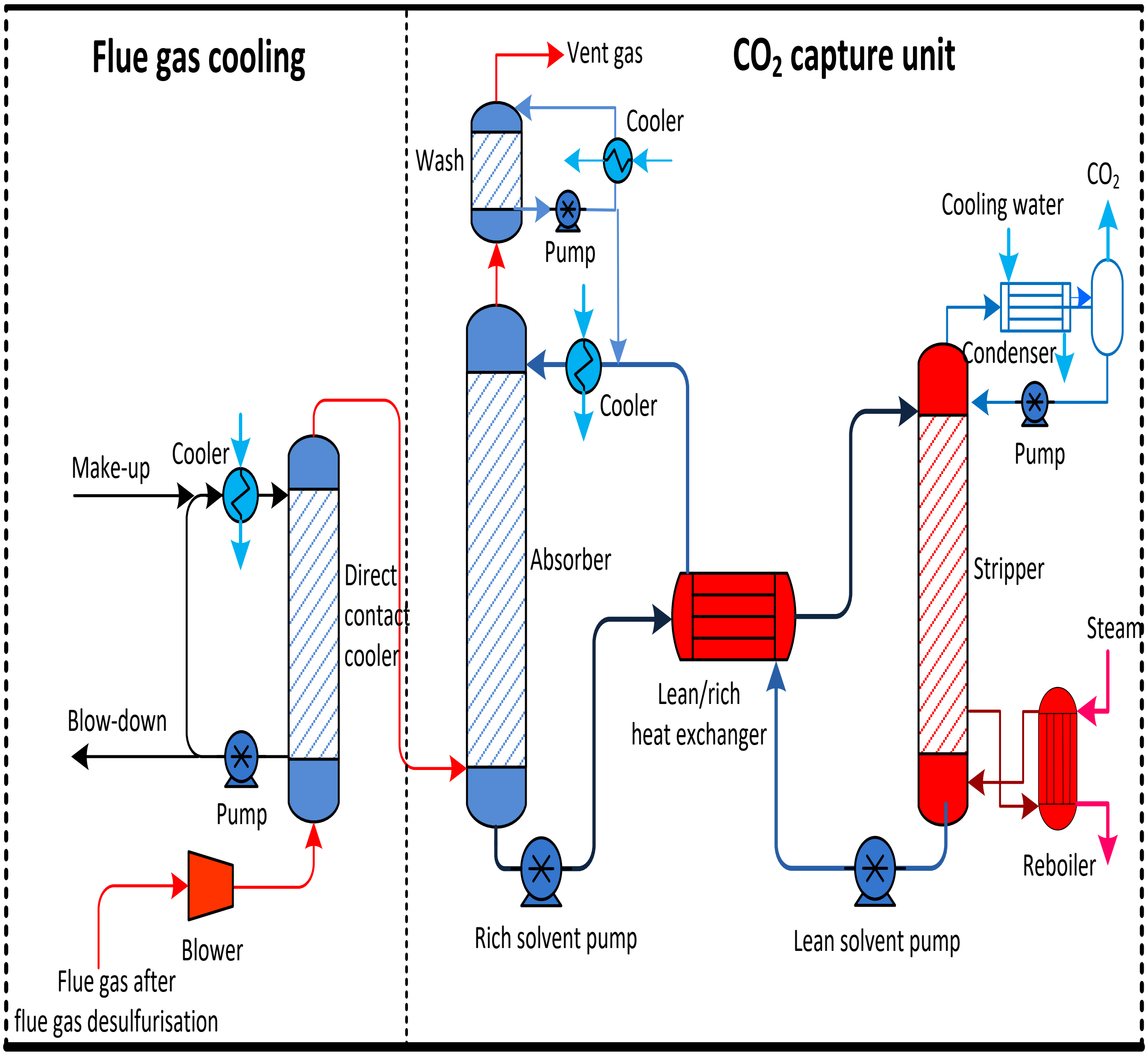


Figure 9 Flow sheet of the conventional aqueous amine-based post-combustion capture process

3.2 Assumptions for LCA study

After determination of the system boundary, an LCA analysis was carried out using mass and energy balances of the whole system. The following assumptions are made for the LCA analysis:

- Reference power-station CO_2 emission factor: 1040 kg CO_2/MWh (SimaPro software for NSW power station)
- The flue gas pre-treatment, CO_2 transport and storage, production process of brine waste, bicarbonate product use are not considered within the boundary of this LCA.
- Average transport distance of raw material inputs, for example, waste brine from coal mine, calcium hydroxide from power plant fly ash etc. and the outputs from the electrochemical process, for example bicarbonate product to utilisation point etc. are taken to be 200 km.
- CO_2 capture efficiency by amine processes: 90%
- Belt-type filter press used for recovery of sodium bicarbonate solids has an energy consumption of 80 kWh/t of bicarbonate product
- Platinum catalyst amount requirement 0.088 mg/cm^2 of electrode[80]
- Pump efficiency 75% with 10m pumping head (all transfer pumps)
- Energy consumption of instrumentation and control system in electrochemical CO_2 utilisation process was assumed to be 10% of total energy input.
- 25% downtime in operation (maintenance)
- The material and unit operation have been based on a 30-year life
- Cell components are replaced every 6 years
- Chemical amine make-up for CO_2 capture process: 1.5 kg/tonne CO_2 processed (0.54 kg CO_2/tonne CO_2 processed)
- CO_2 compression from 2 bar to 150 bar for geological storage

3.3 LCA inventory data

CO_2 emissions from coal-fired power stations are a major contribution to the increase of atmospheric CO_2 concentration. The global warming potential is expressed in kg CO_2/t CO_2 processed in this study. The entire life cycle in the proposed process can be divided into four sections: coal extraction, power generation with CO_2 emission, CO_2 capture and CO_2 utilisation. CSIRO has previously investigated the LCA of coal mining and transportation, coal-fired power generation, amine-based CO_2 capture process,[69] which is used as reference in this study.

The associated life cycle inventory (LCI) data and their CO_2 footprint are shown in Table 5. The total CO_2 footprint for the coal-fired power station coupled with CO_2 capture process is 522.91 kg CO_2/ t CO_2 processed, of which the energy penalty accounts for 71% of the total CO_2 footprint. Energy can be categorised into two groups in the proposed system. The first is the energy demand for CO_2 capture and utilisation, which includes the electricity consumption for pumps, blowers and compressor. It also includes the steam consumption to regenerate the absorbent solution that would normally be used for electricity generation. While this energy consumption does not emit CO_2 directly, the CO_2 emission density per MWh will increase due to the reduced power station output, which contributes to the CO_2 emission in an indirect way. The overall energy consumption for the CO_2 capture process is 359.0 kWh/t CO_2. The second category is the energy harvested from the electrochemical CO_2 utilisation process (not shown in Table 5), which will contribute to the energy efficiency improvement and a subsequent reduction of CO_2 footprint.

Table 5 LCI data for coal mining and transportation, coal-fired power generation, amine-based CO_2 capture process

Item	unit	Value	Note
Coal mining	kg $CO_{2\text{-equivalent}}$ / t CO_2 processed	35.7	CSIRO LCA study[69]
Coal transport	kg $CO_{2\text{-equivalent}}$ / t CO_2 processed	0.37	CSIRO LCA study[69]
CO_2 emission before PCC	kWh/t CO_2 emitted	961	SimaPro software[76]
Pumping for cooling tower in power station	kWh/t CO_2 processed	0.04	CSIRO LCA study[69]
Pumps for amine-based PCC	kWh/t CO_2 processed	4.9	Li et al.[77]
Blowers for amine-based PCC	kWh/t CO_2 processed	30.1	
Regeneration duty (equivalent to electric work) in MEA process	kWh/t CO_2 processed	213.6	
Regeneration duty (equivalent to electric work) in PZ/AMP process*	kWh/t CO_2 processed	213.6	Dash et al.[81]
CO_2 compression duty from 2 bar to 150 bar	kWh/t CO_2 processed	110.4	Li et al.[77]
MEA makeup	kg CO_2/t CO_2 processed	0.54	Based on 0.38 kg CO_2-eq/kg amine
PZ/AMP makeup	kg CO_2/t CO_2 processed	0.54	
Results of CO_2 footprint			
CO_2 emission to air	kg CO_2/t CO_2 processed	111.1	90% CO_2 capture
CO_2 footprint of energy penalty	kg CO_2/t CO_2 processed	373.4	Based on 1040 kg CO_2/MWh
Chemical consumption	kg CO_2/ t CO_2 processed	0.54	
Total CO_2 footprint of PCC coupled power station	kg CO_2/ t CO_2 processed	522.91	

*the energy requirement for the PZ/AMP process in standard absorption-regeneration configuration is assumed to be 3.7 GJ/tonne CO_2 from Dash et al.,[81] which is the same as MEA process[77] for a consistent comparison.

3.3.1 Electrochemical reaction cell

This section examines the impact of the electrochemical CO_2 utilisation process on the CO_2 footprint of the entire process. Table 6 provides the LCI data for the important processes, equipment and chemicals associated with the electrochemical reaction cell process.

Table 6 LCI data for the electrochemical CO_2 utilisation process

Materials	Value	Unit	Notes	Source
Carbon electrode	15.05	kg CO_2-e/kg electrode		[66]
Pt as catalyst	14.5	kg CO_2-e/kg platinum		[76]
Current collector	3.27	kg CO_2-e/kg copper		[76]
PPE end plate	7.79	Kg CO_2-e/kg PPE		[76]
Graphite distribution plate	3.43	Kg CO_2-e/kg graphite		[76]
IEMs (AEM and CEM)	11,925	kg CO_2-e/m^2 membrane		[76]
$Ca(OH)_2$ from flyash	0.095	kg CO_2-e/kg calcium hydroxide	Assuming 20% from flyash including transport up to 200km	[76]
Brine transport from mine	0.11	kg CO_2-e/t km	Transport up to 200km using 20 T truck	[76]
$CaCl_2$ transport	0.11	kg CO_2-e/t km	Transport up to 200km using 20 T truck	[76]
Sodium bicarbonate product transport	0.11	kg CO_2-e/t km	Transport up to 200km using 20 T truck	[76]
Filter press	80	kWh/t solids		[82]

With the determination of LCI data, the CO_2 footprint for the electrochemical CO_2 utilisation process was analysed. Table 7 and Table 8 shows the LCA results of electrochemical reaction cell process for MEA and AMP/PZ cases, respectively.

Table 7 LCA CO_2 footprint for the electrochemical reaction cell process for MEA case

Item	Amount required	Unit	CO_2 footprint (kg CO_2/t CO_2 processed)
Cell components/ important chemicals			
Carbon electrode	8,608.8	kg	4.6326E-05
Pt catalyst	60.6	kg	3.1395E-07
IEMs (AEM and CEM)	30,000	m^2	0.1141
PPE end plate	108,000	kg	0.00027
current collector	538,800	kg	0.00056
Graphite distributor plate	255,000	kg	0.00028
$Ca(OH)_2$	0.055	kmol/s	0.11
Brine transport	0.11	kmol/s (as pure NaCl)	0.16
$CaCl_2$ transport	0.055	kmol/s	0.038
Sodium bicarbonate transport	0.11	kmol/s	0.049
Energy consumption			
Pumps	402	kW	0.0331
Filter press	80	kW/t	0.1588
Instrumentation	10	% of total energy	0.0192
Energy generated			
Electricity production from cell	2.57	MW	-0.7424^a
CO_2 utilisation			
Sodium bicarbonate production	0.11	kmol/s	-28.20^b
Total CO_2 Footprint			-28.26

Note: ^{a}based on 1040 kg CO_2/MWh which is equivalent to 0.2889 kg CO_2/MW;
^{b}based on the processed CO_2 rate of 617.8 tonne/h from 660 MW coal-fired power station.

Table 8 LCA CO_2 footprint for the electrochemical reaction cell process for AMP/PZ case

Item	Amount required	Unit	CO_2 footprint (kg CO_2/t CO_2 processed)
Cell components/ important chemicals			
Carbon electrode	8,608.8	kg	8.4495E-05
Pt catalyst	60.6	kg	5.7305E-07
IEMs (AEM & CEM)	30,000	m^2	0.23331
PPE end plate	108,000	kg	0.00055
current collector	538,800	kg	0.00115
Graphite distributor plate	255,000	kg	0.00057
$Ca(OH)_2$	0.15	kmol/s	0.364
Brine transport	0.3	kmol/s (as pure NaCl)	0.473
$CaCl_2$ transport	0.15	kmol/s	0.0468
Sodium bicarbonate transport	0.3	kmol/s	0.1575
Energy consumption			
Pumps	402	kW	0.0273
Filter press	80	kW/t	0.1588
Instrumentation	10	% of total energy	0.0186
Energy generated			
Electricity production from cell	6.25	MW	-1.8056[a]
CO_2 utilisation			
Sodium bicarbonate production	0.3	kmol/s	-76.92[b]
Total CO_2 footprint			-77.24

Note: [a]based on 1040 kg CO_2/MWh which is equivalent to 0.2889 kg CO_2/MW;
[b]based on the processed CO_2 rate of 617.8 tonne/h from 660 MW coal-fired power station.

It can be seen that the electrochemical CO_2 utilisation process has a positive impact on the CO_2 footprint. While the chemicals and cell components associated with the electrochemical reaction cell process add to the CO_2 footprint onto the process, the power generation from electrochemical process can offset their CO_2 footprint. For instance, in the MEA case the materials used for electrochemical cell has a CO_2 footprint of 0.68 kg CO_2/t CO_2 processed. The power generation from the electrochemical process improves the power plant efficiency, resulting in a negative CO_2 footprint of -0.74 kg CO_2/t CO_2 processed. This compensates for the CO_2 footprint addition caused by the electrochemical cell. The same result applies to PZ/AMP case that has more power output and results in a more negative CO_2 footprint of -1.8 kg CO_2 /t CO_2 processed. More importantly, the electrochemical process utilises CO_2 and turns it into sodium bicarbonate which is considered as a carbon sink in the present study. This results in reduction of CO_2 footprint of -28.20 kg CO_2/t CO_2 processed for the MEA case and -76.92 kg CO_2 /t CO_2 processed for the PZ/AMP case. The power generation and $NaHCO_3$ production contribute to the total negative CO_2 footprint of -28.26 kg CO_2/t CO_2 processed for MEA case and -77.24 kg CO_2/t CO_2 processed for PZ/AMP case. It should be mentioned that the higher impact of the PZ/AMP case is due to its higher concentration of HCO_3^- in the electrolyte, which increases the power production and $NaHCO_3$ production rate, resulting in more reduction of the CO_2 footprint.

3.3.2 Capacitive cell

This section examines the impact of the capacitive cell process on the CO_2 footprint of the entire process. Table 9 shows the CO_2 emission results for the capacitive cell electrochemical process using CO_2 rich solution that is supplied from the MEA process. By cycling CO_2 rich and CO_2 lean solutions, the calculated energy harvest through the capacitive cell process was higher (19.4 MW) compared to the electrochemical reaction cell process (2.57 MW in MEA case and 6.25MW in PZ/AMP case). Although the process itself has CO_2 emissions, the process has a negative emission footprint of -33.25 kg CO_2/t CO_2 processed due to its power generation and CO_2 utilisation.

Table 9 LCA CO_2 footprint for the capacitive cell process for CO_2 supplied from the MEA based capture plant

Item	Amount	Unit	CO_2 footprint (kg CO_2/t CO_2 processed)
Cell components/ important chemicals			
Carbon electrode	39,170	kg	0.00038
IEMs (AEM & CEM)	11,000	m^2	0.08555
PPE End plate	39,600	kg	0.0002
current collector	197,560	kg	0.00042
Graphite distributor plate	93,500	kg	0.00021
Brine transport	0.11	kmol/s(as pure NaCl)	0.16
Sodium bicarbonate transport	0.11	kmol/s	0.058
Energy consumption			
Pumps	726	kW	0.0596
Filter press	80	kW/t	0.1588
Instrumentation	10	% of total energy	0.0218
Energy generated			
Electricity production from cell	19.4	MW	-5.6
CO_2 utilisation			
Sodium bicarbonate production	0.11	kmol/s	-28.20*
Total CO_2 footprint			-33.25

*Assuming that the sodium bicarbonate production rate is the same as the electrochemical reaction cell due to the same solution chemistry in the MEA process

3.4 Life cycle impact assessment

The CO_2 footprint investigation above only considers the electrochemical CO_2 utilisation process (reaction cell and capacitive cell), which leads to a negative emission footprint. If the LCA analysis extends to the whole system, the emission footprint will be more realistic. Table 10 provides the results of CO_2 footprint for the power station integrated with CO_2 capture and electrochemical CO_2 utilisation processes. For the power station coupled with CO_2 capture, the CO_2 footprint is 522.91 kg CO_2/t CO_2 processed. The majority of this total CO_2 emission comes from the energy penalty due to power loss for capture solvent regeneration and CO_2 compression (71%) and the CO_2 emission of the vent gas directly to the air (21.2%). This indicates that reducing the energy requirement of CO_2 capture is critical for a low CO_2 footprint in coal-fired power station.

When the electrochemical CO_2 utilisation is integrated with CO_2 capture process, the total CO_2 footprint is reduced. For example, it is reduced to 489.27 kg CO_2/t CO_2 processed for the MEA-based electrochemical reaction cell, a 6.4% reduction compared to reference scenario. This CO_2 footprint reduction is attributed to the three factors: (i) the power generation from the electrochemical process; (ii) CO_2 utilisation in a format of $NaHCO_3$ product; (iii) the reduction of regeneration energy duty resulting from the decreased amount of CO_2 for desorption because part of CO_2 is used for $NaHCO_3$ production. When the PZ/AMP solvent is used for CO_2 capture and electrochemical CO_2 utilisation process, the CO_2 footprint can be further reduced to 429.92 kg CO_2/t CO_2 processed (17.8% reduction). This is due to the increase of bicarbonate formation in PZ/AMP solution, resulting in the improvement of energy harvesting performance and the increase of $NaHCO_3$ production rate.

As for the scenario of capacitive cell using CO_2 rich solution, the total CO_2 footprint is reduced to 484.29 kg CO_2/t CO_2 processed. This value is slightly less than that of electrochemical reaction process (489.27 kg CO_2/t CO_2 processed) using the MEA solvent, which is attributed to the increased amount of electricity generated from the capacitive cell.

Table 10 Results of CO_2 footprint for different electrochemical CO_2 utilisation cases (unit: kg CO_2/t CO_2 processed)

Items	Power station with CO_2 capture	Power station with CO_2 capture & utilisation			Note
		Electrochemical reaction cell - MEA	electrochemical reaction cell – PZ/AMP	Capacitive cell-MEA	
CO_2 emission to air	111.1	111.1	111.1	111.1	90% capture rate
Coal mining	37.5	37.5	37.5	37.5	CSIRO LCA study
Coal transport	0.37	0.37	0.37	0.37	CSIRO LCA study
Materials makeup	0.54	1.16	1.17	1.18	0.38 kg CO_2-eq/kg amine
Energy penalty of PCC	373.4	367.4	357.0	367.4	1040 t CO_2-eq/MWh
Materials for electrochemical cell	-	0.68	1.48	0.54	
Harvested energy	-	-0.74	-1.8	-5.6	
CO_2 utilisation $NaHCO_3$	-	-28.2	-76.9	-28.2	
Total	522.91	489.27	429.92	484.29	

3.5 Towards a better CO_2 footprint

The assessment of CO_2 footprint identified the three major components that affect the emission footprint: CO_2 emission to air, the energy consumption for the CO_2 capture process and the CO_2 utilisation. The first two add to the CO_2 emission footprint to the whole system whilst the later reduces the emission footprint. One can anticipate that improvement in these three areas would have the large impact in reducing the CO_2 footprint (Figure 10). For instance, if the CO_2 capture rate is increased to 95%, the CO_2 emission footprint to air can be reduced from 111.1 kg CO_2/t CO_2 processed at 90% capture rate to 52.6 kg CO_2/t CO_2 processed. The present LCA is based on conventional amine process with a high reboiler duty of 3.7 GJ/tonne CO_2 for both MEA and PZ/AMP processes. CSIRO's investigation on amine-based CO_2 capture indicates that the process improvement can significantly reduce the regeneration duty, for example, in the MEA process the advanced process configuration of stripper inter-heating and cold rich split decreases the regeneration duty from 3.7 GJ/t CO_2 to 3.1 GJ/t CO_2.[77] This will lead to a CO_2 footprint reduction of 34.6 kg CO_2/t CO_2 processed. In the PZ-based CO_2 capture process, a further reduction to 2.5 GJ/t CO_2 is achievable when using an advanced flash stripper,[83] which would decrease the CO_2 footprint by 69.3 kg CO_2/t CO_2 processed.

Regarding the electrochemical CO_2 utilisation process, the CO_2 footprint can be reduced by maximizing the electricity generation and sodium bicarbonate production rate. As discussed in previous section 2.1-2.4, the energy harvesting and $NaHCO_3$ production are largely dependent on the amount of HCO_3^- in the CO_2-rich solvent. The maximization of HCO_3^- can be achieved by formulating the amine absorbent. For instance, AMP is beneficial for the HCO_3^- formation. A high ratio of AMP to PZ (for example, 3.2M AMP/0.8M PZ) would increase the concentration of HCO_3^- to 1.0 M for coal-fired flue gas conditions. This would lead to an increased electricity generation to 12.6 MW (-3.7 kg CO_2/t CO_2 processed) and $NaHCO_3$ production rate to 0.61 kmol/s (-155.6 kg CO_2/t CO_2 processed), decreasing the total CO_2 footprint to 365.1 CO_2/t CO_2 processed. Combining the benefits from increased CO_2 capture rate and energy efficiency improvement, the total CO_2 footprint has the potential to be reduced as low as 237.3 kg CO_2/t CO_2 processed. Note that the detailed benefits of CO_2 emission reduction from these process improvements should be investigated on a case-by-case basis.

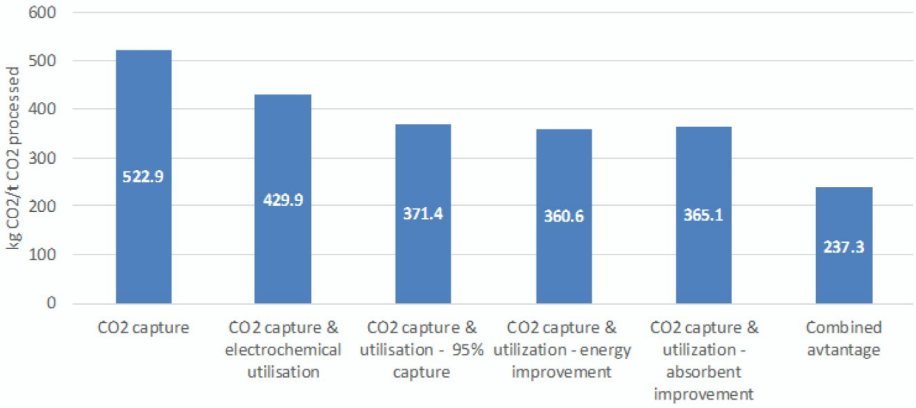


Figure 10 Potential improvement of CO_2 footprint by improving the CO_2 capture rate and capture energy efficiency and electrochemical CO_2 utilisation performance. Base scenario: 90% CO_2 capture using 1.5M PZ/3M AMP with the electrochemical reaction process

4 Preliminary Economic Assessment

4.1 Methodology

Based on the technical performance, a preliminary economic assessment was performed to investigate the impact of electrochemical CO_2 utilisation processes on the overall post-combustion CO_2 capture (PCC) process integrated with a 660MW coal-fired power station. Two amine processes (MEA and PZ/AMP) and two electrochemical CO_2 utilisation processes (electrochemical reaction cell and capacitive cell) are assessed in this study.

4.1.1 Estimation of capital investment

The methodology used for estimating the total capital investment in this economic assessment follows the guideline proposed by United States Department of Energy (US DOE),[84] with the detailed capital costing calculation illustrated in Figure 11. The Aspen Capital Cost Estimator® (ACCE) was employed to calculate the main equipment costs involved in the amine-based CO_2 capture process, such as columns, packings, blowers, cross heat exchangers, pumps, compressors, solvent storage tanks, etc. Previous investigation revealed that equipment costs estimated from the ACCE agree well with the cost results from the detailed DOE economic study for a MEA-based CO_2 capture plant,[77] providing us with the confidence to reliably estimate equipment costs for the PZ/AMP process. The total material cost includes all the equipment in the electrochemical CO_2 utilisation-coupled CO_2 capture plant, and the associated costs for piping, civil engineering, structural steel, instrumentation, electrical wiring, insulation and paint. The process contingency and project contingency are included in cost estimates to compensate the process uncertainties and unknown costs due to a lack of complete project definition and engineering. The percentages used to calculate the total investment cost were under the guidelines of US DOE economic analysis[85] and the Association for the Advancement of Cost Engineers International Recommended Practice,[86] with an expected accuracy of total capital cost of ±30-50%.

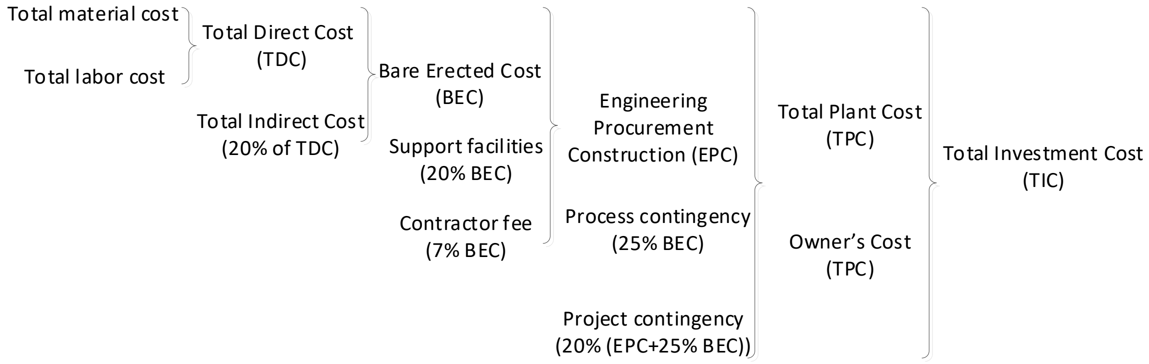


Figure 11 Capital costing methodology for the electrochemical CO_2 utilisation coupled PCC plant (Source: United States Department of Energy)

As the equipment costing derived from ACCE is based on United State (US) conditions, we employed a generic method developed by WorleyParsons and Schlumberger[87] to evaluate the regional economic performance of the proposed processes. The following three steps describe the principles of converting the reference US costs to the Australia-based costings:

1) Calculating capital costs in a reference location (US);

2) Transferring the projects to the Australian location using the regional cost indices and the currency exchange factor;

3) Performing the subsequent economic analysis as regularly based on the requirement of project.

GHD developed various location factors used to convert the capital costs from the reference location, i.e. US to other locations outside US.[88] These conversion indices were utilised to estimate the regional costs of three major cost elements, including equipment, materials and labour. The Australian cost factors for the equipment, materials, labour, currency exchange are provided in Table 11. The Chemical Engineering Plant Cost Index (CEPCI) was used to convert the dollar of past years to 2018 year.

Table 11 Regional cost indices to transfer the project from US to Australia.

Region	Capital, operating and maintenance			Currency exchange [89]
	Equipment	Materials	Labour	
US	1.00	1.00	1.00	1
Australia	1.08	1.08	2.422	1.32

4.1.2 Economic assumptions and cost indexes

Table 12 lists the primary economic assumptions for the assessment of the electrochemical CO_2 utilisation coupled PCC process integrated with the coal-fired power plant. This assumption follows the criteria set out by the IEAGHG for technical and economic assessment of power plants with low CO_2 emissions.[90]

Table 12 Primary economic assumptions of the electrochemical CO_2 utilisation coupled PCC process integrated with the coal-fired power plant

Parameter	Value
Present value	2018 AU dollars
Plant life	30 years
Capital cost	Calculated
Discounted cash flow rate	8%
Construction time	3 years
Fuel cost	$1.8/GJ
Budget allocated in construction year 1, 2, 3	40%, 30% and 30%
Plant capacity factor	85%
Plant capacity factor of first year’s operation	50%
Fixed O&M cost	3.5% of total capital investment
Cooling water	$0.48/m^3 [77]

Demineralised water for solvent	$2.74/m^3
MEA solvent [a]	$1 500/tonne
PZ solvent [b]	$10 000/tonne
AMP solvent [c]	$12 000/tonne
CaO price [d]	$150/tonne
$NaHCO_3$ sale price [e]	$ 300/tonne

Note: [a] MEA price quote from Shandong Baovi Energy Technology Co., Ltd. https://chembh.en.alibaba.com/?spm=a2700.details.cordpanyb.4.1f36360cRdSbrW;

[b] PZ price quote from Jinan Yudong Trading Co., Ltd. https://jnyudong.en.alibaba.com/?spm=a2700.details.cordpanyb.4.66e167a7HRsaqn

[c] AMP price quote from Hangzhou Sartort Biopharma Co., Ltd. https://sartortbiopharma.en.alibaba.com/?spm=a2700.details.cordpanyb.4.585f5d66z6qLA0

[d] CaO price quote from Inner Mongolia Youfang Industrial Co., Ltd. https://nmgyoufang.en.alibaba.com/?spm=a2700.wholesale.cordpanyb.2.411352d87ocJfG

[e] $NaHCO_3$ sale price quote from Tianjin Credit International Co., Ltd. https://credit-chem.en.alibaba.com/?spm=a2700.details.cordpanyb.4.52794e163T8L9F

The economic assessment is conducted based on the calculation of net present value to achieve a breakeven electricity-selling price, termed the levelised cost of electricity (LCOE). This is the minimum price sold to the grid system so that the power plant owner can receive the revenue to cover all capital investments and O&M costs during the plant life. It should be mentioned that the electrochemical CO_2 utilisation process produces elecricity which can be integrated into power plant for sale and also produces $NaHCO_3$ which can be sold in the market. The energy and byproduct benefits are regarded as revenue income, which will be reflected by the decrease of LCOE. The LCOE calculation is shown in equation 11.

$$LCOE = \frac{\sum_t [\frac{(Capital\ Expenditure)_t}{(1+r)^t} + \frac{Fixed\ O\&M_t}{(1+r)^t} + \frac{Variable\ O\&M_t}{(1+r)^t}]}{\sum_t \frac{(Electricity\ and\ sodium\ bicarbonate\ Sold)_t}{(1+r)^t}} \tag{11}$$

where (capital expenditure)$_t$ is the capital cost invested in the construction of power plant with and without PCC in year t, ($); fixed O&M$_t$ is the fixed O&M cost in year t, ($); variable O&M$_t$ is the variable O&M cost in year t, ($); (electricity sold)$_t$ is the produced and sold electricity in year t, (MW); and r is the discounted rate.

The CO_2 avoided cost ($/tonne CO_2) was then calculated to quantify the economic performance of the overal CO_2 capture and utilisation process based on the LCOE and CO_2 emission before and after CO_2 capture and utilisation. Note that the CO_2 emission after PCC considers the utilisation of CO_2 for production of $NaHCO_3$ which is regarded as CO_2 fixing, though it will release CO_2 when $NaHCO_3$ is used. The calculation of CO_2 avoided cost is shown in equation 12.

$$Cost\ of\ CO_2\ avoided = \frac{(LCOE)_{PCC} - (LCOE)_{Ref}}{(CO_2\ emission)_{Ref} - (CO_2\ emission)_{PCC}} \tag{12}$$

where $(LCOE)_{PCC}$ and $(LCOE)_{Ref}$ are the LCOE exported from the power plant with and without PCC, respectively, ($/MWh); and $(CO_2\ emission)_{PCC}$ and $(CO_2\ emission)_{Ref}$ are the CO_2 emission intensity from the power plant with and without PCC, respectively, (tonne CO_2/MWh). Note that the avoided cost excludes the costs of CO_2 transportation and storage, as these costs vary from case to case depending on location, geological formations, topography and socioeconomic aspects.

For the electrochemical CO_2 utilisation unit, it has the sale revenue of $NaHCO_3$ product and electricity which produces a positive cash flow. The payback period is calculated based on capital investment and the net profit in the electrochemical CO_2 utilisation process (equation 13).

$$Payback\ period = \frac{Captial\ budgeting}{net\ profit\ /year} \tag{13}$$

4.2 Economic performance of electrochemical CO_2 utilisation coupled PCC process integrated with power station

The economic assessment of the overall CO_2 capture and utilisation process follows the process flow starting from the coal-fired power station, amine-based CO_2 capture process, and then the electrochemical CO_2 utilisation process.

4.2.1 Coal fired power station

The coal-fired power station is assumed to have a power output of 660 MW with a CO_2 emission density of 686 tonne/h CO_2. Table 13 summarises the technical performance and cost information for the reference power station. The specific total plant cost of the power plant was sourced from a CO2CRC report[91] and converted to 4th quarter of 2018 cost basis using the appropriate Chemical Engineering Plant Cost Index.

Table 13 Technical and cost information (2018 AUD) of the 660-MW greenfield coal-fired power station

Parameter	Unit	Value
Net electricity output	MW	660
CO_2 flow rate	tonne/h	686
Total capital investment	AUD million	2,355
Total capital cost per Kw	AUD/kw	3,568
Fixed operation & maintenance (O&M) cost	AUD million-year	79.0
Variable O&M cost	AUD million-year	33.3
Levelised cost of electricity (LCOE)	AUD/MWh	88.1

4.2.2 Amine-based PCC process (MEA and PZ/AMP)

The amine-based PCC process is designed with a 90% CO_2 removal efficiency from 686 tonne/h CO_2 emission from the power station. Due to the large flue gas flow rate, in MEA process four parallel process trains are proposed, each treating ~1.2 million tonne CO_2 per annum. This CO_2 capture capacity is between the commerical CCS projects of Boundary Dam (1.0 million tonne/year) in Canada and Petro Nova (1.4 million tonnes/year) in the USA.[92, 93] The techno-economic performance of MEA-based process has been detailed in our previous work,[77] whilst the techno-economic performance of the PZ/AMP based process has been reported by the International Energy Agency Greenhouse Gas

R&D.[68] Table 14 summarises the important technical and economic performance of MEA and PZ/AMP based CO_2 capture processes, which were taken as reference for the following electrochemical CO_2 utilisation process. Note that the economic performance of PZ/AMP was adjusted using the present economic assumptions for a consistent comparison.

Table 14 Summary of technical and economic performance of MEA and PZ/AMP based CO_2 capture processes

	MEA	PZ/AMP
Energy consumption in CO_2 capture process		
Pumps, kWh/tonne CO_2	4.9	4.8
Blowers, kWh/tonne CO_2	30.1	23.1
Absorbent regeneration, kWh/tonne CO_2	213.6	213.6
CO_2 compression, kWh/tonne CO_2	110.4	105.2
Others, kWh/tonne CO_2	12.8	23.5
Total energy consumption, kWh/tonne CO_2	371.8	370.2
Total energy consumption, MW	228.9	227.9
Capital cost of CO_2 capture plant		
Total capital investment, million AU$	872	769
Fixed O&M cost, million AUD/year	30.5	26.9
Variable O&M cost, million AUD/year	34.6	30.5
Economic performance		
LCOE of power station, AUD/MWh	88.1	88.1
LCOE of power station and PCC plant, AUD/MWh	183.9	174.7
CO_2 avoided cost, AUD/tonne CO_2	109.1	98.5

As shown in Table 13, the LCOE of the power station is significanlty increased when it is integrated with a CO_2 capture plant. This is due to the high energy conusmption and large captial investment of the PCC process. The LCOE of the PCC coupled power station rose from 88.1 to 183.9 AUD/MWh for the MEA process and to 174.7 AUD/MWh for the PZ/AMP process, resulting in CO_2 avoided costs of 109.1 and 98.5 AUD/tonne CO_2, respectively. It should be mentioned that the economic assessment of MEA and PZ/AMP processes is based on a standard process configuration without any process optimisation. It is anticipated that process improvements can greatly benefit the economic performance, for instance, in CSIRO's investigation of the PZ/AMP process with absorber intercooling and rich split enables the energy consumption to decrease to 0.244 MWh/tonne CO_2.[94] This leads to a lower LCOE of 148.1 AUD/MWh and a lower CO_2 avoided cost of 66.4 AUD/tonne CO_2.

4.2.3 Electrochemical CO_2 utilisation process

The present study employs two electrochemical systems, i.e. capacitive cell and electrochemical reaction cell for power generation and $NaHCO_3$ production. The process description has been detailed in the chapter 2. The electrochemical configuration is akin to a flow battery, which is mainly composed of the following elements: endplates, current collector, flow channel plates, electrodes (cathode and anode) and ion exchange membranes (AEM and CEM). These important components constitute the majority of the capital investment of the electrochemical system.

Endplates: The endplates require chemically stable materials that have no reactions with the amine and its CO_2-loaded solution. Polyphenylene ether (PPE) materials that we used in our previous electrochemical experiments with high hardness and chemical resistance to amine are considered in the present economic assessment.[95]

Electrodes: The electrodes play an important role in harnessing electricity from the electrochemical CO_2 utilisation processes. In the capacitive cell, the CSIRO carbon composite electrode[75] is used, whilst in the reaction cell the platinum/carbon electrodes are used for H_2 redox reactions by which electricity is generated.

Current collector: A current collector is used to collect the current through the electrodes for power output. A copper plate is usually used for current collectors.

Plates with flow channel: The surfaces of the plates contain a "flow field" which is a set of channels machined or stamped into the plate to allow the electrolyte to flow over the electrode. Graphite grooved with flow channel is used as the base materials.

Membrane: The AEM and CEM are essential in the electrochemical system to allow anion or cation migration while preventing the diffusion of electroactive species between compartments. The use of a selective membrane helps to produce the $NaHCO_3$ by-product with Na^+ from the brine travelling through CEM, and HCO_3^- from the CO_2-loaded amine solution travelling through the AEM.

The auxiliary components of the electrochemical cell include a solvent tank for solution buffering and storage, and a space gasket for cell sealing. With respect to the CO_2 utilisation unit, it requires a heat exchanger for solvent cooling, a settling tank for $NaHCO_3$ production, a press filter for $NaHCO_3$ dehydration, etc. Table 15 summarises the capital investment of each piece in the capacitive cell and electrochemical reaction cell for CO_2 utilisation. The total capital investment for the capacitive cell is estimated as 100.1 million AUD, and the capital cost of the reaction cell is 91.9 million AUD for the MEA process and 236.8 million AUD for the PZ/AMP process. Of the three electrochemical processes, the reaction cell using PZ/AMP has the highest capital cost due to it having the largest cost of platinum (used as catalyst) and producing the largest amount of $NaHCO_3$. It should be mentioned that the electrochemical CO_2 utilisation is integrated with the coal-fired power station and a project life of 30 years is assumed for the CO_2 capture plant. However, some parts of the electrochemical cell such as electrode, membrane etc., may not be operated over 30 years and these components would need to be replaced periodically. As there is no electrochemical CO_2 utilisation in operation at present, we estimated the component replacement based on the commercial H_2O electrolyser. The U.S. DOE[96] suggest that in a water electrolysis system the electrolyser cells should be replaced every 7 years with the capital replacement being 25% of the total capital investment. The present study assumes a periodic replacement of 6 years, which means the electrochemical cell needs to be replaced 4 times over the whole 30-year project. This results in the capital replacement cost of the electrochemical components (electrode, membrane, current collector, endplate, flow channel, etc) of 49.1 million AUD in the capacitive cell, 41.0 million AUD in MEA-based reaction cell and 103.6 million AUD in the PZ/AMP-based reaction cell. With the inclusion of cell replacement, the total capital investment of the overall project is increased to 149.1 million AUD in capacitive cell, 132.9 million AUD for the MEA-based reaction cell and 340.4 million AUD for the PZ/AMP-based reaction cell.

Table 15 Technical performance and capital investment of the capacitive cell and electrochemical reaction cell. Costs are in 2018 AUD

Technical specifications	Capacitive cell	Reaction cell		Note
		MEA	PZ/AMP	
CO_2 utilisation rate, kmol/s	0.11	0.11	0.3	
$NaHCO_3$ production rate, kmol/s	0.11	0.11	0.3	
Electricity output, MW	19.4	2.57	6.25	
Pump energy consumption, MW	0.24	0.24	0.22	Proportional to solvent pump energy in PCC
Cooling duty for $NaHCO_3$ production, MW	3.8	3.8	3.7	10K difference, coefficient of performance of 5 for cooling
Electrode area, m^2 *	11,000	11,000	30,000	Including anode and cathode
Electrode mass, kg	39,169	3,540	8,609	
Platinum on the electrode, kg	0	24.9	60.6	
Graphite distributor with flow channel, kg	93,500	93,500	255,000	
Membrane area, m^2	11,000	11,000	30,000	Including AEM and CEM
Endplate area, m^2	11,000	11,000	30,000	Including the cathode and anode sides
Capital cost of each equipment				
Electrode price, AUD /kg	370	370	370	Ref: http://www.graphitestore.com/carbon-fiber-laminate-uni-zero-0-014t
Cost of electrode, million AUD	14.5	1.3	3.2	
Platinum powder price, AUD/g	-	415	415	Price quote from Easmaterial Group Limited, China
Cost of platinum as catalyst, million AUD	0	10.3	25.1	
AEM price, AUD /m^2	127.2	127.2	127.2	Price quote from Selemion Company, Japan
Cost of AEM, million AUD	0.7	0.7	1.9	5 500 m^2 for AEM
CEM price, AUD /m^2	254.4	254.4	254.4	Price quote from Selemion Company, Japan
Cost of CEM, million AUD	1.4	1.4	3.8	5 500 m^2 for CEM
Space gasket, AUD /m^2	3.0	3.0	3.0	Price quote from Tianjian Qiangtongda Rubber product, Co. Ltd
Cost of space gasket, million AUD	0.033	0.033	0.09	Double membrane area
Graphite with flow channel, AUD/kg	4	4	4	Price quote from Huixian Maibang Graphite Product Co., Ltd. China

Cost of graphite, million AUD	0.37	0.37	1.02	
PPE endplate price, AUD /kg	1.5	1.5	1.5	Price quote from Shanghai Hanliang Industry, Co. Ltd
Cost of PPE endplate, million AUD	0.5	0.5	1.4	3 cm in thickness
Current collector price, AUD/kg	10	10	10	Price quote from Ningbo Powerway Alloy Material, Co. Ltd.
Cost of current collector, million AUD	2.0	2.0	5.5	0.2 cm in thickness
Anolyte/catholyte tanks, million AUD	0.68	0.68	0.65	Aspen costing, two solvent tanks
Pumps cost, million AUD	0.24	0.24	0.22	Aspen costing
Heat exchanger, million AUD	0.32	0.32	0.30	Aspen costing
Bicarbonate Settling tank, million AUD	1.2	1.2	3.3	
Filter press, million AUD	17.8	17.2	47.6	
Summary of capital investment				
Total direct cost (TDC)	39.7	36.5	94.1	
Total indirect cost (TIC)	7.9	7.3	18.8	0.2 TDC
Bare erected cost (BEC)	47.7	43.8	112.9	TDC + TIC
Engineering, procurement, construction (EPC)	60.6	55.7	143.4	1.27 BEC
Total plant cost (TPC)	87.0	79.9	205.9	1.2 EPC + 0.3 BEC
Total capital investment, million AUD	100.1	91.9	236.8	1.15 TPC
Capital replacement of cell, million AUD	49.1	41.0	103.6	25% capital of electrochemical cell with replacement every 6 year
Total project capital cost, million AUD	149.1	132.9	340.4	

Note: *the surface area of electrode is the geometric area that is the same as the area of endplate and membrane

Table 16 summaries the economic parameters of the electrochemical CO_2 utilisation processes. As indicated in the process description, the electrochemical process utilises the absorbed CO_2 to produce $NaHCO_3$ which is a valuable product for sale. The MEA based process has a CO_2 utilisation rate of 0.11 kmol/s, which equals 248 kilotonne/year of $NaHCO_3$. This will contribute to a sale revenue of 74.4 million AUD/year given the market price of 300 AUD/metric tonne of $NaHCO_3$.[97] The PZ/AMP process enables a higher sale revenue of 203 million AUD/year if all the $NaHCO_3$ is sold to market. The electrochemical CO_2 utilisation processes also produces electricity, particularly in the capacitive cell and the PZ/AMP based reaction cell which have net power outputs of 15.36 MW and 2.33MW respectively. The produced electricity can be sold to the grid, enabling revenue from electricity sale. Although the electrochemical processes require capital investment, operating and maintenance costs, chemicals etc., the revenue compensates for these costs and enables positive net profits over the project. The sale revenue is 74.2 million AUD/year for the capactive cell, 56.6 million AUD/year for the MEA based reaction cell, and 205.6 million AUD/year for the PZ/AMP based reaction cell. Accordingly, the pay back period of the electrochemical CO_2 utilisation process is estimated to be 2.0 years for the capactive cell, 2.3 years for the MEA based reaction cell, and 2.1 year for the PZ/AMP based reaction cell, under the conditions adopted.

It should be mentioned that the present economic assessment focuses only on the electrochemical CO_2 utilisation unit, and the net profits are based on the assumption that there is no cost for the raw materials such as brine, fly ash containing CaO and CO_2-rich solvent. The following section will therefore incorporate the CO_2 capture process to explore the effect of the electrochemical process on the economics of overall process.

Table 16 Summary of the important economic parameters of the electrochemical CO_2 utilisation processes

Techno-economic performance	Capacitive cell (MEA)	Reaction cell MEA	Reaction cell PZ/AMP
Cash out			
Capital investment, million AUD	149.1	132.9	340.4
Fixed O&M cost, million AUD/year	5.2	4.7	11.9
Variable O&M cost, million AUD/year	6.0	5.3	13.6
Wastewater treatment, million AUD/year [a]	6.2	6.2	16.8
Cash in			
Power consumption for CO_2 utilisation, MW	4.04	4.04	3.92
Power generation from CO_2 utilisation, MW	19.4	2.57	6.25
Net power output from CO_2 utilisation, MW	15.36	-1.47	2.33
Sale revenue from the power, million AUD/year [b]	17.2	-1.6	2.6
Sale revenue of $NaHCO_3$, million AUD/year	74.4	74.4	203.0
Total sale revenue, million AUD/year	91.6	72.8	205.6
Net cash			
Net profits from CO_2 utilisation, million AUD/year	74.2	56.6	163.3
Payback period, years	2.0	2.3	2.1

Note: [a]the wastewater treatment is based in AUD 2/m^3; [b] the revenue of power output is based on the electricity price of 0.15 AUD/kWh

4.2.4 Economics of overall process

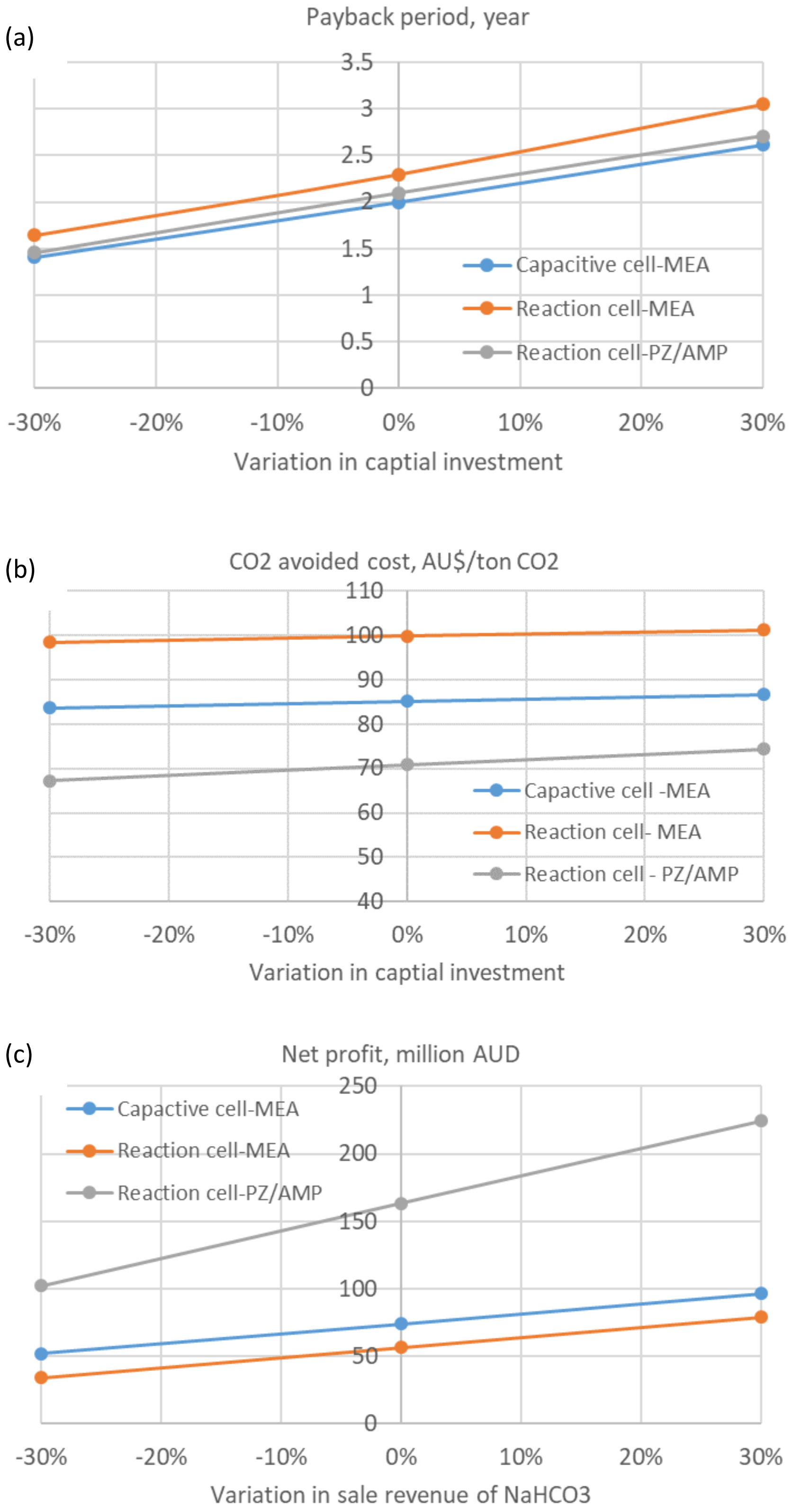
Table 17 summarises the economic performance of the overall process including a power station, amine-based capture plant, and electrochemical cell with CO_2 utilisation. The results show that integration of the electrochemical CO_2 utilisation process has significant effect on reducing the CO_2 avoided cost, i.e. the cost is decreased from AUD 109.1 to AUD 85.1 /tonne CO_2 for the capacitive cell, and the cost is reduced further for the electrochemical reaction cell when using PZ/AMP from AUD 98.5 to AUD 70.8 /tonne CO_2. This cost reduction is attributed to the electrochemical CO_2 utilisation process that produces power and turns the CO_2 into a valuable product. Of the three electrochemical systems, the PZ/AMP based reaction cell is more favourable for electrochemical CO_2 utilisation, resulting from its high content of bicarbonate species and high sale revenue from the $NaHCO_3$ product. It is expected that the economic performance of the reaction cell using PZ/AMP can be further improved when tuning the ratio of PZ and AMP that favours the formation of bicarbonate. Future work is suggested to focus on the experimental investigation on the electrochemical CO_2 utilisation using an optimised PZ/AMP formula to make this practically applicable.

Table 17 Summary of the techno-economic performance of an overall process including a power station, amine-based capture plant, electrochemical cell with CO_2 utilisation.

Techno-economic performance	Capacitive cell (MEA)	Reaction cell	
		MEA	PZ/AMP
Power station			
Net electricity output, MW	660	660	660
Total capital investment, million AUD	2,355	2,355	2,,355
Levelised cost of electricity, AUD/MWh	88.1	88.1	88.1
Amine based process with power station			
Total energy consumption, MW	228.9	228.9	227.9
Total capital investment, million AUD	3,227	3,227	3,124
Levelised cost of electricity, AUD/MWh	183.9	183.9	174.7
CO_2 avoided cost, AUD/ton CO_2	109.1	109.1	98.5
Overall process including power station, CO_2 capture and electrochemical utilisation			
Energy consumption of CO_2 capture, MW	226.2	226.2	219.8
Energy output of electrochemical cell, MW	15.36	-1.47	2.33
Total energy consumption, MW	210.8	227.7	217.5
Total capital investment, million AUD	3,376.1	3,359.9	3,464.4
Net profits from CO_2 utilisation, million AUD/year	74.2	56.6	163.3
Levelised cost of electricity, AUD/MWh	163.4	175.8	150.5
CO_2 avoided cost, AUD/ton CO_2	85.1	99.8	70.8

4.2.5 Sensitivity analysis

The sensitivity analysis was performed to understand how the electrochemical CO_2 utilisation process would affect the economic performance of the overall process. As indicated in Table 16, the capital investment of the electrochemical CO_2 utilisation unit and the sale revenue of $NaHCO_3$ are the two most significant factors influencing the economic performance. The sensitivity analysis therefore focuses on these two factors with ±30% variation. Figure 12 shows the effect of capital investment and sale revenue of $NaHCO_3$ on the payback period, net profits of the electrochemical process and the CO_2 avoided cost of the overall process.


(a)
Payback period, year
3.5
3
2.5
2
1.5
1
0.5
0
Capacitive cell-MEA
Reaction cell-MEA
Reaction cell-PZ/AMP
-30%
-20%
-10%
0%
10%
20%
30%
Variation in captial investment
(b)
CO2 avoided cost, AU$/ton CO2
110
100
90
80
70
60
50
40
Capactive cell -MEA
Reaction cell- MEA
Reaction cell - PZ/AMP
-30%
-20%
-10%
0%
10%
20%
30%
Variation in captial investment
(c)
Net profit, million AUD
250
200
150
100
50
0
Capactive cell-MEA
Reaction cell-MEA
Reaction cell-PZ/AMP
-30%
-20%
-10%
0%
10%
20%
30%
Variation in sale revenue of NaHCO3

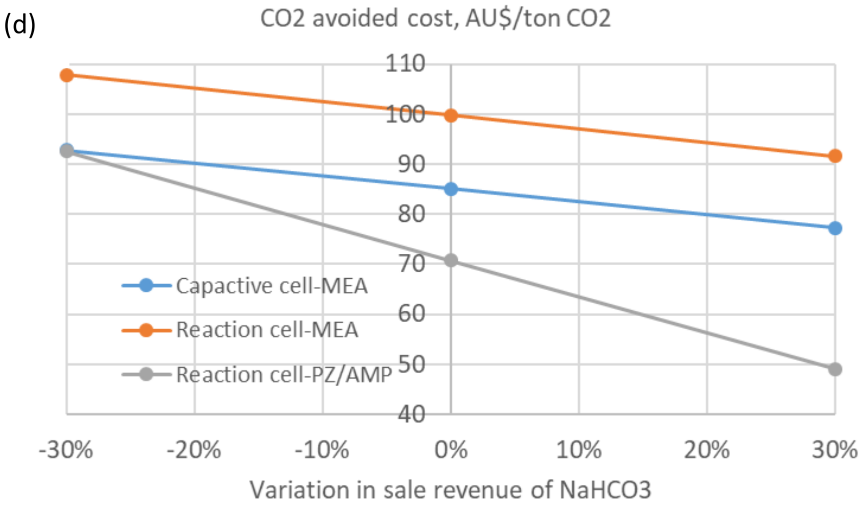


Figure 12 Sensitivity of capital investment (±30% variation) on (a) payback period of electrochemical CO_2 utilisation process and (b) CO_2 avoided cost; sensitivity of $NaHCO_3$ sale revenue (±30% variation) on (c) net profits of electrochemical CO_2 utilisation process and (d) CO_2 avoided cost.

The capital investment has important influence on the payback period of the electrochemical CO_2 utilisation process. It is intuitive that a decrease in capital cost benefits a short payback period whilst an increase in capital cost adds heavy financial burden with longer payback period. The sensitivity study shows that a variation of capital investment by ±30% leads to payback period of 1.4-2.6 years for the capacitive cell, 1.6-3.1 years for the MEA-based reaction cell and 1.5-2.7 years for the PZ/AMP-based reaction cell. The capital investment of electrochemical systems also affects the CO_2 avoided cost of the overall process, but the influence is not significant. For instance, a variation of capital investment by ±30% leads to a change in CO_2 avoided cost of AUD 83.6-86.6/tonne CO_2 for the capacitive cell, AUD 98.4-101.2/tonne CO_2 for the MEA-based reaction cell and AUD 67.2-74.3/tonne CO_2 for the PZ/AMP-based reaction cell. This small change is due to the factor that the capital investment of the electrochemical systems accounts for a small proportion of the capital of the overall process, i.e. 4.4% for the capacitive cell, 4% for MEA-based reaction cell and 9.8% for the PZ/AMP-based reaction cell.

The sale of $NaHCO_3$ is the most important revenue for the electrochemical CO_2 utilisation process, and the variation of sale revenue of the $NaHCO_3$ product significantly influences the net profit of the electrochemical systems. Specifically, a ±30% variation in $NaHCO_3$ sale revenue results in net profit changes of 51.9-96.5 million AUD/year for the capacitive cell, 34.3-78.9 million AUD/year for MEA-based reaction cell and 102.4-224.2 million AUD/year for the PZ/AMP-based reaction cell. This significantly affects the CO_2 avoided cost of AUD 77.3-92.8/tonne CO_2 for the capacitive cell, AUD 91.6-107.9/tonne CO_2 for the MEA-based reaction cell and AUD 49.0-92.6/tonne CO_2 for the PZ/AMP-based reaction cell. This sensitivity analysis indicates that the sale of $NaHCO_3$ to the market is the determining factor for the profitability of the electrochemical system and to ensure a low CO_2 avoided cost. Of the three electrochemical CO_2 utilisation systems, the PZ/AMP-based reaction cell exhibits the best economic performance in terms of net profit and CO_2 avoided cost which deserves further investigation towards technology development.

5 Path to Commercialisation

Sodium bicarbonate is an important industrial feedstock for the production of soda ash, magnesium carbonate and other compounds. It is used as a liquid and slurry or as dry powder. It is used in various industries such as food, agriculture and animal feed, pharmaceutical, medical etc. Sodium carbonate (soda ash) and bicarbonates are also used in making glass. The sodium bicarbonate market according to end-use is shown in Figure 13.[98] Significant portion of its use is in the food and beverage industry and animal feed products. Also, there is an increase in demand for its use in detergents and cleaning products, in personal care and cosmetics, and pharmaceutical applications.[99, 100] As it is an environmentally friendly natural product, it is also used in agrochemicals. Other end-uses include fire extinguishers, textiles, leather, etc. Its liquid formulation is also used in flue gas treatment.

The sodium bicarbonate market was expected to be about USD 1.2 billion in 2018[99] and there is a growing demand of about 2-5% annually up to 2025. Asia Pacific region is currently the largest market in the world for sodium bicarbonate and other regions of significant consumption are Europe and North America.[98] In Australia, Penrice is the largest sodium bicarbonate producing company and domestic sales according to 2012 figures were about 30,000 tonnes with a revenue of AUD 25M and about 100,000 tonnes per annum in exports.[101]

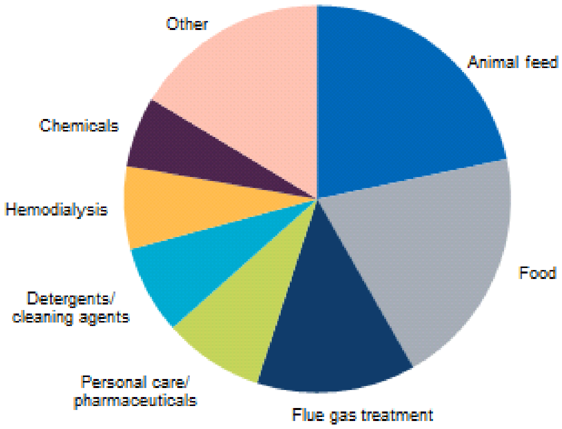


Figure 13 World consumption in 2016 of sodium bicarbonate by end-use[98]

Some of the other global producers include Solvay, Henan Zhongyuan, Novacap, Church & Dwight Company, Tata Chemicals, Natural Soda, Ciner Group and its subsidiary Kazan Soda Elektrik Uretim. In 2015, Solvay group announced opening a 100,000 tpa sodium bicarbonate plant in Thailand to meet the growing demand in Asia Pacific.[102] Presently, from the information available, three companies are associated with carbonate mineralisation technology using industrial wastes;[87]

1. Carbonfreechem, also known as Skynoic, has developed patented technologies for the capture and utilisation of CO_2 in mineral form. Its proprietary processes result in products such as carbonate/bicarbonate materials. The SkyMine® technology[103] began operations in March 2015 in San Antonio, Texas at Capitol Aggregates cement plant. The plant aims to reduce its carbon emissions by 15 percent or 83,000 tonnes of CO_2 annually.

2. Calera: Calera's uses an aqueous precipitation process with flyash as the source of alkalinity and converting it into a solid form of cementous materials thereby sequestering the CO_2. Calera's CO_2 capture and conversion

pilot plants produced up to 2 tonnes of CO_2-containing calcium carbonate product per day using raw flue gas without needing concentration of the CO_2.[104] Each tonne of mineral carbonation and cement formed by the Calera mineralisation process contains 0.5 tonne of CO_2.[87]
3. Blue Planet utilises waste CO_2 as a raw material to produce lightweight coarse and fine aggregates that are used in concrete, roofing, and solar-reflective cool pigments. Blue Planet produced calcium carbonate powder as a replacement for expensive titanium oxide, which was earlier used as a high solar reflective material.[105]

In Australia, Mineral Carbonation International, is developing a carbon utilisation technology combining waste streams and transforming them into value added products.[106] The process uses serpentine (composed of magnesium silicate mineral) as feedstock for mineral carbonation along with sodium bicarbonate to produce magnesium carbonate, as cement substitute.[107-109] Field studies have been reported using ultramafic mine tailings containing magnesium rich silicate and hydroxide minerals for sequestering CO_2.[110]

The electrochemical CO_2 utilisation process evaluated in this study also uses industrial wastes as raw materials in the process to produce sodium bicarbonate. An additional advantage is the electrical energy harvest. The purity of the sodium bicarbonate produced from this process is expected to be of similar quality to the existing products in the market. So environmental gains outweigh commercial gains from this perspective. In addition to utilising CO_2, waste streams such as brine and flyash are used, thereby reducing the environmental disposal. Mine water extracted, for example, from coal mines in Australia are predominantly sodium-containing brackish water and require moderate treatment before returning to the environment or reuse.[40] The sodium-rich waste brines are generally stored on-site in large dams that can be utilised as raw materials for the electrochemical process. Some mines adopt treatment technologies to desalinate the mine water to recover reusable water and concentrate the brine to reduce the on-site storage volume. For example, Centennial mine in NSW applies desalination followed by a brine concentrator and crystalliser to recover water and salt crystals.[111] Potential application of the electrochemical process can provide additional advantage of energy harvesting. Integration of such CO_2 utilisation technologies with the mining Industry could be one development pathway and is potentially beneficial as it would also encourage sustainable development of this industry by addressing greenhouse gas mitigation and waste management. Waste brine from abandoned legacy mine pits can also potentially be utilised. This technology and equipment can also be integrated with base power plants. For example, this could also provide synergies with coal mine and coal fired power plants. In Australia, major coal producing basins occur in New South Wales and Queensland and there are number of coal-fired power plants that are in close proximity to some of the major coal mines.[112] This could provide significant economic advantage in minimising transportation and environmental benefit in waste utilisation while adopting this CO_2 utilisation technology. This would also provide an alternative to CO_2 transport and storage, especially where suitable storage facilities are still being evaluated. From this theoretical study, about 2.8% of the captured CO_2 is used in the utilisation process for the MEA case. For AMP/PZ, about 7.7% of the input CO_2 is utilised as bicarbonate.

The next step in the development of this electrochemical CO_2 utilisation technology would be a lab scale experimental study to validate the technical feasibility in the sodium bicarbonate formation and energy harvest, especially utilising actual industrial waste materials. The experimental results would help confirm the assumption and theoretical results from this feasibility studies. It will also help to develop effective strategies to increase the utilisation proportion of the captured CO_2. Upon successful validation, the potential stages towards technology development would be a pilot scale electrochemical CO_2 utilisation unit, followed by a demonstration plant (about 5000-10,000 tonnes CO_2) before commercial uptake. An early business case would involve both energy and mining industries to play an important role for the development of this novel electrochemical CO2 utilisation technology. It was estimated that in some areas of inland desalination treatment, every 1% reduction of their brine volume offered a savings of about \$1M in disposal costs.[113] Brine disposal cost and lack of a disposal options would be important cost drivers for the mines to seek alternate brine utilisation technologies. The electrochemical process combines the use of brine waste as a potential resource and the captured CO_2 in producing value added bicarbonate to achieve a circular industrial economy. A small portion of the input captured CO_2 is being utilised by the electrochemical process as seen in the feasibility study. This must be experimentally verified, and strategies developed for enhancing the input CO_2 utilisation to form bicarbonate and reduce the dependence on the desorber, compression and storage route. Nevertheless, there is an economic and CO_2 footprint reduction benefit in integrating the electrochemical process to the power station with CO_2 capture plant, that is attributed to the electrical power generation and sodium bicarbonate product from the electrochemical technology.

Some of the barriers or challenges for the development of this technology would include:

- The chemicals that are added as raw reactants such as CO_2, sodium from brine, calcium hydroxide from alkaline waste flyash, must be fully sourced from industrial wastes in a real process to make it commercially viable.
- The presence of other contaminants in the industrial raw materials could interfere in the process efficiency.
- The requirement of precious metal catalysts must be minimised. Hence this study also evaluated an alternate electrochemical process without the use of catalyst and with fewer raw materials.
- Obtaining a constant source of high-concentration CO_2 can also be an issue.
- Successful market uptake would also be governed by the demand for sodium bicarbonate produced from this process. However, given the various industrial applications and use of sodium bicarbonate, and the growing demand for this product, it looks like this would not be an issue.
- Securing initial investment for the technology development could be difficult. Suitable partnerships would also be required between the mining industry, power station and CO_2 capture facility in the development and successful deployment of this technology.
- Carbon pricing would provide an additional incentive for industry uptake.

6 Conclusion and Recommendations

6.1 Conclusion

A theoretical feasibility study of a novel electrochemical CO_2 utilisation technology to produce a value-added sodium bicarbonate product and simultaneously harvest electrical energy was carried out. Two electrochemical CO_2 utilisation methods, a cyclic mixing energy capacitive cell process and the CO_2 mineralisation reaction cell process, were studied. A preliminary life cycle assessment and economic evaluation were carried out to assess the feasibility of these processes.

A theoretical prediction using chemical reactions and activity models applied to the CO_2 electrochemical reaction cell process for two different amines, MEA and AMP/PZ scenarios, showed a sodium bicarbonate yield of 0.11 kmol/s and 0.3 kmol/s respectively, and an electricity generation of 2.57 MW and 6.25 MW respectively. For the capacitive cell CO_2 utilisation electrochemical process with carbon composite porous electrodes, the maximum theoretical electrical energy harvest with 54% process efficiency was found to be 19.4 MW.

The electrochemical processes were integrated with post combustion amine-based CO_2 capture in a 660 MW coal-fired power station to carry out a preliminary LCA study. The CO_2 footprint for the reference case of power station coupled with CO_2 capture without the electrochemical process was 522.91 kg CO_2/t CO_2 processed. Integration of the electrochemical reaction cell process showed a reduction in the CO_2 footprint of about 6.4% (489.27 kg CO_2/t CO_2 processed) for the MEA system, and by about 17.8% (429.92 kg CO_2/t CO_2 processed) for the AMP/PZ system. Similarly, integration of the capacitive cell process based on MEA showed a reduction in CO_2 footprint of about 7.4% with 484.29 kg CO_2/t CO_2 processed. This CO_2 footprint reduction is attributed to the combined effects of electricity recovery from the electrochemical process, CO_2 fixing through its utilisation with the sodium bicarbonate formation, and the reduction of capture process regeneration energy duty resulting from the decreased amount of CO_2 for desorption because part of the CO_2 is used for $NaHCO_3$ production. For MEA, about 2.8% of the captured CO_2 is fixed by the utilisation process. For AMP/PZ, about 7.7% of input CO_2 is fixed. With further modification to the CO_2 rich amine electrolyte composition, for example, changing the ratio of AMP/PZ, the bicarbonate yield and the electricity generation would be further increased. This could have additional scope for further reduction in the overall CO_2 footprint.

Based on the obtained theoretical performance, a preliminary economic evaluation was carried out for the two electrochemical CO_2 utilisation processes to reveal their impact on the PCC process integrated with a power plant. The capital cost of the electrochemical capacitance cell was estimated to be AUD 100.1 M and the reaction cell was AUD 91.9 M and AUD 236.8 M for the MEA and AMP/PZ systems respectively. Considering periodic replacements of electrochemical cell components every 6 years, the capital investment for the 30 year period, was found to be AUD 149.1 M for the capacitance cell MEA system, and AUD 132.9 M and AUD 340.4 M for the reaction cell with MEA and AMP/PZ systems respectively. Among the three cases, the reaction cell using PZ/AMP had the highest capital due to increased sodium bicarbonate throughput and the associated equipment and component costs such as increased platinum catalysts requirements. The electrochemical process requires capital investment, fixed and variable operating and maintenance costs, chemical consumption, etc. However, the sale revenue from the power production, and more notably from the sodium bicarbonate produced is able to compensate these costs and enable net positive revenue over the project, with an estimated payback period of 2-3 years, under the study conditions adopted.

The levelised cost of electricity and the CO_2 avoided cost from the overall integrated system of the electrochemical cell and the power station with amine-based PCC showed that the PZ/AMP based CO_2 utilisation reaction cell process was found to be most economically favourable followed by the capacitive cell process as given below:

Parameter	Power plant+ amine-based PCC		Power plant+ MEA-based PCC and capacitive cell process	Power plant+ amine-based PCC and reaction cell process	
	MEA	AMP/PZ		MEA	AMP/PZ
Levelised cost of electricity, AUD/MWh	183.9	174.7	163.4	175.8	150.5
CO_2 avoided cost, AUD/tonne CO_2	109.1	98.5	85.1	99.8	70.8

In Australia, the mining industry with suitable partnerships, could be one implementation pathway for this electrochemical CO_2 utilisation technology and potentially beneficial as it would also encourage sustainable development of this industry by addressing greenhouse gas mitigation and waste management.

In summary, a feasibility study was carried out and found that through the theoretical analysis of the electrochemical CO_2 utilisation process, which when integrated in a power station with CO_2 capture, improves CO_2 emission reduction and lowers the overall CO_2 mitigation costs, compared to an equivalent system without the electrochemical process.

6.2 Recommendations

Future work is suggested to focus on the lab-scale experimental investigation on the electrochemical CO_2 utilisation capacitive and reaction cell processes to verify the theoretical assessment of the bicarbonate production and electricity generation from this study. Further to the verification, effective strategies must be developed to increase the utilisation proportion of the captured CO_2 through experimentation. The experimental work must use actual industrial wastes as the feedstock to evaluate the proof-of-concept and assess the technical performance of the system including the recovery efficiency and the purity of the sodium bicarbonate obtained. A parametric evaluation and optimisation are required using experimentation on various operating parameters such as electrochemical reactor and electrode design, reactant concentrations, cycle time, reaction kinetics etc. to maximise bicarbonate production and electricity generation. In the theoretical study, an assumption is made that 100 % of the HCO_3 in the rich absorbent reacts to form $NaHCO_3$. Experimental work is required to determine the actual performance. Also, experimental data is critical to have reliable equilibrium constants that can then be incorporated and verified using the modelling tools. Further, in the capacitive process, a catalyst is not used, however in the reaction cell, replacing the platinum catalyst with, for example, graphite could reduce the cost of the electrochemical process during industrial scale up.

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Appendix 1

Table 1A and 1B shows the parameters of the CO_2 rich MEA and AMP/PZ streams from the CO_2 capture plant respectively.

Table 1A CO_2 rich MEA stream from the CO_2 capture plant

Streams	Units	Parameters
Water	kmol/s	22.53
Carbon Dioxide	kmol/s	1.55
MEA	kmol/s	3.29
Nitrogen	kmol/s	0.00
Nitric Oxide	kmol/s	0.00
Oxygen	kmol/s	0.00
Formate (HSS)	kmol/s	0.30
Total Flow		27.66
Frac Vapor		0.00
Molec Wt		24.88
Temperature	Celsius	43.01
Pressure	kPa	105
Mass Flow	kg/s	688.23
Volume Flow	cum/s	0.61

Table 1B CO_2 rich AMP/PZ stream from the CO_2 capture plant

Streams	Units	Parameters
Water	kmol/s	15.65
Carbon Dioxide	kmol/s	1.23
Piperazine	kmol/s	0.78
AMP	kmol/s	1.56
Nitrogen	kmol/s	0.00
Nitric Oxide	kmol/s	0.00
Oxygen	kmol/s	0.00
Formate (HSS)	kmol/s	0.235
Total Flow		19.45
Frac Vapor		-
Molec Wt		28.41
Temperature	Celsius	44.7
Pressure	kPa	105
Mass Flow	kg/s	552.6
Volume Flow	cum/s	0.5

Table 1C and 1D shows the mass balance for the CO_2 rich stream for MEA and AMP/PZ respectively.

Table 1C Mass balance for the CO_2 rich MEA stream from absorber[+]

Parameters		CO_2 rich absorbent from absorber	Na rich brine	Aqueous $Ca(OH)_2$	$Ca(OH)_2$ reduced flow	Na lean brine	CO_2 lean flow to settling tank	CO_2 reduced rich absorbent to STR	Solid $NaHCO_3$ produced
T	C	44.54	25.00	25.00	-	-	-	25.00	25.00
P	kPa-a	108.70	105.00	105.00	-	-	-	101.00	101.00
total mass flow	kg/s	1062.54	220.7	2360.21	2363.08	216.1	1051.66	1045.05	6.61
H_2O	kmol/s	34.99	12.2	130.82	130.90	12.2	34.99	34.99	0.00
CO_2	kmol/s	2.45	0.00	0.00	0.00	0.00	2.37	2.37	0.00
MEA	kmol/s	5.08	0.00	0.00	0.00	0.00	5.08	5.08	0.00
NaCl	kmol/s	0.00	0.09	0.00	0.00	0.016	0.00	0.00	0.00
$Ca(OH)_2$	kmol/s	0.00	0.00	0.05	0.01	0.00	0.00	0.00	0.00
$CaCl_2$	kmol/s	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00
$NaHCO_3$	kmol/s	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.08

[+] using ProTreat model

Table 1D Mass balance for the CO_2 rich AMP/PZ stream from absorber[+]

Parameters		CO_2 rich absorbent from absorber	Na rich brine	Aqueous $Ca(OH)_2$	$Ca(OH)_2$ reduced flow	Na lean brine	CO_2 lean flow to tank	CO_2 reduced rich absorbent to STR	Solid $NaHCO_3$ produced
T	C	42.28	25	25	-	-	-	25	25
P	kPa-a	108.70	105	105	-	-	-	101	101
total mass flow	kg/s	685.5	396.3	4238.9	4244	388.1	678	666.1	11.87
H_2O	kmol/s	19.09	21.9	234.95	235.09	21.9	19.09	19.09	0
CO_2	kmol/s	1.75	0	0	0	0	1.61	1.61	0
PZ	kmol/s	0.95	0	0	0	0	0.95	0.95	0
AMP	kmol/s	1.90	0	0	0	0	1.9	1.9	0
NaCl	kmol/s	0	0.17	0	0	0.028	0	0	0
$Ca(OH)_2$	kmol/s	0	0	0.085	0.014	0	0	0	0
$CaCl_2$	kmol/s	0	0	0	0.071	0	0	0	0
$NaHCO_3$	kmol/s	0	0	0	0	0	0.14	0	0.14

[+] using ProTreat model

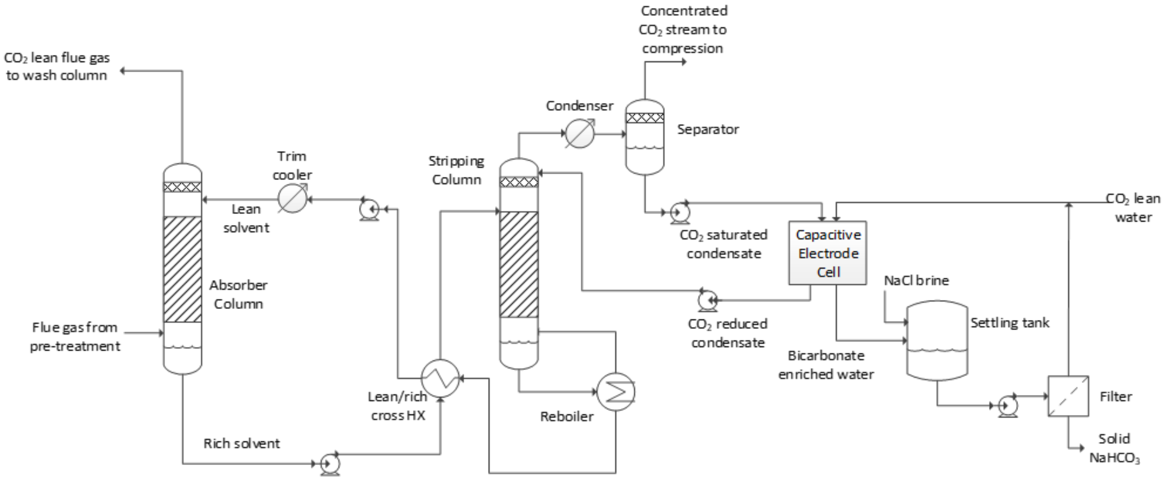

Figure 1A Schematic of the CO_2 capture and regeneration with capacitive electrode cell configuration applied to CO_2 saturated stripping column condensate

Appendix 2

List of Publications

No publication has been produced at the time of the submission of the report. The project outcomes and findings are planned to be disseminated through a Journal and/or conference publication.

Appendix 3

List of Staff Engaged on the Project

Ramesh Thiruvenkatachari, Senior Research Scientist, CSIRO
Kangkang Li, Research Scientist, CSIRO
Ashleigh Cousins, Senior Research Scientist, CSIRO
Yonggang Jin, Team Leader, CSIRO
Nawshad Haque, Senior Research Scientist, CSIRO
Shi Su, Team Leader, CSIRO
Paul Feron, Group Leader, CSIRO
David Randall, Project Manager, Centennial Coal

Appendix 4

Sign Off

I, the undersigned, being a person duly authorised by the Grantee, certify that:

a) the above information is true and complete,
b) the expenditure of the funding received to date has been used solely on the project; and
c) there is no matter or circumstances of which I am aware that would constitute a breach by the Grantee or, if applicable the End Recipient and Subcontractors, of any term of the Funding Deed.

Signature:

Position: Principal Research Scientist, CSIRO

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