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Retrofitting calcium carbonate looping to an existing cement plant for CO₂ capture: a techno-economic feasibility study

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Acknowledgments

Executive Summary

The cement industry is a major source of industrial carbon dioxide (CO_2) emissions, contributing to around 8% of global CO_2 emissions. In a carbon constrained future, carbon capture, utilisation and sequestration (CCUS) will be required to achieve deep emission reductions from the cement industry. However, the application of carbon capture technologies in the cement industry is at an early stage of development. CO_2 capture technologies being studied in the cement industry include direct separation (DS), calcium carbonate looping (CCL), oxyfuel and post-combustion capture (PCC). Current PCC technologies being investigated include chemical absorption, adsorption, membrane, and mineralisation. There are only a few pilot-scale research developments for CO_2 capture from cement production worldwide, with none of them in Australia.

CCL has a number of advantages over other CO_2 capture technologies for its application in the cement industry, including (1) abundant, cheap and environmentally benign raw materials (i.e. limestone); (2) high sorption capacity of CO_2; (3) lower energy consumption with additional steam cycle driving; (4) no need for flue gas pre-treatment; and (5) synergies with cement manufacture. CCL is based on the reversible reaction between lime (CaO) and CO_2. The most studied CCL configuration employs an oxy-fired combustion at 900-950°C to release a high purity CO_2 stream. This oxy-fired CCL (Oxy-CCL) process has been subject to extensive R&D in the past two decades and established a few pilot-scale plants in the world, mainly for application in power plants. Despite the advantages, Oxy-CCL is still an energy- and capital-intensive process, with a significant portion of energy consumption and capital costs associated with the air separation unit (ASU) required for oxy-fired combustion. It is imperative to further improve the commercial viability of the CCL technology.

This project aims to carry out a techno-economic feasibility study of retrofitting a novel CCL process to an existing cement plant in New South Wales for deeply reducing CO_2 emissions. The reference cement plant is based on a dry process with 4 stages of pre-heaters, a pre-calciner and a rotary kiln with a clinker production of 184 t/h. Specific objectives of this project are:

- Technology survey of CO_2 capture technologies being studied in the cement industry and overview of pilot development of CCL;
- Site investigation to collect relevant technical information and understand its current operation; and
- Techno-economic feasibility assessment to understand the technical feasibility and economic costs and CO_2 emissions reduction.

The project commenced in January 2019 and was successfully completed by the end of May 2020, with all the research tasks successfully accomplished on budget. Technology surveys of the state-of-the-art R&D in CO_2 capture in the cement industry and pilot-scale Oxy-CCL plants were carried out to better understand the latest technological development in decarbonising the cement sector. Site investigation was also successfully carried out with relevant operating data and technical information collected, which were used to perform the techno-economic assessment and assess the retrofitability.

Aiming to eliminate the need of the energy-intensive ASU in the Oxy-CCL process, a novel indirect-heated CCL (IH-CCL) process was assessed and applied to the reference cement plant. The IH-CCL process involves the limestone decomposition in an indirect-heated calciner where the heat required is indirectly transferred from air combustion of fuel. The separation of limestone

decomposition and air combustion of fuel leads to a pure CO_2 stream. The retrofit of IH-CCL to the reference cement plant can be achieved through the following three different configurations:

- **Downstream integration** involves a standalone IH-CCL plant that is placed after the raw mill and treats flue gases at ~120°C, with almost no impact on the existing cement production. The integration level is 50%, meaning that the spent CaO flow from the CCL process is fed into the pre-calciner to replace 50% of CaO in raw meals for clinker production

- **Tail-end integration** involves a standalone IH-CCL plant that is placed after the pre-heaters and treats flue gases at ~370°C, requiring some of the existing piping to be rerouted. The CO_2 lean flue gas from the IH-CCL process is fed into the raw mill to pre-heat raw meals. Similarly, the integration level is 50%. This configuration has deeper thermal integration with cement production than the downstream integration.

- **Full integration** is achieved by replacing the existing pre-calciner and pre-heaters with the IH-CCL plant. The flue gas from the rotary kiln that remains unchanged is firstly directed to the indirect-heated calciner to assist the limestone decomposition. The carbonator treats flue gases from the rotary kiln and the calciner. The CO_2 lean flue gas is sent to the raw mills to pre-heat the raw meals. The indirect-heated calciner produces a H_2O/CO_2 stream and a CaO stream that is partly fed to the kiln for clinker production and partly to the carbonator for cyclic CO_2 capture. This configuration requires significant modifications to the existing kiln system.

In all three configurations, the thermal input is partially recovered by driving a steam cycle. The technical feasibility and economic viability of the three configurations were evaluated in terms of the specific primary energy consumption for CO_2 avoided (SPECCA), technical retrofitability, cost of clinker (CoC), and cost of CO_2 avoided (CCA). Key results from the techno-economic assessment are presented in the table below.

	Ref plant	Downstream integration	Tail-end integration	Full integration
SPECCA, MJ/t clk	--	4,124.32	2,264.18	1,396.71
Cost of clinker (CoC), $/t clk	119.19	235.78	216.78	175.69
Cost of CO_2 avoided (CCA), $/t CO_2	--	80.83	58.68	65.88

The best SPECCA was obtained for the full integration (1,396.71 MJ/t clk), followed by the tail-end integration (2,264.18 MJ/t clk) and downstream integration (4,124.32 MJ/t clk). The retrofit of IH-CCL resulted in significant increases in the calculated CoC from 119.19$/t for the reference plant without CO_2 capture to 175.69$/t for full integration, 216.78$/t for tail-end integration, and 235.78$/t for downstream integration. The significant increases are mainly attributed to the high Capex, which seems a common problem for all CO_2 capture technologies. Among all three configurations, the tail-end IH-CCL configuration has the lowest CCA of 58.68$/t and the full integration case shows a slightly higher CCA of 65.88$/t. The downstream integration case has the highest CCA of 80.83$/t. Compared with other PCC technologies, the IH-CCL tail-end and full integration cases have the potential to significantly improve the commercial viability of CO_2 capture from cement production.

The retrofitability of the three configurations was also qualitatively assessed through six criteria based on the technical assessment results. Although the downstream and tail-end configurations are expected to have much larger footprint than the full integration, all the three configurations should be able to fit in the reference plant based on the site investigation. Also, both the downstream and tail-end configurations involve a standalone IH-CCL plant with very minor impact on the existing cement production and negligible impact on the clinker quality. In contrast, the full integration case requires significant modifications to the existing kiln system, and the impact on the clinker quality is currently unclear due to changes in gas atmosphere and temperatures. Moreover,

additional dust removal may be required for the downstream and tail-end configurations due to the high fuel consumption. Lastly, the handling of steam, operation of new auxiliaries including the steam cycle and CO_2 compression unit are required in all cases and are different skill set to the operators.

The economic index relies on assumptions related to the discount rate, electricity price, fuel price, process contingencies and steam cycle efficiency. A sensitivity analysis of the CCA was performed, showing a strong dependency on all variables for both the downstream and tail-end configurations. In comparison, the CCA for the full integration was more sensitive to the discount rate and steam cycle efficiency than other variables.

In summary, the IH-CCL tail-end integration is recommended for retrofitting to existing cement plants due to the lowest CCA and very minor impact on the existing cement manufacture process. The full integration offers the lowest SPECCA and CoC but requires significant modifications to the existing kiln system and a long stop of cement production. For this reason, the full integration case may be better suited to greenfield cement plants.

For the first time the IH-CCL technology is investigated for CO_2 capture in the Australian cement industry. Based on the techno-economic assessment, the novel IH-CCL technology can be retrofitted to an existing cement plant for deeply cutting CO_2 emissions in a cost competitive manner. To further progress the IH-CCL technology, the following R&D is recommended:

- Fundamental R&D

  The IH-CCL technology eliminates the need of the energy-intensive ASU but possibly needs larger size of reactors due to the higher fuel consumption. As a result, the capital costs associated with the reactors represents the largest share of the total plant cost. A thorough thermodynamic analysis is therefore required to minimise the fuel consumption and the associated Capex.

  On the other hand, it is still unclear at this stage that how the retrofit might impact the clinker quality in the full integration case due to changes in gas atmosphere, temperature and/or other conditions. Some lab-scale experimental work should be carried out to understand the impact and ensure the clinker quality.

- Pilot-scale prototype unit demonstration

  Although the Oxy-CCL process has been demonstrated through a number of pilot-scale plants, the operational experience associated with IH-CCL is scarce and its TRL is low. A pilot-scale IH-CCL prototype unit needs to be erected to gain engineering and operational experience to reduce the high Capex for the future deployment in the cement industry. The pilot-scale IH-CCL prototype unit also needs to be demonstrated at a cement plant using real flue gases.

Lay Summary

The cement industry is a high-emitting industry, contributing to around 8% of global CO_2 emissions. In a carbon constrained future, carbon capture, utilisation and sequestration (CCUS) will be required to achieve deep emission reductions from the cement industry. However, the application of carbon capture technologies in the cement industry is at an early stage of development and requires very high upfront capital investment.

The project studies the retrofit of a novel calcium carbonate looping process into an existing cement plant for deep CO_2 emissions reduction in a cost competitive manner. The novel calcium carbonate looping process is based on the reversible reaction between the lime (CaO) and CO_2 and is more compatible with cement production than other post-combustion capture (PCC) technologies, as the spent materials can be re-used for clinker production. Nationally, there has been no research on retrofitting existing cement plants with calcium carbonate looping in an industrial setting. Successful completion of this project would help bridge this gap and potentially lead to a near-zero emission cement plant in NSW.

The project include technology surveys to better understand the latest technological development in reducing carbon emissions from the cement sector, site investigation to collect relevant technical information and understand its current operation, and techno-economic feasibility assessment to understand the technical retrofitability, economic viability and potential CO_2 emissions reduction.

The retrofit of the novel calcium carbonate looping process was achieved through three different integration configurations including the downstream integration, tail-end integration and full integration. The tail-end integration that involves a standalone calcium carbonate looping based CO_2 capture plant to treat cement plant flue gases from the pre-heaters, is recommended for the retrofit due to the lowest cost of CO_2 avoided and very minor impact on the existing cement production. The full integration, in which the existing kiln system is replaced by the calcium carbonate looping process, offers the lowest energy consumption and clinker cost. But due to the significant modifications, the full integration may be better suited to greenfield cement plants.

The novel calcium carbonate looping process is an advanced carbon capture technology and can reduce the carbon emissions from the existing cement plant by more than 80%. It is also more cost competitive than other PCC technologies. The uptake of the technology would help the cement industry achieve net-zero emissions and improve its environmental sustainability and resilience.

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Nomenclature

Abbreviations			
Abbreviations		SWDF	Solid waste derived fuel
ASU	Air separation unit	TDC	Total direct cost
BAT	Best Available Technology	TPC	Total plant cost
BFB	Bubbling fluidised bed	tpd	Tonne per day
CAP	Chilled ammonia process	tph	Tonne per hour
Capex	Capital expenditure	TRL	Technology readiness level
CCA	Cost of CO_2 avoided	*Symbols*	
CCL	Calcium carbonate looping	e_{CO2}	Direct CO_2 emissions from the cement plant [kg/s or kg/t]
CCUS	Carbon capture, utilisation and Storage	$e_{CO2,el}$	Indirect CO_2 emissions associated to power consumption [kg/s or kg/t or kg/MWh]
CFB	Circulating fluidised bed	$e_{CO2,eq}$	Equivalent CO_2 emissions of the cement plant [kg/s or kg/t]
$CF_{process}$	Process contingency factor	F_0	Molar flow of $CaCO_3$ in the preheated raw meal entering the calciner [kmol/s]
$CF_{project}$	Project contingency factor	F_R	Sorbent molar flow from the calciner to the carbonator [kmol/s]
COC	Cost of clinker	F_{CO2}	Molar flow of CO_2 entering the carbonator [kmol/s]
CPU	CO_2 purification unit	m	Mass flow rate [kg/s or tpd]
DS	Direct Separation	Pe	Electric power [MW_e/tclk]
EC	Equipment cost	q	Direct fuel consumption in the cement plant [MJ_{HHV}/t clk]
ECRA	European Cement and Research Academy	q_{clk}	Direct specific primary energy consumption [MJ_{HHV}/t clk]
ESP	Electrostatic precipitator	$q_{el, clk}$	Indirect fuel consumption associated to power consumption [MJ_{HHV}/t clk]
HHV	High heating value	$q_{clk, eq}$	Equivalent fuel consumption of the cement plant [MJ_{HHV}/t clk]
HRSG	heat recovery steam generation	*Greek letters*	
ID	Induced draft	η_{el}	Electric efficiency
IH-CCL	Indirect-heated calcium carbonate looping	*Subscripts*	
INCF	Indirect cost factor	cem	Cement
OCF	Owner's cost factor	clk	Clinker
Opex	Operating expenditure	e	Electric
Oxy-CCL	Oxy-fuel combustion calcium carbonate looping	eq	Equivalent
PCC	Post combustion capture	th	Thermal
ref	Reference		

1 Introduction

1.1 Background

The global climate system is showing unequivocal signs of warming, leading to significantly adverse impacts on natural systems (e.g. water cycle and ecosystems) and human activities (e.g. agriculture and human health). The soaring concentrations of greenhouse gases have been linked to global warming: CO_2 is the anthropogenic emission that makes the largest contribution.[1, 2]

Since the beginning of the Industrial Revolution, the CO_2 concentration in the atmosphere has increased from 280 ppm to 400 ppm, and is expected to reach 500 ppm by 2050 even if CO_2 emissions are stable for the next few decades.[3] Nearly 44% of CO_2 emissions are emitted from the processing of fossil fuels (e.g. coal and natural gas) to generate electricity. Unfortunately due to the increasing demands for more energy intensive lifestyles and growing population, fossil fuels would still be the dominant source as other energy sources (e.g. biomass-based fuels, solar energy and nuclear energy), which are CO_2 neutral or do not emit CO_2, still cannot replace fossil fuels on a large scale in a short term.[4] Therefore, it is necessary that any CO_2 mitigation strategy accounts for continued use of fossil fuels.

The cement industry is a major source of industrial CO_2 emissions. Globally, ~4 billion tonnes of cement were produced in 2015, contributing to around 8% of global CO_2 emissions.[5] In Australia, cement production was ~10.4 million tonnes in 2018-19 with 5.1 million tonnes CO_2-e emissions.[6] Australian cement production has been building steadily since the Global Financial Crisis in 2007-08 before reaching record levels in 2018-19 – primarily on the back of growing demand from major infrastructure projects and the construction market in general.[6]

The manufacture of cement involves the decomposition of limestone, complex solid reactions and fuel combustion. The limestone decomposition and fuel combustion are two main sources of CO_2 emissions from the cement production process. In an Australian context, around 60% of the total CO_2 emissions comes from limestone decomposition, 30% from fuel combustion, and the remaining 10% from the consumption of electricity across the facilities.[6]

Recognising the challenge that a changing climate poses to the natural environment, the Australian cement industry has been taking actions in reducing its energy consumption and CO_2 emissions through a variety of different techniques, including but not limited to: (1) increased energy efficiency; (2) utilisation of alternative fuels; (3) application of alternative raw materials; and (4) a lower clinker/cement ratio. As a result, the emissions intensity of cement manufacturing expressed in terms of total CO_2 emissions per tonne of clinker produced on site in 2018-2019 is 17% lower than the level in 2010-11.[6] These techniques will only be able to partly contribute to the emission reductions required to meet global climate change goals. In a carbon constrained future, carbon capture, utilisation and sequestration (CCUS) will be required and has the potential to achieve the reduction in global CO_2 emissions of 50-80% by 2050.[7]

The application of carbon capture technologies in the cement industry is at an early stage of development. CO_2 capture technologies being studied in the cement industry include the direct separation (DS) technology, calcium carbonate looping (CCL), oxyfuel and post-combustion capture (PCC). The DS technology was proposed by Calix and employs a specifically designed reactor to replace the traditional pre-calciner, where limestone is decomposed in steam and the resulting pure CO_2 can be captured. However, the CO_2 from fuel combustion in the rotary kiln and the DS reactor

is not captured.[8] PCC where CO_2 is separated from flue gases could be applied to both greenfield construction and to retrofit existing plants. Oxyfuel, where fuel is burnt in oxygen to produce a CO_2 rich exhaust stream, presents a relatively lower cost of CO_2 avoided, but requires extensive retrofitting to the kiln system.[9] Current PCC technologies being investigated include chemical absorption, adsorption, membrane, and mineralisation. There are only a few pilot-scale research developments for CO_2 capture from cement production worldwide, with none of them in Australia.

Among the CO_2 capture technologies, CCL has been seen as a next generation CO_2 capture technology and attracted significant R&D interests over the past two decades, due to a number of advantages including (1) abundant, cheap and environmentally benign raw materials (i.e. limestone); (2) high sorption capacity of CO_2; (3) lower energy consumption with additional steam cycle driving; (4) no need for flue gas pre-treatment; and (5) synergies with cement manufacture. The conventional CCL process exploits the reaction that takes place at medium temperatures (650-700°C) between CaO and CO_2 to form $CaCO_3$ which can be reversed at higher temperatures (900-950°C) to release a CO_2 stream of high purity in an oxy-fired atmosphere. The oxy-fired CCL (Oxy-CCL) technology has been demonstrated through several pilot-scale Oxy-CCL plants worldwide. To date, most of the research in the CCL technology is associated with the CO_2 capture from coal-fired power plant flue gases. Very limited research into the practicalities of integrating the CCL process with a cement plant has been published. On the other hand, Oxy-CCL is still an energy- and capital-intensive process, with a significant portion of energy consumption and Capex associated with the air separation unit (ASU) required for oxy-fired combustion. It is still imperative to improve the commercial viability of the CCL technology.

In Australia, it is expected that the domestic cement demand will remain steady in the future.[6] Hence, it is unlikely that new cement plants will be built in the near future. Under such a context, deep CO_2 emissions reduction from the cement industry can be achieved by retrofitting the CCL process to existing cement plants.

1.2 Project Description

This project aims to carry out a techno-economic feasibility study of retrofitting a novel CCL process to an existing cement plant for reducing CO_2 emissions. The reference cement plant is based on a dry process with 4 stages of pre-heaters, a pre-calciner and a rotary kiln with a clinker production of 184 t/h. Specific objectives of this project are:

- Technology survey of CO_2 capture technologies being studied in the cement industry and overview of pilot development of CCL;
- Site investigation to collect relevant technical information and understand its current operation; and
- Techno-economic feasibility assessment to understand the technical feasibility and economic costs and CO_2 emissions reduction.

1.3 Project Status

Table 1 lists all the milestones, their status, and brief descriptions of achievements. Overall, all the milestones have been successfully completed on budget. The project activities for each milestone are described in detail in the following chapters.

Table 1: Project status summary

Milestone ID	Milestone Title	Status (%)	Relevance to project and achievement
1	Technology survey	100	Technology surveys of the state-of-the-art R&D in CO_2 capture in the cement industry (this is out of the original scope) and pilot-scale CCL plants were carried out. Better understanding of the latest technological development in CO_2 capture and the development of CCL technology in the cement industry were achieved.
2	Site investigation	100	Site investigation was successfully carried out with relevant operating data and technical information collected, which were used to assess the retrofitability and perform the techno-economic assessment.
3	Techno-economic feasibility assessment	100	A thorough techno-economic feasibility assessment was successfully performed. A novel CCL process that avoids the energy- and capital-intensive ASU was successfully developed and showed potential to reduce the energy consumption. The novel CCL process was then retrofitted to the reference cement plant through three different configurations. Based on the techno-economic assessment results, the tail-end integration and full integration cases showed lower SPECCA (Specific Primary Energy Consumption for CO_2 Avoided) and cost of CO_2 avoided compared to other CO_2 capture technologies.
4	Management and reporting	100	Final report successfully completed.

2 Technology survey of CO_2 capture in the cement industry

Technology surveys were carried out in this chapter to better understand the current cement manufacture process and the state-of-the-art R&D in CO_2 capture from the cement industry. Then the development of the conventional Oxy-CCL technology, as a promising next generation CO_2 capture technology, was reviewed, with a focus on a number of pilot-scale CCL plants erected worldwide.

2.1 State-of-the-art of CO_2 capture in the cement industry

2.1.1 The cement manufacture process

Cement is a binding material used for construction that sets, hardens and adheres to other materials (i.e. fine and coarse aggregates, and water) to form aggregate. Although it has different types, modern cement is often referred to as hydraulic cement, such as Portland cement. Cement is made of a mixture of silicates and oxides, as shown in Table 2.

Table 2: The primary constituents of cement clinker [10]

Constituent	Formula	Weight percentage, %		
		Min	Average	Max
Tricalcium silicate (Alite)	Ca_3SiO_5 or $3CaO \cdot SiO_2$	45	62	75
Dicalcium silicate (Belite)	Ca_2SiO_4 or $2CaO \cdot SiO_2$	5	15	35
Tricalcium aluminate (Aluminate)	$Ca_3Al_2O_6$ or $3CaO \cdot Al_2O_3$	4	11	15
Tetracalcium aluminferrite (Ferrite)	$Ca_4Al_2Fe_2O_{10}$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	4	8	15
Free calcium oxide	CaO	0.1	1	4
Free magnesium oxide	MgO	0.5	1.5	4.5

The production of cement accelerated rapidly worldwide after World War II, reaching 4 billion tonnes in 2015[11], and is expected to continue to increase to more than 5.5 billion tonnes by 2030.[12] However, the increase in cement production is more likely to occur in those developing countries due to the increasing demand and cheaper resources.

The manufacture of cement is a three-step process,[13] including:

- Raw material preparation: grinding a mixture of raw materials to make a 'raw meal';
- Clinker production: heating the raw meal to a sintering temperature of >1400°C in a cement kiln to produce 'clinker'; and
- Cement production: grinding the resulting clinker with gypsum and other additives to make cement.

The most common raw materials used for cement manufacture include limestone, marls and clay, although other raw materials with similar compositions can be used. During the process, significant amounts of carbon dioxide (CO_2) are released from limestone decomposition and fuel combustion.

The average emissions intensity of Australian cement manufacturing was 0.77 t CO_2-e/t cement in 2018-19.[6]

There are four main process routes for the manufacture of cement:[10, 13]

- The dry process, in which the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln;
- The semi-dry process, in which the dry raw meal is pelletised with water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses;
- The semi-wet process, in which the slurry is first dewatered in filter presses. The resulting filter cake is extruded into pellets and then fed either to a grate preheater or directly to a filter cake dryer for raw meal production; and
- The wet process, in which the raw materials (often with a high moisture content) are ground in water to form a pumpable slurry. The slurry then is either fed directly into the kiln or first to a slurry dryer.

The choice of process is, to a large extent, determined by the state of the raw materials (dry or wet). Although a large part of global clinker production is still based on wet processes, the dry process is generally the more efficient, energy saving and lower carbon intensive option. In Europe, more than 90% of cement production is based on dry processes due to the availability of dry raw materials. In Australia around 98% of clinker is produced using highly efficient dry processes.[6]

The dry cement manufacture process typically employs a kiln system consisting of various stages of preheaters, and/or a pre-calciner, and a rotary kiln, in which the raw materials are preheated and burnt at high temperatures to produce clinker. The main types of kiln systems are: (a) kiln without pre-heater; (b) kiln with pre-heater; (c) kiln with both pre-heaters and a pre-calciner. Pre-heaters are a series of vertical cyclones in which the raw material is passed in counter-flow with exhaust gases from rotary kiln and/or pre-calciner so that heat is transferred from the hot gas to the raw material, which is therefore preheated and even partially or fully calcined before entering the rotary kiln. Most common pre-heater kilns have between 4 and 6 cyclone stages. The kiln is usually equipped with a cooler to cool down clinker with air. Part of the exhaust air of temperature at 1,000°C is recirculated to the pre-calciner through a tertiary air duct for fuel combustion. The higher the number of cyclone stages, the more heat is recovered.[14] Also, it should be noted that most of the CO_2 capture studies in cement plants is based on the European Best Available Technology (BAT) dry process with 5 cyclone stages and a pre-calciner, as shown in Figure 1.
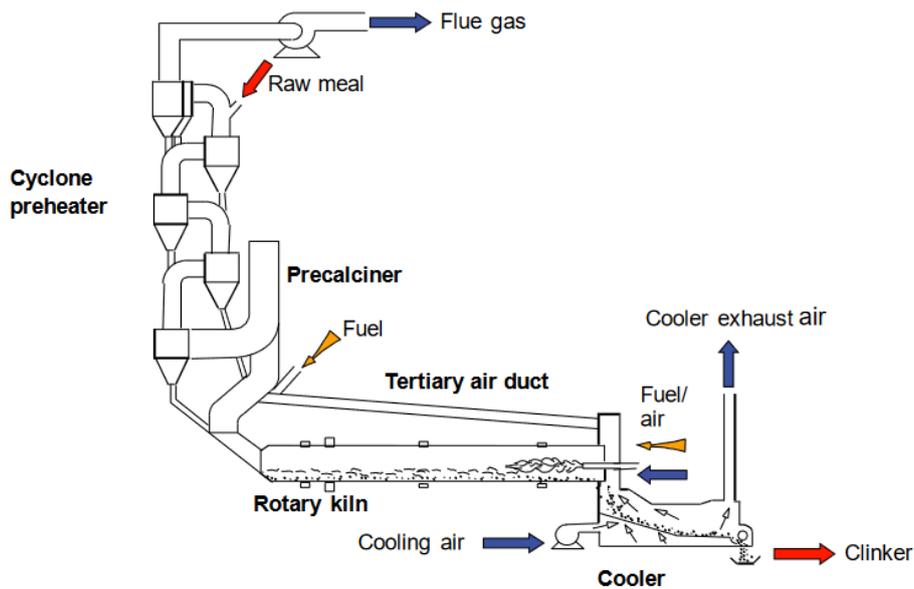
Figure 1: Principle of an European BAT standard dry process cement plant[15]

The production of clinker involves complex solid reactions over a wide temperature range, as shown in Table 3. In the dry process, it is generally accepted that limestone decomposes to a significant extent in the pre-calciner before entering the rotary kiln. The resulting CaO then reacts with SiO_2, Al_2O_3 and Fe_2O_3 in the rotary kiln to form clinker.

Table 3: Chemical reactions in clinker formation [16, 17]

Chemical reaction	Temperature required, ºC	Enthalpy changes (25ºC) ΔH, kJ/kg solid products
$CaCO_3=CaO+CO_2$	600-900	+2964
$2CaO+SiO_2=2CaO·SiO_2$	600-1300	-603
$2CaO·SiO_2+CaO=3CaO·SiO_2$	1350-1450	-448
$3CaO+Al_2O_3=3CaO·Al_2O_3$	800-1300	-37
$4CaO+Al_2O_3+Fe_2O_3=4CaO·Al_2O_3·Fe_2O_3$	1200-1300	-109

2.1.2 R&D activities in CO_2 capture in the cement industry

The cement industry has been showing increased interest in CO_2 capture technologies in recent years, especially in Europe where the European Cement Research Academy (ECRA) has been actively carrying out CCUS research since 2007.[18] CO_2 capture from cement plants is still at an early stage of development, compared to the extensive R&D activities in power plants. In general, CO_2 capture technologies are categorised into: (1) pre-combustion capture, (2) post-combustion capture, and (3) oxy-fired combustion capture. Different to power plants where CO_2 emissions are from fuel combustion only, the cement production process has two main sources of CO_2 emissions from fuel combustion and limestone decomposition. Therefore, a significant disadvantage of pre-combustion capture is due to the fact that only the CO_2 from fuel combustion would be captured. This means that about 60% of total CO_2 emissions from cement industry would remain unbated.[15] Therefore, pre-combustion capture is not further discussed here.

Table 4 presents the worldwide R&D activities in CO_2 capture from the cement industry. It can be clearly seen that the European cement and R&D community has been a major driving force for progressing the CO_2 capture technologies in the cement industry.

Table 4: Worldwide R&D activities in CO_2 capture in the cement industry

Project	Technology provider	Location	Technology	Scale	Fund	Duration	Ref.
ECRA CCS	ECRA	Europe	PCC	Research study	€1.4m	2007-22	9, 18
			Oxy-fuel				
Norcem CO_2 capture	Aker Clean carbon	Norway	Chemical absorption	Pilot	€12.5m	2013-16	19
	RTI		Adsorption	Small pilot-scale			
	DNV GL/NTNU/Yodfat		Membranes	Small pilot-scale trial			
	ALSTOM		Calcium looping	De-risking study			
LEILAC	Calix	Belgium	Direct separation	10tph CO_2 demonstration plant	€12m	2016-20	8, 20, 21
CEMCAP	GE power Sweden/ETHZ	Europe	Chilled ammonia process	1 ton/day pilot plant	€10m	2015-18	18, 22, 23
	SINTEF Energy Research/TNO		Membrane-assisted liquefaction				
	Politecnico di Milano/CSIC/University of Stuttgart (IFK)		CCL-tail-end configuration	Demonstration in an industrial environment			
CLEANKER	13 research organizations from seven countries	Europe	CCL-integrated configuration	Advance the TRL to 7	€9.2m	2017-21	18, 24
SkyMine	Skyonic Corp	USA	Mineralisation by "SkyMine®"	Pilot plant 75,000tpa CO_2	USD$23m	2010-15	25
Calera	Calera Corporation	USA	Mineralisation by aqueous precipitation	Pilot plant 1tpd CO_2	USD$22m	2010-14	26-28
HECLOT	ITRI/Taiwan Cement Corp.	Taiwan	CCL	1.9MW$_{th}$ pilot plant	--	--	29, 30
Baimashan CCS	Anhui Conch Cement Company	China	Amine scrubbing	50,000 tpa CO_2 capture plant	CNY50m	2015-	31

ECRA CCS project

ECRA was founded in 2003 as a platform upon which the cement industry supports, organises and undertakes research activities in the context of the production of cement and its application in concrete. ECRA has been working on carbon capture research since 2007 in a long-term project designed to examine the capture of CO_2 as a prerequisite for the safe geological storage of CO_2. ECRA's CCS project comprises the following six phases:[18]

- Phase I: Literature study (January -June 2007);
- Phase II: Study about technical and financial aspects of CCS projects, concentrating on oxyfuel and post-combustion technology (2007 –2009);
- Phase III: Laboratory-scale / small-scale research activities (2009 –2011)
- Phase IV: Prepare pilot plant (2012-2015);
- Phase V Build and operate pilot plant (time-frame: 3-5 years)
- Phase VI: Demonstration plant (time-frame: 3-5 years)

Phases I, II, III, and IV have been completed. Built on the previous research outcomes, ECRA is planning an industrial-scale oxyfuel kiln.[32]

Norcem CO_2 capture project

The Norcem CO_2 capture project in Norway aims to test four various PCC technologies on real cement conditions. The technologies studied are:

- Solid sorbent technology by RTI
- Amine technology by Aker Solutions
- Membrane technologies by a consortium under the lead of the Norwegian University of Science and Technology (NTNU)
- Calcium carbonate looping by Alstom Power

CEMCAP project

CAMCAP is a project funded by the European Union (EU) Horizon 2020 Programme addressing CO_2 capture from cement production by the demonstration of different CO_2 capture technologies in an industrially relevant environment (TRL 6) based on the previous work of ECRA and Norcem.[18] CO_2 capture technologies studied in this project include:[33]

- Chilled ammonia process (CAP)
- Membrane-assisted liquefaction (MAL)
- Calcium carbonate looping-tail-end configuration

CLEANKER project

CLEANKER started in 2017 and is also funded by the EU's Horizon 2020 Programme. It addresses CO_2 capture from cement production by demonstrating the CCL technology in the cement plant, aiming to achieve a TRL of 7.[24] This project is focused on the full integration configuration.

LEILAC project

The LEILAC (Low Emissions Intensity Lime and Cement) project funded by the EU is testing the Direct Separation technology (not a CCL process) invented by Calix Australia at a cement plant in Belgium. A pilot plant with a capacity of 240tpd cement raw meal is being erected.[8, 21] It should be noted that an European BAT cement plant has a capacity of 4,500tpd raw meal for producing 2,900tpd clinker.

SkyMine project

The SkyMine project was mainly funded by the US Department of Energy (DoE) and managed by the Skyonic Corporation (now known as Carbonfree Chemicals), aiming to demonstrate its patented SkyMine® process to remove CO_2 from industrial waste streams and generate saleable carbonate and/or bicarbonate materials. The project consisted of two phases, resulting in a commercial scale pilot plant to directly capture 75,000tpa CO_2 and produce various chemicals, such as Hydrochloric Acid, Sodium Bicarbonate, etc.[25]

Calera project

The Calera project was also mainly funded by the US DoE and managed by the Calera Corporation, aiming to demonstrate an innovative process to directly mineralise CO_2 in flue gases to carbonates and convert them to construction materials, such as aggregates and cementitious substitutes. The process used a novel membrane electrolysis process to produce sodium hydroxide for use in a CO_2 absorber. A CO_2 Conversion to Material Products (CCMP) pilot plant was constructed and operated to capture and convert 1 tpd CO_2 into stable construction materials.[26-28]

HECLOT project

Taiwan's Industrial Technology Research Institute (ITRI) developed a High Efficiency Calcium Looping Technology (HECLOT) and demonstrated through a 1.9MWth pilot plant that was erected in 2013 for CO_2 capture from cement plants. This is currently the largest CCL demonstration project.[29, 30]

Baimashan CCS project

The Anhui Conch Cement Company commenced the Baimashan CCS project in 2015. A commercial scale pilot plant using the amine technology was constructed in 2017 to capture 50,000 tpa CO_2 from the Baimashan cement factory.[31]

2.1.3   Overview of CO_2 capture technologies in the cement industry

Through the projects as summarised in Section 2.1.2, the following CO_2 capture technologies have been or are being studied for decarbonising the cement production:

- Oxyfuel technology
- Chemical absorption (e.g. amine scrubbing, chilled ammonia process)
- Membrane technologies
- Adsorption technologies
- Mineralisation
- Direct separation
- Calcium carbonate looping (CCL) process

The principles and current development status of these technologies are overviewed in the following section.

Oxyfuel technology

Oxyfuel, as shown in Figure 2, uses pure oxygen from an ASU instead of air for fuel combustion and results in a comparatively pure CO_2 stream. To maintain an appropriate flame temperature, a certain amount of flue gas has to be recirculated. This integrated system would have a huge impact on the clinker burning process, mainly an energy shift caused by the different gas properties as well as the ratio between the enthalpy flow of the kiln gas and the energy needed for the preheating of the kiln feed. In an optimised operation, this influence and the variable oxygen concentration could even benefit the clinker burning process by increasing its thermal energy efficiency. There are some experiences from cement kilns which were operated with oxygen enrichment (to increase the production capacity or enhance the use of alternative fuels).[34] Furthermore, oxyfuel has been investigated at power plants in recent years, so that some of the results obtained may be transferrable to cement kilns.[35] Nevertheless, there is a need for further research before the technology can be applied on an industrial-scale. Due to its advantages of improving energy demand compared to other capture methods the oxyfuel technology is seen as a long-term prospect. ECRA has planned to implement the oxyfuel technology at full scale in two cement plants in Europe.[18]
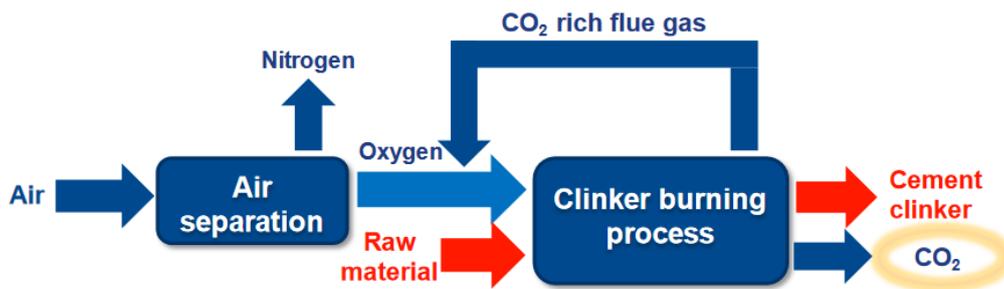
Figure 2: Oxyfuel technology with flue gas recirculation[10]

Chemical absorption

Chemical absorption is the leading technology and commercially proven method for flue gas CO_2 capture. The chemical solvents (e.g. amines), however, have some issues such as the secondary environmental impact to be addressed. Amine scrubbing has been established for over many decades in the chemical and oil industries, for removal of hydrogen sulphide and CO_2 from gas streams. This experience is largely on natural gas streams and/or with chemically reducing (primarily oxygen deficient) gases but there are several facilities in which amines are used to capture CO_2 from flue gas streams today. As a typical end-of-pipe technology, a retrofit to existing cement kilns would be feasible. High CO_2 recovery rates of up to 98% can be achieved with a purity of > 99%. Typically, prior to the CO_2 removal stage, the flue gas from the stack is cooled and treated to reduce the levels of particulates and other impurities, such as NO_x, SO_x and O_2. The pre-treatment system could be complex and expensive depending on the flue gas characteristics. Afterwards the scrubbing process is carried out as follows, as shown in Figure 3.[9, 36]

- An aqueous alkanolamine solution is contacted in an absorber column with CO_2 containing flue gas from combustion processes;
- The basic amine reacts with the acidic CO_2 vapours to form a dissolved salt. The purified flue gas exits the absorber;
- The CO_2 rich amine solution is regenerated in a stripper column (desorber), where the pressure is reduced and/or the temperature increased to roughly 120°C in order to release the CO_2 and to yield a concentrated gas stream; and
- Lean solution is cooled and returned to the absorber so that the process is repeated in a closed loop.
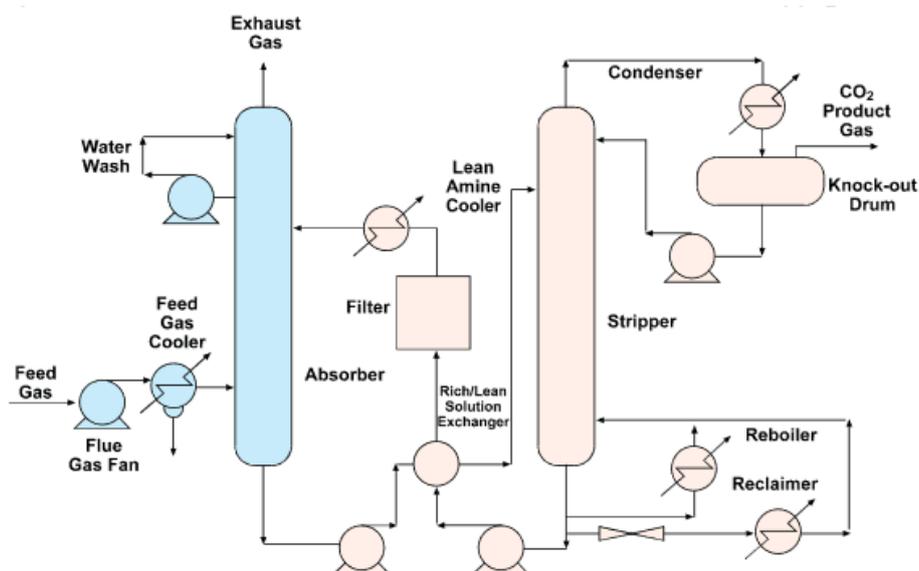
Figure 3: Schematic diagram of CO$_2$ capture with chemical solvents[36]

Commercially available solvents may be grouped into 'first generation' and 'second generation' solvent systems. Solvents of the first generation are binary mixtures of water and amine or water and inorganic salt as monoethanolamine (MEA), diethanolamine (DEA), triethanol-amine (TEA) or potassium carbonate (K$_2$CO$_3$). While especially MEA still plays an important role, blended alkanolamines (second generation solvents) are used to increase the absorption rate constant and to lower the regeneration energy.[37] Ammonia is another solvent that has gained significant R&D focus, due to the advantage over amines with respect to high absorption capacity, oxidative resistance and thermal degradation. However, ammonia losses can be large due to its high vapor pressure. In general, one of the main disadvantages associated with chemical absorption is high energy demand for solvent regeneration and the very large equipment sizes.[34, 37]

As part of the Norcem CCS project, Aker Solutions' Mobile Test Unit (MTU) was installed at Norcem's cement plant, as shown in Figure 4. The MTU is a custom-built mobile test CO$_2$ capture facility, based on a conventional amine absorption/desorption process with full packing height absorber and desorber columns. Several novel features are installed such as Aker Solutions' ACCTM Energy Saver, Anti-Mist Design and Emission Control technology. The MTU was also equipped with an electrically powered reboiler, which allows for accurate quantification of the energy consumption. A tie-in point was installed on Norcem's flue gas duct just before the flue gas enters the stack, i.e. downstream of all existing emission control devices, including a Selective Non-Catalytic Reduction (SNCR) unit, an Electrostatic Precipitator (ESP), a Flue Gas Desulfurisation (FGD) unit and a bag house filter. The MTU can be fed with a slip stream of flue gas from the cement kiln of up to 1,000 Sm^3/h.[38] Aker Solutions operated its MTU from May to Nov 2014. After around 2,700 h of operations, the proprietary amine-based solvent 'S26' employed in this test showed a low build-up of degradation products and stable performance above 90% capture. Aker Solutions presented heat requirements for solvent regeneration as low as 2.7 MJ/kg CO$_2$ with 90% capture, expecting a further reduction down to 2 MJ/kg CO$_2$ when heat integration with CO$_2$ compression is enabled. The testing had been extended till September 2015 and the MTU has achieved 5,500 h of operation without solvent reclaiming by the date of reporting in 2015.[39]

Figure 4: The Aker Solution's MTU installed at Norcem's cement plant[39]

The largest carbon capture demonstration plant using amine scrubbing for the cement sector is located at Baimashan Cement Factory in Wuhu China, as listed in Table 4. The construction commenced in October 2017 and the plant shown in Figure 5 started operation in October 2018.[31] The plant performance has not yet been reported.

Figure 5: The 50,000 tpa amine-based CO_2 capture plant in China[31]

Membrane technology

Membrane technology, as shown in Figure 6, is a physical separation process where gas mixtures consisting of two or more components are separated by a semipermeable barrier into a retentate stream and a permeate stream. One of the main advantages of membrane separation over other

technologies is that no regeneration is required. The membrane system is also compact, modular, and flexible in operation and maintenance.[9,40,41]
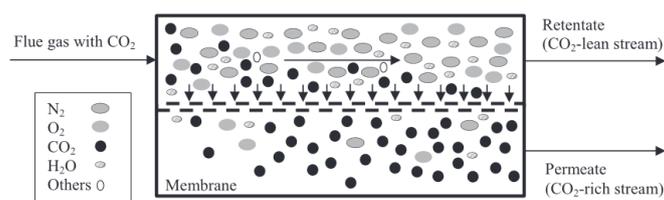
Figure 6: Schematic diagram of membrane-based CO_2 separation process from flue gas streams[40]

A number of solid polymer membranes are commercially available for CO_2 separation, primarily for natural gas sweetening. The driving force for the separation is the CO_2 partial pressure difference across the membrane, which is favoured in the cement industry as the flue gas from the cement manufacture process contains higher CO_2 than power plants. To this end, compression or vacuum or combined is required to provide the driving force for permeation. However, there are still challenges on the application of membranes for CO_2 capture related to (1) the limitation of membrane separation performance (the trade-off between gas permeance and selectivity of most polymeric membranes) and (2) the poor membrane stability and short lifetime when exposd to a gas stream containing the impurities of acid gases such as SO_2 and NOx.[42]

As part of the Norcem project, the three partners DNV GL (previously known as KEMA), NTNU, and Yodfat Engineers joined forces to develop a membrane technology for cement application. In the project, (1) DNV GL was responsible for the modelling and holds the partner coordination role, (2) NTNU was responsible for the membrane production and carried out the planned test programme, and 3) Yodfat Engineers was responsible for the design and construction of the test pilot. A one stage membrane module was deployed where handmade poly-vinyl-amine based, fixed-site carrier (FSC) membranes, produced as flat sheets, were placed in 12 cassettes inside the membrane module (two sheets in each cassette). The total membrane area was approximately 1.5 m^2. A 6-month test program was carried out to treat a 17% (wet basis) CO_2 flue gas in a cement factory. The test results revealed that it was difficult to achieve a stable operation, and that a CO_2 purity up to 72% was achieved for short periods when all process parameters were well controlled in the single stage FSC membrane system.[43] It should also be noted that proper pre-treatment processes (e.g., particle filtering, water condensation) were always required to protect the membrane system for CO_2 capture in the cement factory.[44]

Adsorption technology

CO_2 capture by adsorption is in general referring to the use of solid adsorbents, such as activated carbons, zeolites and meso-porous silicates, alumina, metal oxides, etc. Adsorption processes operate on a repeated cycle with the basic steps being adsorption and regeneration.[45] In the adsorption step, gas is fed to a bed of solids that adsorbs CO_2 and allows other gases to pass through. When a bed becomes fully saturated with CO_2, the feed gas is switched to another clean adsorption bed and the fully saturated bed is regenerated to remove the CO_2. On account of industrial application, an effective and less energy-consuming regeneration of the CO_2 captured adsorbents needs to be developed. The regeneration techniques include (1) pressure swing adsorption (PSA), (2) vacuum swing adsorption (VSA), (3) temperature swing adsorption (TSA), (4) electric swing adsorption (ESA), the increase of temperature by conducting electricity through the conductive adsorbents; (5) pressure and temperature hybrid process (PTSA), and (6) washing.[46] Among these regeneration options, pressure swing is now a widely accepted and commercial technology for a

number of applications. It is generally accepted that the regeneration step is the most energy intensive part of the adsorption process.[47]

As part of the Norcem CCS project, the US company, Research Triangle Institute (RTI) was tasked with demonstrating their advanced solid sorbent technology at the Norcem's cement plant, as shown in Figure 7a. The RTI solid sorbent technology is based on a cyclic, thermal swing, absorption-desorption CO_2 capture process using a CO_2-philic poly-amine based sorbent.[19,48] To ensure efficient heat management in the CO_2 absorber (removal) and sorbent regenerator (addition), a fluidised, moving-bed arrangement was employed, as shown in Figure 7b. The fluidised bed adsorption/desorption process was tested with actual cement plant flue gases at a sorbent circulation rate of 100 kg/h and CO_2 capture rate of 0.11tpd.[49] The prototype system was operated for >150 h of CO_2 capture experimentation with a steady CO_2 capture rate in the range of 80-90% at baseline conditions.[48]
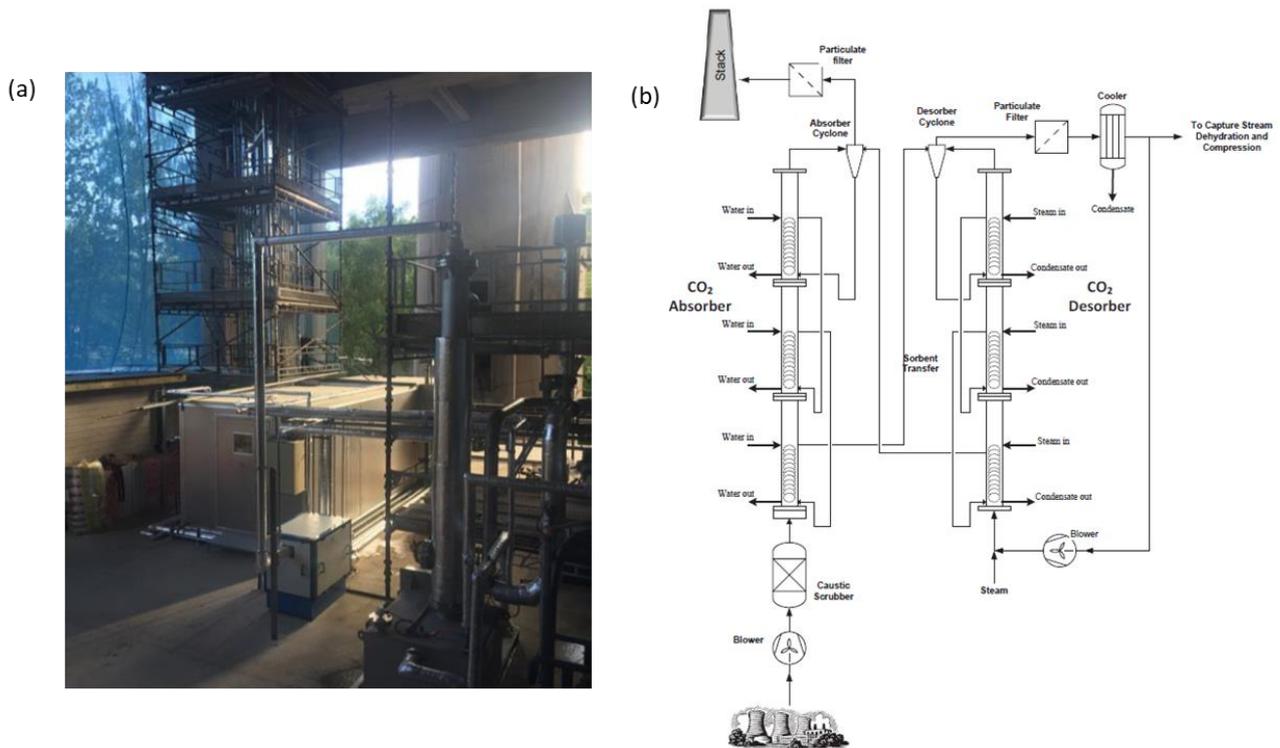
Figure 7: (a) RTI's prototype solid sorbent CO_2 capture test unit installed at Norcem's cement plant, (b) its flow diagram[48]

Mineralisation – SkyMine® process

The SkyMine® technology is developed by Skyonic (now known as Carbonfree Chemicals).[50] The SkyMine® technology has been developed at a commercial-scale pilot plant at the Capitol Aggregates, Ltd., cement plant in San Antonio, Texas, U.S. As shown in Figure 8, salt and water are electrolysed in this process to produce hydrogen and chlorine gases and sodium hydroxide solution, which is reacted with CO_2 in flue gas to produce sodium bicarbonate. Sodium bicarbonate has many uses and can be sold on the market.[51] This plant is expected to directly remove CO_2 (~75,000tpa) from industrial waste streams through co-generation of carbonate and/or bicarbonate materials (~143,000tpa) for use in bio-algae applications to become a profitable process. In addition to capturing and mineralising CO_2, the SkyMine® process can remove SOx, NO_2 and heavy metals such as mercury from existing power plants and industrial plants.[25]
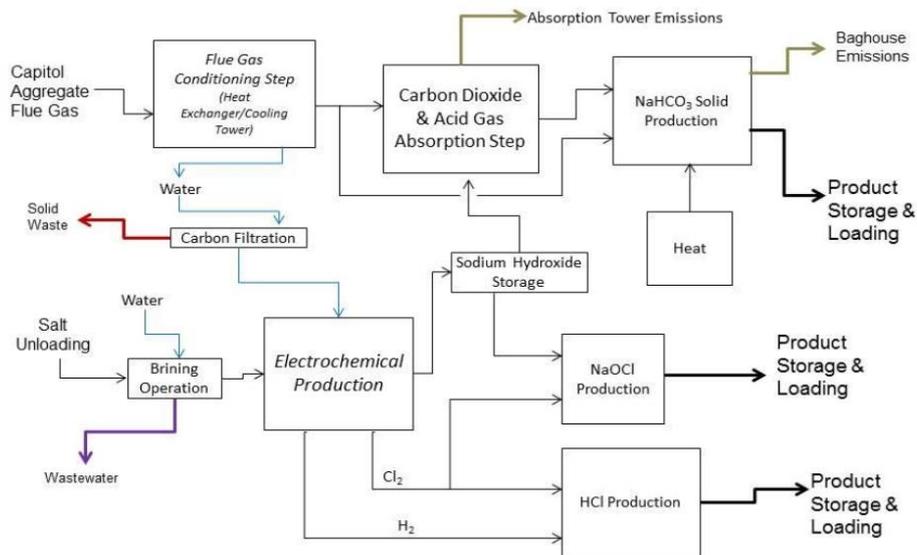
Figure 8: Schematic diagram of the SkyMine process[25]

Mineralisation-Calera process

The idea of the Calera process is that CO_2 is bound into a product called 'calcium carbonate cement'. The process imitates the formation of 'marine cement' by corals which takes calcium and magnesium from the seawater to build their shells and reefs. It is claimed that for every tonne of 'cement', half a tonne of CO_2 is sequestered, so that it would be an effective measure for CO_2 capture and storage. To produce the 'calcium carbonate cement', only seawater and flue gas containing CO_2 is needed. The waste heat of the flue gas is used for drying the resulting slurry. The final product is calcium carbonate. Calera Corporation has designed, constructed and operated two pilot plants to utilise the flue gas from coal-fired power plants to produce calcium carbonate. The flue gas is contacted in a scrubber with an aqueous alkaline solution that effectively removes the CO_2 (capture step) and a calcium source that results in the formation of the calcium carbonate product.[27, 52]

Direct separation

Figure 9 shows the overall concept of the LEILAC project, which focuses on the development of Calix's Direct Separation (DS) technology. The outside of the calciner tube is heated, in the case of the pilot by natural-gas fuelled burners. Limestone or cement raw meal enters the calciner tube and the particles are heated by both conductive and radiative heat transfer from the reactor wall, causing them to calcine. The particles and released CO_2 continue to make their way down the calciner. At the base the solids and gases are separated. By keeping the process gases separate from the flue gas stream, pure CO_2 (in the case of pure limestone) can be captured.

The pilot plant is being erected at HeidelbergCement Group's Lixhe cement plant in Belgium. Once constructed, the pilot is expected to have a capacity of 240 t/d cement raw meal or 190 t/d limestone. It is planned to run the plant for around two years, carrying out a range of tests. The quality of the CO_2 separated will be assessed, though it is currently planned to be subsequently released. Investigating the impact on the resulting cement and lime products will be an important finding of the project. Compared to other CO_2 capture technologies, the DS technology does have a lower overall CO_2 capture rate as only the CO_2 from limestone decomposition is captured.[8, 20, 21] To increase the overall CO_2 capture rate, an additional CO_2 capture process must be employed to capture CO_2 from fuel combustion.
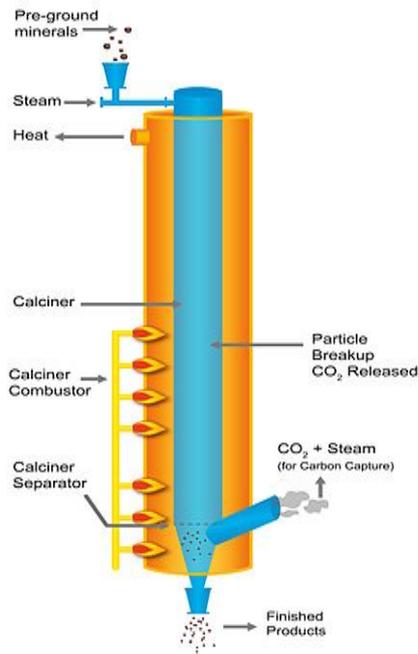
Figure 9: A design concept of the LEILAC direct separation reactor[8]

Calcium carbonate looping

The schematic diagram of the CCL process is shown in Figure 10. It employs the cyclic carbonation and calcination reactions between CaO and CO_2 as expressed in the following equation:

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \qquad \Delta H_{r,298K} = -178 \; kJ/mol \qquad (1)$$
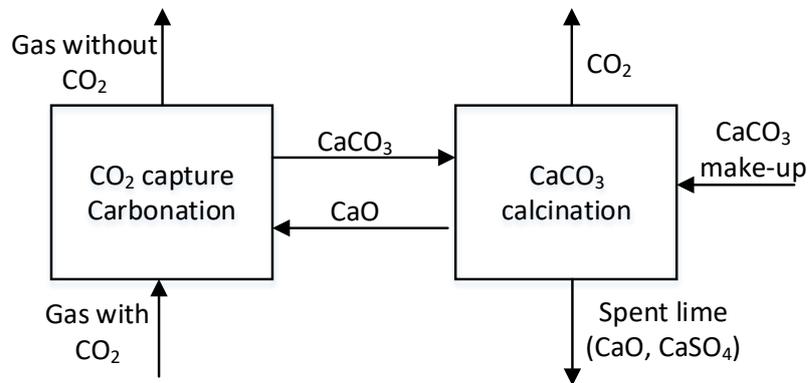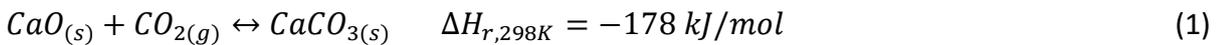
Figure 10: Schematic diagram of a typical calcium carbonate looping process

The carbonation reaction takes place at medium temperatures while the calcination reaction occurs at higher temperatures to release CO_2. To obtain high purity CO_2 from $CaCO_3$ decomposition, oxy-fired combustion is proposed to provide external energy required for the calcination. Due to the high CO_2 partial pressure, the calcination reaction is usually performed in the temperature range of 900-950°C. Critically, the external energy input can be partially recovered by driving additional high temperature steam cycles via utilising the reaction heat released from the carbonation of CaO and CO_2. Due to the loss-in-capacity of sorbents in CO_2 capture, a make-up flow of fresh limestone is usually required to maintain the chemical activity.

The conventional Oxy-CCL process is the most studied configuration and is accomplished in two interconnected moving or fluidised-bed reactors, although other types of reactors and configurations are also feasible for implementing the CCL process, such as the alternating packed bed reactors and the rotating reactor.[55, 56]

Technology summary

The current carbon capture technologies as introduced in Section 2.1.3 have been demonstrated to various extent. Among them, the conventional Oxy-CCL process has attracted significant R&D interests over the past two decades, due to the following advantages:

- Abundant, cheap and environmentally benign raw materials

  The CCL process uses natural materials (i.e. limestone) as CO_2 sorbents, which are abundant, cheap, and environmentally benign. Other PCC technologies, such as amine scrubbing, use expensive materials and may cause secondary environmental problems.

- High sorption capacity of CO_2

  Theoretically, CaO has a very high CO_2 capture capacity (i.e. 0.79 kg CO_2/kg CaO), leading to smaller reactors and thus lower upfront investment. Although the CO_2 capture capacity decreases over a few cycles, a make up flow of fresh materials can be employed to maintain the activity. Due to the low cost of the raw materials, the Opex is not expected to increase significantly.

- Lower energy consumption with additional steam cycle driving

  Due to the high operating temperature, Oxy-CCL is expected to have lower energy consumptions by driving a steam cycle for heat recovery.

- No need for flue gas pre-treatments

  Another advantage that Oxy-CCL has is that there is no need for flue gas pre-treatments, which however is required for some PCC technologies, such as amine scrubbing and the membrane technology as discussed in Section 2.1.3. The pre-treatment could be complex and expensive depending on the flue gas characteristics and the requirements of the carbon capture technology. CCL is also SO_2 tolerant, the resulting $CaSO_4$ is an ingredient for cement production.

- Synergies with cement manufacture

  Potential synergies between CCL and cement production makes the integration an interesting application. The drawback of the degradation of CaO in CO_2 capture capacity is largely offset as the spent CaO stream can be directed to the kiln system for clinker production.

For above reasons, the Oxy-CCL process has been progressed steadily over the past two decades and achieved a TRL of 6 based on the IEA assessment.[57] Nevertheless, the CCL technology needs further R&D to reduce the investment cost and improve its economic viability. It has been reported that the energy-intensive ASU in the conventional Oxy-CCL process almost accounts for about 1/3 of the total Capex.[58] It is therefore imperative to further reduce the cost of the CCL technology, so that it can be economically applied to the clinker burning process.

2.2 Pilot-scale calcium carbonate looping plants

Over the past two decades, the Oxy-CCL process has been demonstrated with a number of lab-scale test facilities and pilot-scale plants developed worldwide. The lab scale and pilot scale are distinguished on the basis of their scale and heating mode. The lab-scale facilities are within the low kilowatt (kW) range and are generally heated by external means, such as electrical heating systems. The pilot scale plants are larger in scale, and the process heat is generated by combustion of fuel inside the regenerator. Certainly, the pilot-scale plants provide more realistic insights in the operation of the CCL process. Therefore, the pilot-scale Oxy-CCL plants that burn fuel in the calciner are reviewed here. Review of other lab-scale Oxy-CCL plants can be found in the literature.[59-61] Table

5 summarises and compares the main characteristics of those five pilot-scale Oxy-CCL plants that burn fuel in the system to provide heat required for operation, which are introduced in more detail below. Among these pilot plants, only the 1.9MWth pilot Oxy-CCL plant at ITRI was focused on CO_2 capture from cement plant flue gases.

2.2.1 The 200kW$_{th}$ Oxy-CCL plant at University of Stuttgart

The 200kW$_{th}$ pilot-scale CCL plant at the University of Stuttgart was commissioned in 2010. The size of 200 kW$_{th}$ was chosen to follow a consecutive development strategy from lab to pilot scale.[62-64] As shown in Figure 11, for the purpose of experimental flexibility, three connected fluidised-bed reactors were chosen to operate with different fluidisation regimes, leading to two different configurations. Configuration A consists of two fast fluidised circulating fluidised bed (CFB) reactors, which are coupled by two symmetrically arranged loop seals with cone valves to divert the solid flow between the opposed reactor and the internal circulation via the loop seal overflow. In contrast, the carbonator is a turbulent fluidised bed (TFB) in configuration B, and the solid looping is achieved with the combination of an L-valve with overflow and the bottom loop seal arrangement at the TFB. Details of these fluidized bed reactors are given in Table 5.

The calciner is operated as an oxy-fuel-fired CFB combustor with flue gas recycle. The combustion can be controlled by staged oxidant supply and fuel feeding rate. Different fuels, such as coal and biomass, can be used. The circulation rate between both reactors, but also in the internal loop, is measured by measurement ports at the return leg of the CFBs, where the solid flow is stopped and monitored through a sight glass. The ports are designed not to influence the CFB hydrodynamics. In addition, microwave sensors, adapted for high-temperature applications, are installed in the return legs. With the help of these sensors operators can continuously monitor the riser circulation rates. Cooling of the carbonator is achieved by a bed cooler in the bottom region of the reactor and bayonet coolers at the top of the carbonator.

Figure 11b shows the peripheral components of both configurations. After each of the fluidised bed reactors, a secondary cyclone for dust removal, a gas cooler, and a bag filter for final gas cleaning are installed. The pressure level of the single reactor trains is controlled by pressure control valves after the filters, before the induced draft (ID) fan. The regenerator (R1) additionally consists of a flue gas recirculation train to recycle the CO_2-rich flue gas at temperatures of 200 °C for oxy-fuel combustion. All three downstream lines are connected to a common ID fan. The initial heat-up of the facility is conducted by means of an external gas burner, which provides hot flue gas to all reactor trains. Further equipment installed at the facility includes the dosing system, consisting of loss-of-weight feeders that enable automatically controlled fuel and limestone dosing. Both feeds are introduced to the reactor system by a rotary valve. For flue gas and oxidant supply to the carbonator and calciner, water-cooled side channel blowers are used. Both streams are enriched with oxygen for oxy-fuel combustion in the calciner and carbon dioxide required for carbonator synthetic flue gas. Loop seals and L-valves are fluidised with CO_2 and air, respectively. The technical gases are supplied from the tanks, which are part of the oxy-fuel infrastructure at the University of Stuttgart. The steam required for the simulation of realistic power plant flue gas with vapor concentrations of 10-20% after wet flue gas desulfurisation is supplied by a steam generator. It has been reported that as of 2015 the pilot plant has been successfully operated 1400 and 700 h in CO_2 capture mode. Stable oxy-fuel regeneration with flue gas recycle in the calciner was operated for more than 300 h.[60] The previous operation was focused on CO_2 capture from power plants. In a recent study, this 200kWth pilot Oxy-CCL facility has been successfully modified and operated during a 120h experimental campaign investigating cement specific calcium looping operation conditions.[64]
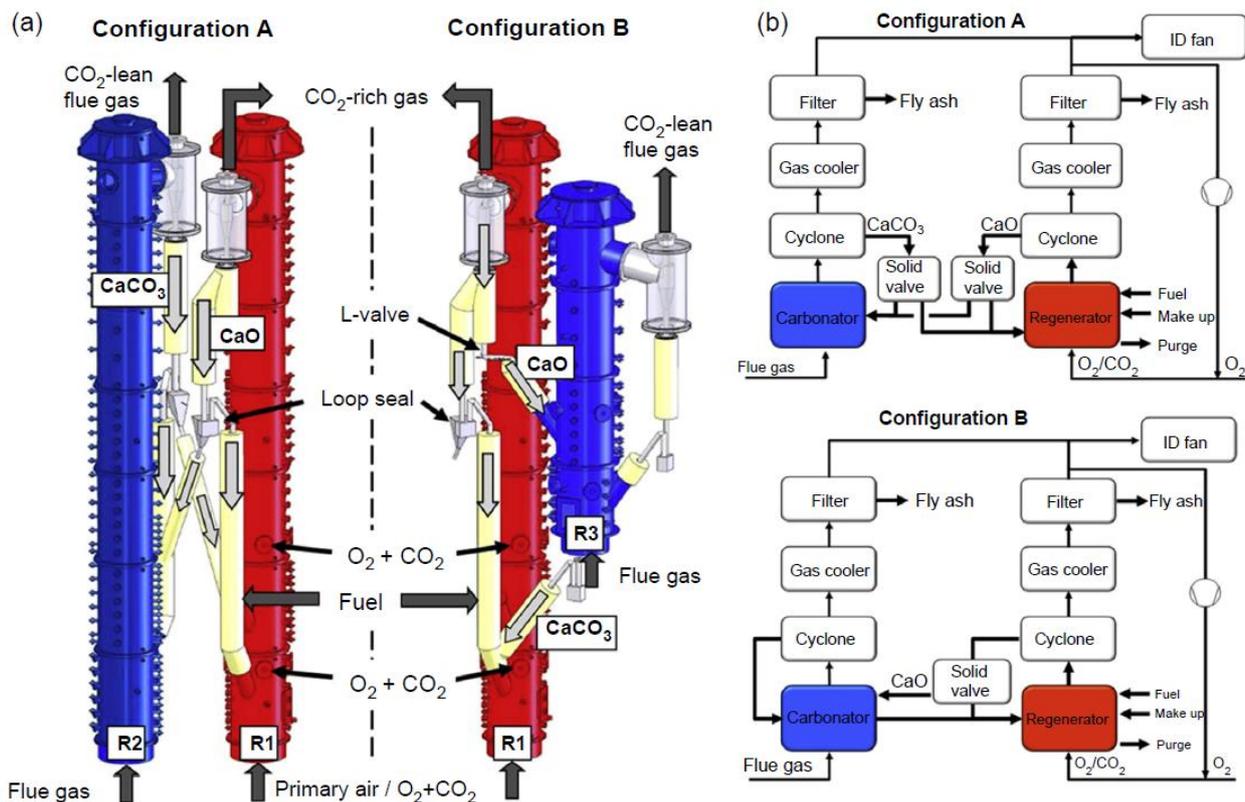
Figure 11: The 200kWth Oxy-CCL pilot plant at University of Stuttgart with its two operational configurations. Configuration A: CFB Carbonator (R2) – CFB calciner (R1). Configuration B: TFB Carbonator(R3)-CFB calciner (R1) [60]

2.2.2 The La Robla 300kW$_{th}$ CCL plant

The 300kW$_{th}$ La Robla pilot CCL plant is located in Leon Spain within the boundary of a 655 MW$_e$ pulverised coal power plant. As shown in Figure 12, it employs two interconnected CFB reactors, a combustor–carbonator and a combustor–calciner. Both reactors are at the same size, i.e. 12 m high and 0.4 m in diameter, as presented in Table 5. These reactors operate at temperatures of around 630-720 °C and 800–950 °C,[65] respectively. Biomass combustion takes place inside both reactors using air, instead of pure oxygen. Different to the conventional CCL process, limestone is continuously fed to the combustor–carbonator in the facility. As shown in Figure 12b, this facility is equipped with primary cyclones which close the main loop. A secondary cyclone is installed at the exit of the combustor–carbonator primary cyclone in order to retain finer solids that escape with the flue gas, contributing to a more accurate closure of the solids mass balance. No secondary cyclone is installed for the gas exiting the combustor–calciner. Instead, a fan blows air into the combustor–calciner gas stream to produce a sharp decrease in temperature and in CO_2 concentration at the exit of the primary cyclone, and ensures a reduction in the residence time of the CaO particles in the duct. This prevents the deposition of carbonate in this region of the facility. Water jackets are installed along the line that carries the solids from the combustor– calciner to the combustor–carbonator (see black-shaded area in Figure 12b) to extract a fraction of the combustion and the carbonation heat from the combustor–carbonator and maintain the reactor at 700 °C.[66]

Table 5 Main characteristics of pilot-scale Oxy-CCL plants worldwide

	Stuggart University (Germany)[60, 62]	La Robla (Spain)[65]	TU Darmstadt (Germany)[67]	La Pereda (Spain)	ITRI (Taiwan)[29, 30]
Capacity	200 kW$_{th}$	300kW$_{th}$	1MW$_{th}$	1.7 MW$_{th}$	1.9 MW$_{th}$
Configuration	CFB-CFB, TFB-CFB	CFB-CFB	CFB-CFB	CFB-CFB	BFB-Rotary kiln
Reactor dimensions	CFB carbonator D: 22 cm, H: 10 m CFB regenerator D: 21 cm, H: 10 m TFB carbonator D: 33 cm, H: 6 m	Carbonator-combustor D: 0.4m H:12m Calciner D: 0.4m H:12m	Carbonator D: 0.6 m, H: 8.6 m Regenerator D: 0.4 m, H: 11.5 m	Carbonator D: 0.65 m, H: 15 m Regenerator D: 0.75 m, H: 15 m	Carbonator D:3.3m, H: 4.2m Rotary kiln (as regenerator) D: 0.9m, L:5m
Reactor temperature	Carbonator 600-700°C Calciner 850-950°C	Carbonator-combustor 630-720°C Calciner: 800-950°C	Carbonator 650°C Calciner 900°C	Carbonator 600-715°C Calciner 820-950°C	Rotary kiln 600 (farthest side of burner)-1330°C
Operating velocities	Carbonator A 4-6 m/s Carbonator B 1-4 m/s Regenerator 4-6 m/s	Carbonator-combustor 0.9-2.8 m/s	Carbonator 2.2-3.3 m/s Regenerator 3-4.1 m/s	Carbonator 2-5 m/s Regenerator 3-6 m/s	Carbonator 0.25-0.35 m/s Rotary kiln Solid residence time: 10-15min, Rotation speed: 3-5RPM
Solid looping mechanism	Loop seal with cone Valve; L-valve and loop seal	Bubbling loop seal	Screw conveyor and loop seal	Double exit loop seals	Storage tanks + pneumatic conveying link
Calciner firing	Coal, biomass, oxy-fuel	Biomass, air-fired	Propane-coal, oxy-fuel	Coal, oxy-fuel	Diesel oil, oxy-fuel
Calciner flue gas circulation	Yes	N/a	No	No	Yes
Flue gas source	Simulated flue gas from power plants	From biomass combustion	Simulated flue gas from power plants	Real flue gas from power plants	Real flue gas from a cement plant
Postprocessing units	Gas coolers, fabric filters	N/a	Gas coolers, fabric filters	Electrostatic precipitator	Bag filter, gas cooling via heat exchanger

Although the calcination of $CaCO_3$ in the conventional Oxy-CCL process is carried out using a mixture of O_2/CO_2, no oxy-calcination takes place in this pilot plant for the sake of simplicity. Continuous and stable operation has been achieved in this 300 kWth pilot-scale CCL plant for 360 h.[66]
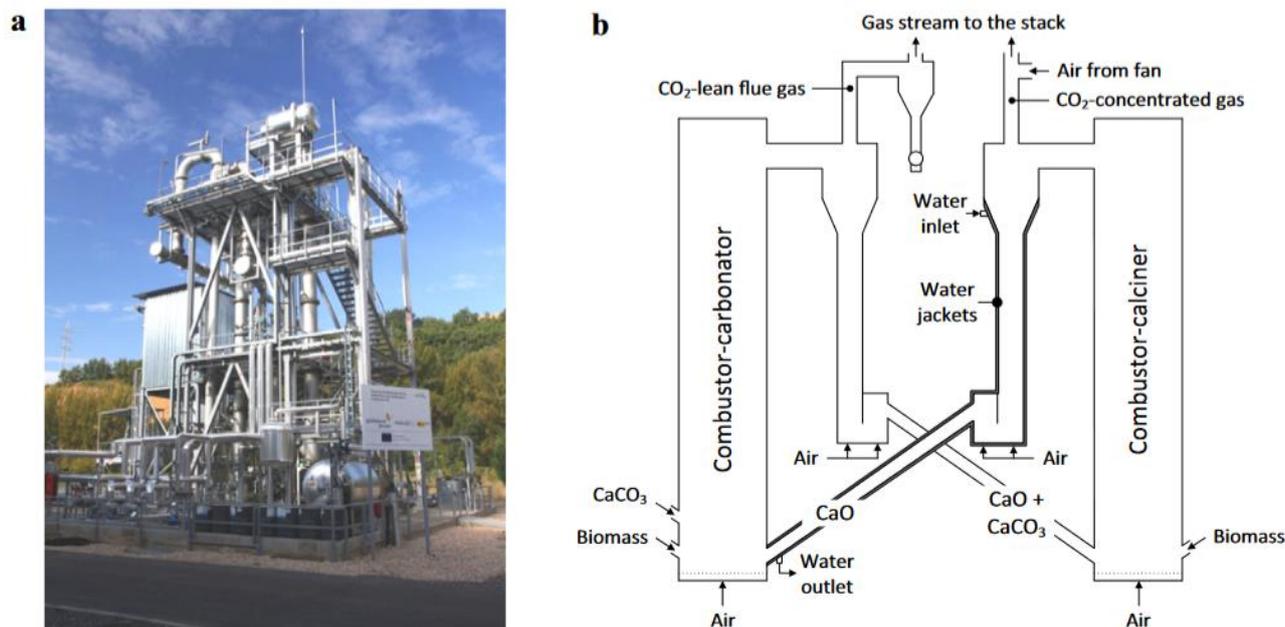
Figure 12: (a) Image and (b) process schematic of La Robla 300 kWth calcium looping pilot plant [66]

2.2.3 The 1 MW$_{th}$ Oxy-CCL plant at TU Darmstadt

The 1MW$_{th}$ pilot Oxy-CCL plant was commissioned at Technical University Darmstadt (TUD) for post-combustion CO_2 capture in 2012. This pilot plant consists of two interconnected CFB reactors. As shown in Table 5, the carbonator has a height of 8.6 m and an internal diameter of 0.6 m. The regenerator is 11.5 m high and has an internal diameter of 0.4 m. The whole reactor system including circulation ducts is refractory lined. As shown in Figure 13, the flue gas supplied to the carbonator is a synthetic mixture of air and CO_2 from gas tanks. After the CO_2 capture in the carbonator, the CO_2 lean flue gas leaves the system through a heat exchanger and filter for dust removal. Gas compositions and flows of the flue gas are continuously measured. Make-up limestone is fed into the carbonator by means of a gravimetric dosing system. The carbonator is equipped with an adjustable, internal bed material cooler in order to remove the reaction heat and to control the temperature in the reactors. The solid looping from carbonator to regenerator is carried out by means of a screw conveyor while the circulation from regenerator to carbonator is achieved by a loop seal.[68]

Different fuels can be burned in the regenerator to provide heat for sorbent regeneration. The reactor can be fired with propane, either by a burner or by a bed lance. The bed lance allows the introduction of propane into the bottom zone of the reactor. Alternatively, the reactor can be fired with pulverised coal up to 150 kg/h, corresponding to approximately 1 MW$_{th}$. In order to vary the oxygen content in the reactor, pure oxygen can be mixed into the primary air. Analogously to the carbonator, the calciner flue gas is released via a heat exchanger and a filter to the environment. Flow and gas composition of the calciner flue gas are continuously monitored. Additionally, the pilot plant is equipped with pressure transducers and thermocouples along the reactor height and in the peripheral components.[67]
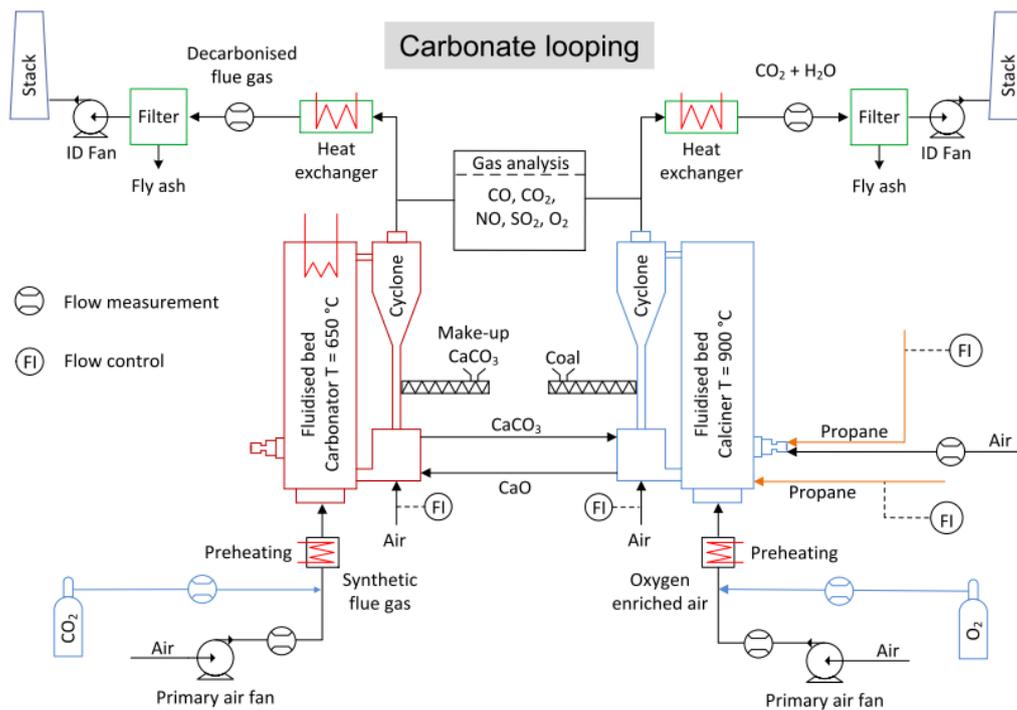
Figure 13: Set up of the 1MW$_{th}$ Oxy-CCL pilot plant at TUD [67, 69]

During the test, a synthetic mixture of air and CO_2 (12 vol. % of CO_2) was used instead of a coal-originated flue gas to enter the carbonator, and two different fuels of propane and pulverised coal were fired with oxygen-enriched air in the calciner to provide heat for the sorbent generation. When the first fuel was used, the total CO_2 capture efficiency was observed to be maintained at 92% when the carbonator was operated at 640-650 °C. A similar CO_2 capture efficiency was also achieved when coal was fired in the calciner. However, when the carbonation temperature was reduced to 610 °C, an obvious decrease in the capture efficiency was observed.[67, 69] According to a recent publication, from the end of 2015 until April 2016, the optimised pilot plant configuration had been operated for 16 weeks. During this period, the interconnected fluidised bed reactors ran for 1,444 h, with 1,219 h of stable CO_2 capture achieved. The feasibility of the carbonate looping process was proven by CO_2 absorption rates over 94 % in the carbonator and an overall CO_2 capture rate over 96 % including the CO_2 introduced by fuel in the calciner.[70]

2.2.4   The 1.7 MW$_{th}$ Pilot Oxy-CCL Plant at La Pareda

The 1.7 MWth pilot Oxy-CCL plant at La Pereda in Spain, known as the CaOling project, is the largest demonstration for power plant applications. In 2009, an agreement between ENDESA (a major European utility), Foster Wheeler (a leading world manufacturer of fluidised bed combustion technology), HUNOSA (the biggest coal mining company in Spain and owner of a CFB power plant) and CSIC (Spanish Research Council) was signed to design and construct a 1.7 MWth pilot plant, to experimentally test the performance of calcium looping. The project was funded by the EU's 7th Framework Programme-FP7 (Dec 2009-Nov 2012) and includes other partners of the Institute of Combustion and Power Plant Technology (IFK) of the University of Stuttgart in Germany, Lappeenranta University in Finland, Imperial College in UK and CanmetENERGY in Canada.[71] The pilot plant was built and integrated with the La Pereda coal-fired power plant, which is owned by HUNOSA and located in Asturias (North of Spain). A circulating fluidised boiler with an installed capacity of 50 MW was used as the source point of flue gas, which has a typical composition of 5.5 vol. % O_2, 12.6 vol. % CO_2, 7.0 vol. % H_2O, and 700 ppm SO_2. A photo of the La Pereda power plant

and the schematic of the carbonator and calciner are shown in Figure 14. The CO_2 capture pilot plant consists of two 15 m high interconnected CFBs with an internal diameter of 0.65 m in the carbonator and 0.75 m in the calciner, as shown in Table 5. Removable cooling bayonet tubes in the carbonator are installed to remove heat from the reactor at different temperatures levels. They are both connected to a high efficiency cyclone and a loop seal. The calciner is able to operate under air combustion or under oxy-fuel combustion conditions, using O_2 and CO_2 coming from tanks of liquefied gases. [72, 73]
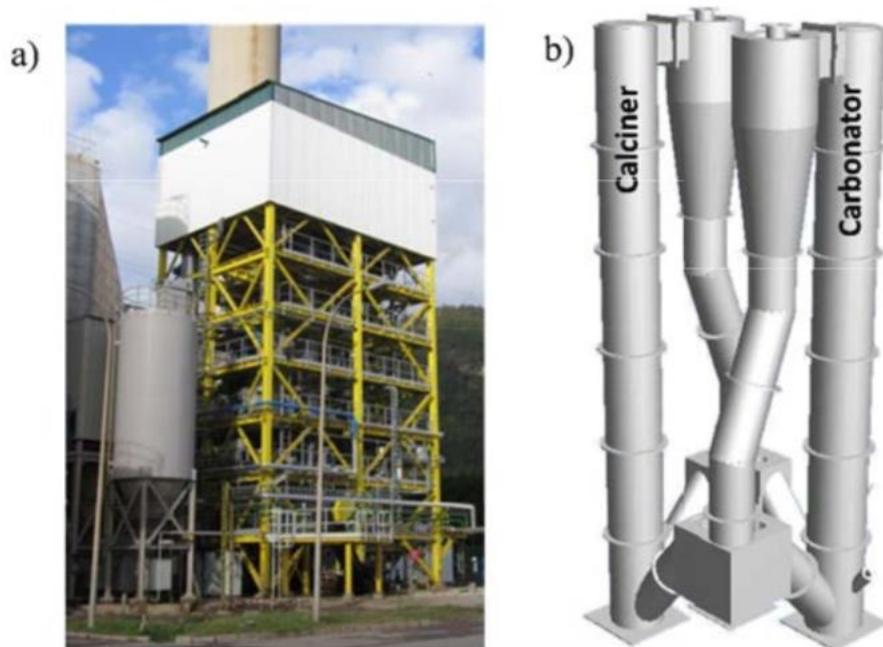
Figure 14: (a) Photo of the La Pereda pilot CCL plant and (b) a schematic of the interconnected dual fluidized bed system [74]

The calciner was operated with the goal of full sorbent conversion to CaO. This has been achieved by operating at sufficiently high calcination temperatures of 20-30°C above the equilibrium temperature of the calcination reaction and an O_2 excess of 5 vol% at the exit of the regenerator to achieve high coal combustion efficiencies in the calciner. The 1.7MWth La Pereda pilot facility entered into operation in 2012 and had accumulated more than 3,100 h of stable operation as of 2017.[74]

2.2.5 The 1.9MW$_{th}$ pilot Oxy-CCL plant at ITRI

A 1.9MW$_{th}$ pilot Oxy-CCL plant was developed and erected by ITRI in Taiwan in 2013 for CO_2 capture from cement plants, as shown in Figure 15a. This is currently the largest Oxy-CCL demonstration project. Different to the conventional Oxy-CCL configuraiton, this pilot plant employs a bubbling fluidised bed (BFB) carbonator and a rotary kiln acting as the calciner, which is very similar to the study by the Ohio State University.[29, 75] As presented in Table 5, the carbonator has a diameter of 3.3 m and a height of 4.2 m. The rotary kiln has a diameter of 0.9 m and a length of 5 m and the solid residence time in the kiln is designed to be at 10-15 min. The transport of solid material takes place via a pneumatic conveying link and storage tanks. The waste solid vented from the cyclone would be transported to the cement plant as a raw material for cement production, which is believed to reduce the sorbent cost of the calcium looping system and the calcination energy consumption of the cement plant.[29, 30]

The rotary calciner is important to the pilot plant and is interconnected with an oxy-fuel combustion system. As shown in Figure 15b, the calciner is driven by a variable speed motor to control the rotation speed in the range of 3-5 RPM. The operating temperature of the calciner is 1,330°C near the burner and drops to 600°C at the end of the kiln on the farthest side of the burner.[30]

It is reported that the accumulated time of unit operation of this pilot plant has been more than 600 h, of which 300 h has been for the fully-continuous looping test[30].
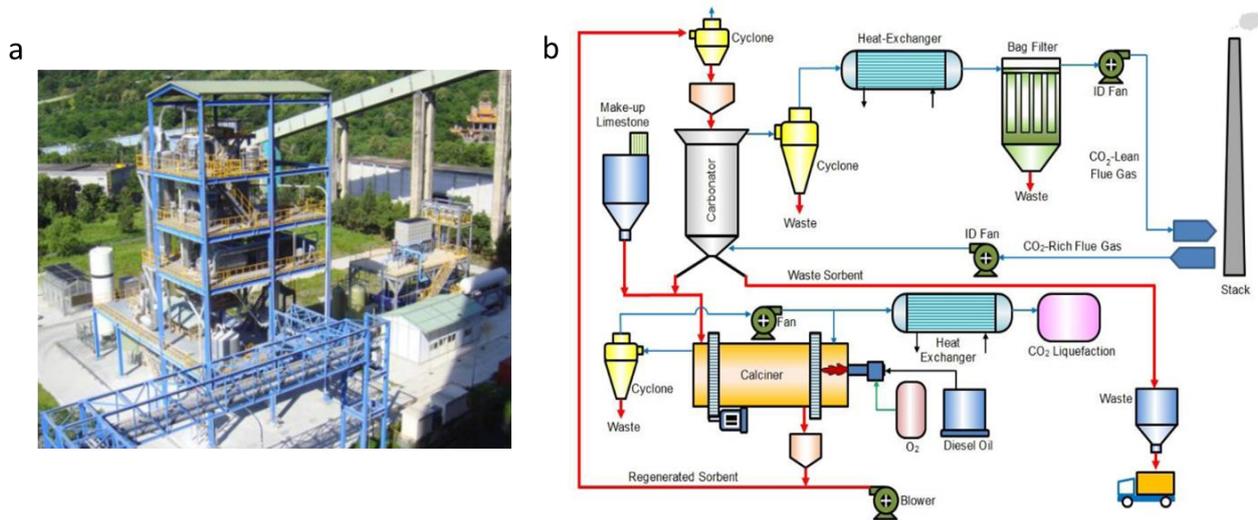
Figure 15: (a) Photo and (b) process schematic of the 1.9MW$_{th}$ CCL plant at ITRI [30]

3 Reference cement plant

A site investigation was carried out at the reference cement plant to understand its operation, collect relevant technical information and operating data. The technical information and operating data were necessary to configure the calcium carbonate looping process with the cement plant and as input parameters for the techno-economic assessment.

3.1 Plant description

The reference cement plant is an integrated clinker and cement manufacturing operation, with main characteristics, as summarised in Table 6. Operating with one kiln, the cement plant takes limestone delivered by rail and, after blending with blue shales, burns it at high temperature to produce 'clinker'. The mass ratio between limestone and blue shale in the raw materials is 85:15. It has an annual production of ~1.4 million tonnes of cement, corresponding to a clinker production of ~183.9 t/h. The clinker/cement factor is 0.88 while the raw meal/clinker factor is 1.61.

The reference cement plant uses Solid Waste-Derived Fuels (SWDFs) (90-95% is wood) as part of its 'fuel mix' which is burnt in the pre-calciner to provide the energy and heat necessary for limestone decomposition. The thermal coal being used together with the SWDF is supplied by a local thermal coal producer and burnt in the rotary kiln.

Table 6: **Characteristics of the reference cement plant**

Parameter	Value
Clinker production, t/h	183.9
Clinker/cement factor	0.88
Raw meal/clinker factor	1.61
Coal feed rate, t/h	12.88
SWDF feed rate, t/h	15.8
Raw material composition	
Limestone, %	85
Blue shale, %	15

The reference cement plant uses a dry kiln process in the manufacture of clinker, as shown in Figure 16. The mixture of raw materials is ground up finely in the raw mills to make raw meal. Hot air from the kiln is drawn through the mills to dry the raw materials. The raw milling is to help the raw materials mix properly and make the mixture easy to burn in the kiln. The raw meal is stored in the homogenising silo. The homogenising silo mixes the raw meal, reducing any variations in the chemistry of raw meal.

The raw meal is then fed to the preheater tower. As the raw meal is heated in the preheater tower and kiln, CO_2 is liberated from the limestone. In the hottest part of the kiln, the burning zone, chemical reactions take place, which convert the raw meal into 'clinker'. Hot gases from the preheater system are quenched in the conditioning towers and then used to dry the raw materials in the raw mills. The gases from the raw mills are de-dusted in either an ESP or bag filter.

The hot clinker that is formed in pieces about the size of large marbles is passed through the cooler where air cools the clinker. Part of the hot air from the cooler is recycled to burn the fuel in the kiln and in the pre-calciner via the tertiary air duct. This helps reduce the amount of fuel needed. Remaining excess cooling air is cooled in an air-to-air heat exchanger then de-dusted in a bag filter.
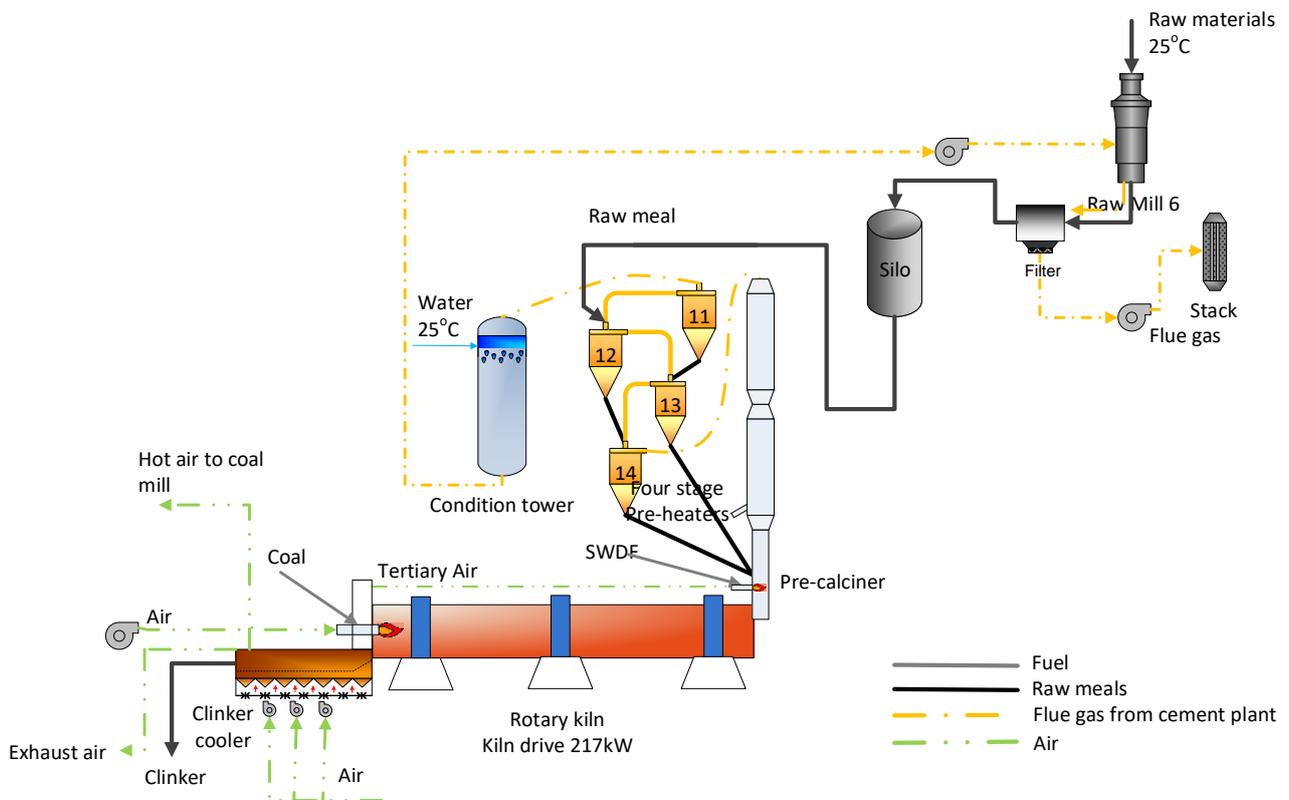
Figure 16: Schematic diagram of the reference cement production process

3.2 Kiln system

Central to the cement manufacture process is the kiln system. The kiln system at the reference cement plant consists of two four-stage cyclone preheaters, a pre-calciner tower with a tertiary duct, a rotary kiln and a clinker cooler. SWDF is burnt in the pre-calciner to bring up the temperature to 1,000-1,050°C, in which limestone is decomposed to CaO and CO_2. The decomposed raw meal enters the rotary kiln at the elevated end. The rotary kiln is inclined at about 3° and has a rotating speed of 3.4RPM. The raw meal stays in the rotary kiln for about 30 min with its temperature rising from 1,000°C to 1,450°C. Clinker is formed at such high temperatures and discharged at the lower end. The chemical compositions of the thermal coal and SWDF are shown in Table 7.

Table 7: Properties of the thermal coal and SWDF used at the reference cement plant

Fuel properties	Unit	Thermal coal	SWDF[b]
Moisture, ar[a]	wt%	6	3.8
Ash, ar	wt%	25.6	0.8
C, ar	wt%	60.1	59
H, ar	wt%	3.4	6
O, ar	wt%	3.2	30
N, ar	wt%	1.2	0.2
S, ar	wt%	0.4	0.2
Total	wt%	99.9	100
HHV	kJ/kg	24,300	13,000
a: ar-as received b: the composition of SWDF is simulated to obtain the HHV given by the ref cement plant			

3.3 Flue gas properties

Flue gases result from the combustion of coal in the kiln and SWDF in the pre-calciner. It travels counter current with raw meals in the rotary kiln and pre-heaters to heat up the solids. After exiting the pre-heaters, flue gas is cooled down in a conditioning tower using water and then introduced into the homogenising & storage silos and raw mills to pre-heat the raw meals, so that the waste heat can be further utilised. Flue gas properties measured at the kiln stack are given in Table 8. The discharging flue gas is in the temperature range of 119-135°C at a mass rate of 650,000 kg/h on a wet basis. The CO_2 concentration is 20.7% on a wet basis. SO_x and NO_x content are low so neither desulfurisation or DeNOx equipment is employed. An ESP and bag filter are used for removing dust from flue gas, reducing the particulate loading to 38.5 mg/m^3.

Table 8: Flue gas properties

Parameters	Value
Mass flow rate (wet basis), t/h	650
Temperature, °C	119-135
Mole fraction (wet), %	
CO_2	20.7
O_2	9.5
H_2O	14-15
N_2	54.8
NO_x, mg/m^3	650
SO_x, mg/m^3	0.71
Particulate, mg/m^3	38.5

4 Techno-economic feasibility assessment

This chapter details the techno-economic feasibility assessment of retrofitting a novel indirect-heated CCL process into the reference cement plant. The indirect-heated CCL process is less energy intensive compared to the conventional Oxy-CCL process and can be integrated with cement product through three different configurations. The three configurations were compared with respect to the energy consumption, technical retrofitability, and economic viability. Also, a sensitivity analysis of the cost of CO_2 avoided to a number of parameters was carried out. Finally, the cost of CO_2 avoided for the novel CCL process was compared with other PCC technologies.

4.1 Technical feasibility study

4.1.1 Selection of calcination options

As mentioned in Section 2.1.3, one of the challenges faced the conventional Oxy-CCL process is the employment of an ASU unit, which is usually based on the cryogenic technology and is energy-intensive. Extensive R&D efforts have been devoted to the development of other CCL processes without the need of oxy-fuel combustion, such as the combined Ca-Cu chemical looping process,[76, 77] the PSA based CCL process,[56] the Endex CCL reactor,[78] etc. Based on the thermodynamic equilibrium of the CaO-CO_2 system, the calcination reaction can be realised by either pressure swing of the CO_2 partial pressure or temperature swing. The swing of CO_2 partial pressure can be achieved with steam addition. The energy required for limestone decomposition can come from direct heating (oxy-fuel combustion) or indirect heating in which energy is transferred from a separate air-fired combustor.[79-81] The indirect heat transfer between the combustor and calciner can be achieved by heat conduction and radiation through metallic walls,[79] heat pipes with an additional heat carrier,[82, 83] or circulation of hot solid streams.[79, 81, 84] Though the indirect calcination has been proposed and discussed through process simulation, its complete integration with cement production has not been fully analysed.

In this project, the following three CCL processes with different calcination options are analysed and compared through process simulation. The simulation was based on the downstream application, in which the CCL process takes flue gases from cement plant stack. The schematic diagrams of these CCL processes are presented in Figure 17.

Indirect-heated wet CCL (IH-CCL-wet)

As shown in Figure 17a, the IH-CCL-wet process employs an indirect-heated calciner which separates the air-fired combustion of fuel and calcination of limestone in the CO_2/H_2O atmosphere. A pure CO_2 stream can be obtained by condensing the steam after exiting the indirect-heated calciner. Part of the CO_2/H_2O gas is recirculated to assist fluidisation in the calciner. Energy required for calcination is provided by air-fired combustion of fuel. The resulting flue gas is then fed to the carbonator for CO_2 capture. The remaining part of the process is the same as the conventional CCL process. The difference is that the carbonator not only treats the flue gas from the upstream cement plant, but also the flue gas from the fuel combustion in the indirect-heated calciner.
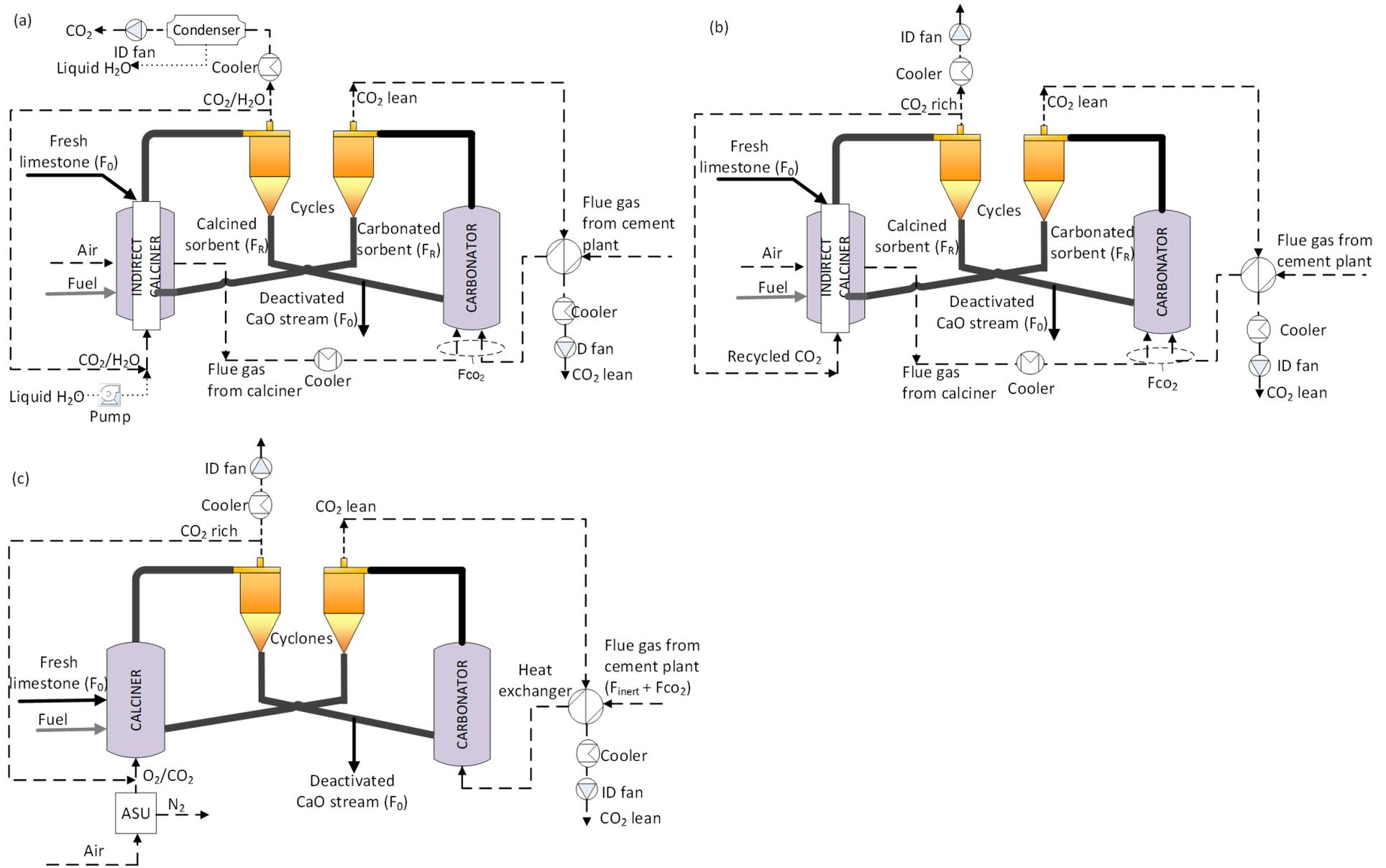
Figure 17: Schematic diagrams of (a) IH-CCL-wet, (b) IH-CCL-dry, and (c) Oxy-CCL

Indirect-heated dry CCL (IH-CCL-dry)

The IH-CCL-dry process (see Figure 17b) is the same as IH-CCL-wet in principle, but the calcination is performed in a dry condition, i.e. 100% CO_2. This calcination option excludes the steam addition, mainly taking into account the high energy associated with steam generation.

Oxy-fired CCL (Oxy-CCL)

This option (see Figure 17c) is the current approach for calcination in the CCL process. To get a pure CO_2 stream, fuel is burnt in an oxygen-rich atmosphere balanced with recycled CO_2. The operating temperature should be above 898 °C (950-1,000 °C) which corresponds to an equilibrium CO_2 pressure of 100 kPa (i.e. 100 vol. % CO_2 at atmospheric pressure). As such, an ASU is required.

The CCL process can be usually characterised using the following parameters[79]:

- The molar flow rate of solid looped between the carbonator and calciner (F_R);
- The molar flow rate of fresh limestone (F_o); and
- The molar flow rate of CO_2 in the flue gas that is fed to the carbonator (F_{CO_2}).

The main simulation boundary conditions for the three configurations are specified in Table 9. The values of F_0/F_{CO_2} and F_R/F_{CO_2} (see Table 9) were chosen to allow good capture efficiency in the carbonator, maintaining under control the heat requirements in the calciner, as well as reasonable sorbent makeup flows. To maintain the mass balance, the deactivated CaO stream exits the process at the same molar flow rate of F_o. In the process simulation, the ash resulting from coal combustion is also removed together with the deactivated CaO stream to prevent accumulation of materials in the system. For comparison, the values of F_0 and F_R in all three processes were set the same. However, the values of F_{CO_2} were different. In the Oxy-CCL process, the carbonator only treats flue gas from the upstream cement production process as the oxy-fired calciner generates a gas stream of high CO_2 purity that is ready for subsequent compression. While in the other two processes, the carbonator not only treats the flue gas from the upstream cement plant, but also the flue gas from the fuel combustion in the indirect calciner. Thus in the simulation, this resulted in the fact that the values of F_0/F_{CO_2} and F_R/F_{CO_2} in these two indirect-heated calcination options were less than that in oxy-fuel combustion, as presented in Table 9.

Table 9: Boundary conditions for these three CCL processes

Item	Unit	Oxy-CCL	IH-CCL-dry	IH-CCL-wet
F_R/F_{CO_2}	--	3.31	0.83	0.93
F_0/F_{CO_2}	--	0.60	0.17	0.19
Carbonator temperature	°C		650	
Carbonator pressure	Bar		1	
Combustor temperature	°C		1150	1050
Combustor pressure	Bar		1	
Excessive air	%	2.5[a]	15	15
Calciner temperature	°C	950	950	850
Calciner pressure	Bar		1	
Air temperature	°C		25	
Air pressure	Bar		1	
a: excessive oxygen				

In the IH-CCL-wet process, with the addition of steam, the CO_2 partial pressure is expected to be lower than that in the conventional oxy-fired calciner. According to the equilibrium curve, the temperature of the calciner was set at 850°C while the combustor was set at 1,050°C, the

temperature difference was to ensure sufficient and fast heat transfer. The carbonator was set at 650°C. In contrast, the indirect-heated dry calcination was performed in the recycled CO_2 stream. The CO_2 partial pressure was set to be very similar to that in the oxy-fuel combustion. Therefore, the calcination temperature for both options was set at 950°C. The combustor temperature for the IH-CCL-dry process was set at 1,150°C.

Air combustion in the combustor was performed with an excessive air of 15% while oxy-fuel combustion was performed with an excessive oxygen of 2.5%[85]. As the process simulation was based on the downstream application to treat all the flue gas from the reference cement plant, the flue gas properties and coal properties as shown in Table 8 and Table 7 were used.

These three calcination options were compared through process simulation using AspenPlus (v10). In the simulation, the energy consumption of oxygen production was assumed at 300 kWh/t O_2.[86] The carbonator efficiency is defined as the amount of CO_2 captured in the carbonator by the amount of CO_2 fed in the carbonator. The total CO_2 capture efficiency is defined as the amount of CO_2 captured in the CCL process by the amount of CO_2 fed and generated in the CCL process.

The mass and heat flows for the three CCL processes are presented in Table 10. During the simulation, it was found that care should be taken to establish the mass and heat balance for the indirect-heated calcination options. This is because the amount of CO_2 introduced to the carbonator was increased due to the flue gas stream from the air-fired combustor. At the same molar flow rates of circulating solids (F_R) and fresh make-up of limestone (F_0), the carbonated fraction of CaO has to be increased to treat the increased amount of CO_2 in the carbonator. However, when the CaO sorbent was regenerated in the calciner, the heat duty was increased as more CO_2 had to be released. Therefore, more fuel was burnt in the combustor, further increasing the amount of CO_2 at the carbonator inlet. It can be seen from Table 10 that the fuel flow rates in the two indirect-heated calcination processes were more than double that in the typical Oxy-CCL process. This effect converged at high energy requirements and could lead to larger size of reactors compared to that in the Oxy-CCL process. It should be noted that the reactors of larger size may have higher investment costs. To understand the impact at the process level, a preliminary cost estimation on the overall process was carried out in Section 4.4. As a result, the carbonated fraction of CaO was increased to 80% in the two indirect-heated calcination processes, higher than 23% in the oxy-fired combustion process. The high carbonated fraction of CaO was still reasonable when the CCL process was integrated with the cement production process, as the molar flow rate of make-up limestone will be maintained at a high rate to meet the requirements of the clinker production process.[79, 87] Nevertheless, the carbonator efficiency and overall CO_2 capture efficiency were found to be lower in the indirect-heated calcination process than that in the oxyfuel combustion. While the overall CO_2 capture efficiency in the oxy-fuel combustion can was as high as 96.25%, the values are 68.71% and 75.18% for the IH-CCL-dry and IH-CCL-wet processes respectively. This however should not be a concern to the IH-CCL processes as the molar flow rates of circulating solids (F_R) can be increased to improve the CO_2 capture efficiency, as demonstrated in Section 4.1.2.

Although the IH-CCL-wet process shows lower CO_2 capture efficiency and higher fuel consumption than Oxy-CCL, it does reduce the energy penalty when a steam cycle is coupled to recover the energy input from fuel combustion. The thermal efficiency of the steam cycle was assumed to be 25% for the Oxy-CCL process, and 35% for the IH-CCL processes. Depending on the thermal input of the steam cycle, and the temperature profile of the heat available, the steam parameters and steam turbine efficiencies could vary significantly. Generally, the smaller the thermal input, the lower the temperature profile, the lower the steam cycle efficiency due to scale effects. In the three CCL processes, the temperature profiles of the heat were very similar as most of the heat recovery is performed at the carbonator that operates at the same temperature of 600-650°C. As the Oxy-CCL process has a much lower thermal input (i.e. fuel consumption), the reactor size is expected to be

much smaller and therefore the steam cycle is likely to be based on a low pressure subcritical steam cycle (steam conditions: 540°C and 12MPa) with a efficiency of 25% on a HHV basis. This efficiency is very typical for coal-fired power plants with power output less than 100MWe, according to the IEA Coal Clean Center's review.[88] In comparison, the IH-CCL processes have thermal inputs that were three times more than that in the Oxy-CCL process, a high pressure subcritical steam cycle with double steam reheats (steam conditions: 560°C with 17.5MPa) can be used to increase the efficiency to 35%.[88-90] The assumption values may seem conservative when compared to the state-of-the-art steam cycles for large-scale power plants. It should be noted, however, that the boiler in the large-scale power plants operates at much higher temperatures of 1,300-1,600°C, allowing the generation of steam with higher parameters and thus higher efficiencies. As shown in Table 10, the energy penalty for IH-CCL-wet is 4.05 GJ/t CO_2, which is lower than that of Oxy-CCL (4.22 GJ/t CO_2) and IH-CCL-dry (5.29 GJ/t CO_2) processes.

Table 10: Mass and heat flows for the three CCL processes

Item	Unit	Oxy-CCL	IH-CCL-dry	IH-CCL-wet
Carbonated fraction	%	23	80	80
Carbonator efficiency	%	90	63.30	70.40
O_2 flow rate	t/h	182.50	--	--
Fuel in the calciner	MW_{HHV}	590.09	1298.19	1062.15
CO_2 generated from fuel combustion	kmol/h	4,378.74	11,707.94	9,992.44
CO_2 generated from $CaCO_3$ decomposition	kmol/h	2,664.64	2,722.72	2,722.72
CO_2 from flue gas	kmol/h	4,387.38	4,387.38	4,387.38
CO_2 captured	kmol/h	11053.45	12929.85	12857.10
Overall CO_2 capture efficiency	%	96.25	68.71	75.18
CO_2 purity in the product gas	%, dry	94.1	100	100
Energy consumption				
Pump	MW_e	0.14	13.78	10.86
ASU	MW_e	28.96	--	--
Energy output by steam cycle	MW_e	-75.04[a]	-476.76[b]	-437.2[b]
Energy penalty	GJ/t CO_2	4.22	5.29	4.05
a: the thermal efficiency of steam cycle is assumed at 25%. b: the thermal efficiency of steam cycle is assumed at 35%.				

Another advantage offered by the IH-CCL processes is that the resulting CO_2 stream from the calciner had 100% purity (dry basis), relatively to 94.1% (dry basis, balanced by 2.5% N_2 and 3.4% O_2) obtained from the Oxy-CCL process. This is because the indirect-heated calcination completely separates the fuel combustion and limestone decomposition, generating a pure CO_2 stream. The impurities in the CO_2 stream would certainly further increase the energy consumption of the downstream CO_2 compression.[91]

In summary, the IH-CCL processes are expected to have the following advantages over the conventional Oxy-CCL process:

- Lower energy penalty for CO_2 capture;
- No need for ASU, possibly leading to lower investment costs; and
- A pure CO_2 stream ready for compression and storage, which minimizes the efforts for downstream CO_2 purification, compression and associated costs;

With the benefits discussed above, the indirect-heated wet calcination option, as referred to as IH-CCL, is therefore adapted in the CCL process for retrofitting into the existing cement plant.

4.1.2 Process integration of IH-CCL with cement production

The reference cement plant was simulated in AspenPlus first to validate the model against operating data. The schematic diagram of the reference cement plant presented in Figure 16. The pre-heating of raw meals in the raw mill and bag filter were also included. The boundary conditions for the reference plant are shown in Table 12.

The simulation results are compared with the operating data in Table 11. The main errors were raw meals flow rate and coal flow rate, as well as the resulting flue gas flow rate and clinker production. It could be caused by the variation in the raw meal composition and/or fuel properties. Also, it should be noted that the temperature of the pre-calciner was set at 950ºC, which could be lower than the actual value and therefore lead to higher coal consumption in the rotary kiln. Moreover, air leaking into the actual cement plant was not considered in this study, which may contribute to the errors. Nevertheless, the input parameters, in general, were in agreement with the operating data of the reference cement plant. The resulting flue gas properties were also reasonably consistent with the operating data. Despite the cement production process being simplified as discussed above, the simulation results demonstrate that the process model established in Aspen plus can reasonably represent the reference cement plant.

Table 11: Key process data from reference cement plant and process simulation

Parameters	Unit	Ref plant	Simulation	Variation
Water flow rate	t/h	22.9	22.8	0.4%
Raw meals flow rate	t/h	307	278.5	9.3%
Clinker production	t/h	183.9	176.1	4.2%
Coal flow rate	t/h	12.88	17.5	35.9%
SWDF flow rate	t/h	15.8	15.8	0
Flue gas properties (wet basis)				
Flow rate	t/h	650	574.2	11.7%
Temperature	ºC	119-135	120	
Mole fraction				
CO_2	%	20.7	21.5	3.9%
H_2O	%	15	12.1	19.3%
N_2	%	54.8	59.7	8.9%
O_2	%	9.5	5.9	37.9%
Total	%	100	99.2	

Based on the reference plant, the IH-CCL process can be integrated in the configurations outlined below. Based on the technical assessment results, the retrofitability of these three different configurations was assessed later in Section 4.2.

Downstream integration

In the downstream integration, as shown in Figure 18, the IH-CCL is placed after the cement production process, in which the flue gas (F'_{CO_2}) exiting the raw mill is fed into the CCL process for CO_2 capture. CO_2-lean flue gas exiting the carbonator is used to preheat the feeding gas via a heat exchanger and then sent back to the bag filter for de-dusting. The CaO generation is carried out through indirect-heated wet calcination with coal combustion. The resulting CO_2-containing flue gas (F''_{CO_2}) is fed into the carbonator for CO_2 capture. Therefore, the CO_2 amount (F_{CO_2}) introduced to the carbonator is a sum of these two CO_2 streams. Due to the exothermic carbonation reaction, the excessive heat is expected to be recovered from the carbonator for steam generation. The spent

CaO flow from the calcium looping process is fed into the pre-calciner and kiln for clinker production, considering that the temperature of the CaO stream from the calciner is almost the same as the pre-calciner. This configuration has almost no impact on the existing cement plant, only the mass and energy balance are expected to re-establish as less raw limestone will be directly fed into the cement production process.
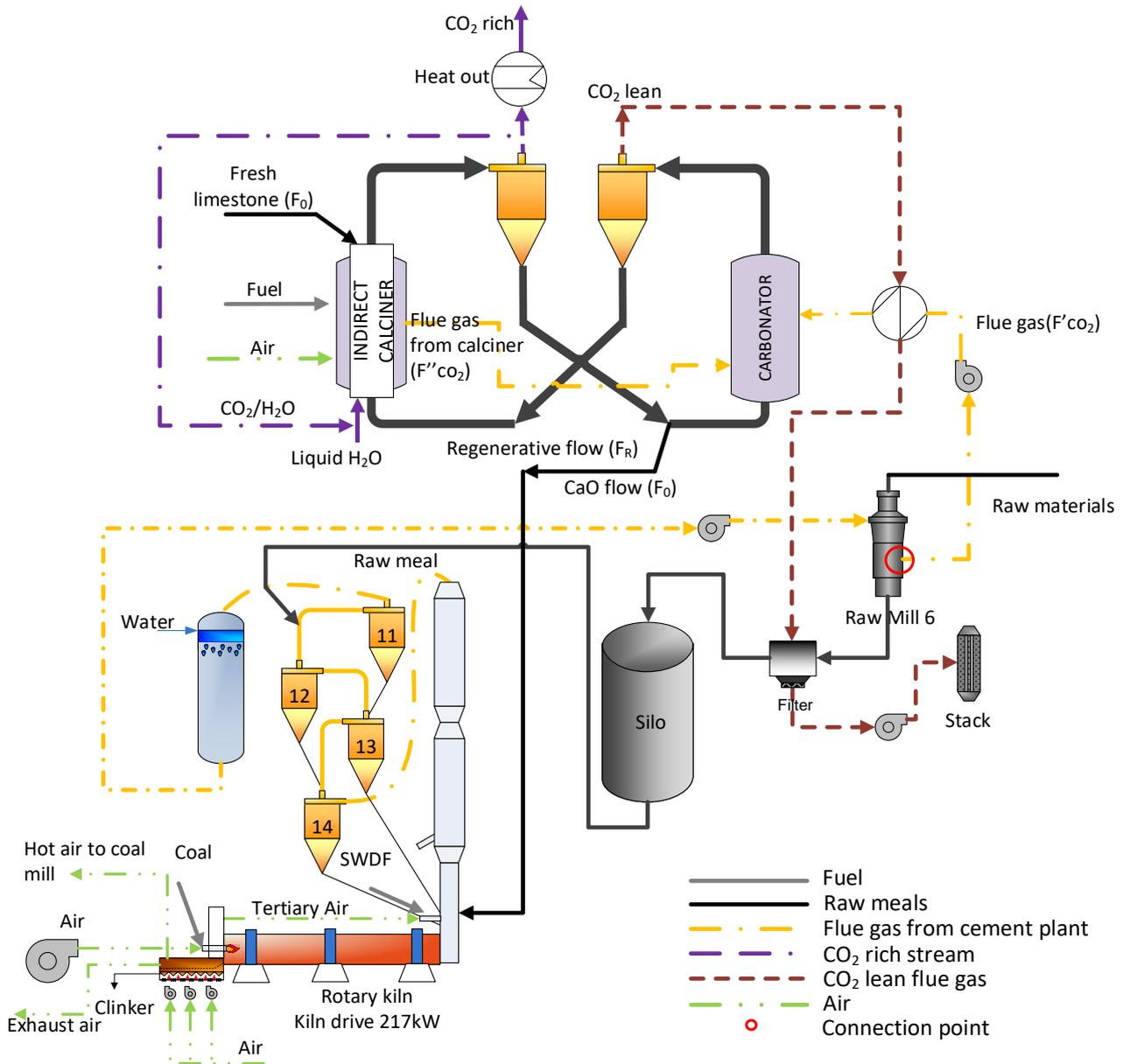
Figure 18: Schematic diagram of the downstream integration of IH-CCL without interrupting the existing cement production

Tail-end integration

The tail-end configuration, as shown in Figure 19, takes the flue gas from cement production from the exit of the pre-heaters, where the flue gas temperature is moderate, about 370°C. By doing so, the cooling tower is no longer required. Similarly, the flue gas is fed into the IH-CCL process through a heat exchanger, which should have a smaller size than the downstream integration due to a lower temperature difference. However, the flue gas exiting the pre-heaters contains a considerable amount of dust (i.e. raw meals) which is detrimental to the operation of the heat exchanger and increases the Opex. Based on the site investigation, the dust in the flue gas from the pre-heaters could be up to 8 wt% of raw meals fed into the pre-heaters. The CO_2 lean flue gas from the IH-CCL

process is instead fed into the conditioning tower and then to the raw mills to pre-heat raw meals. The calcination part is the same as the downstream integration. Also, the excessive heat is expected to be recovered from the carbonator for steam generation. In this configuration the IH-CCL process is still a standalone plant but some of the piping in the existing cement plant needs to be modified.
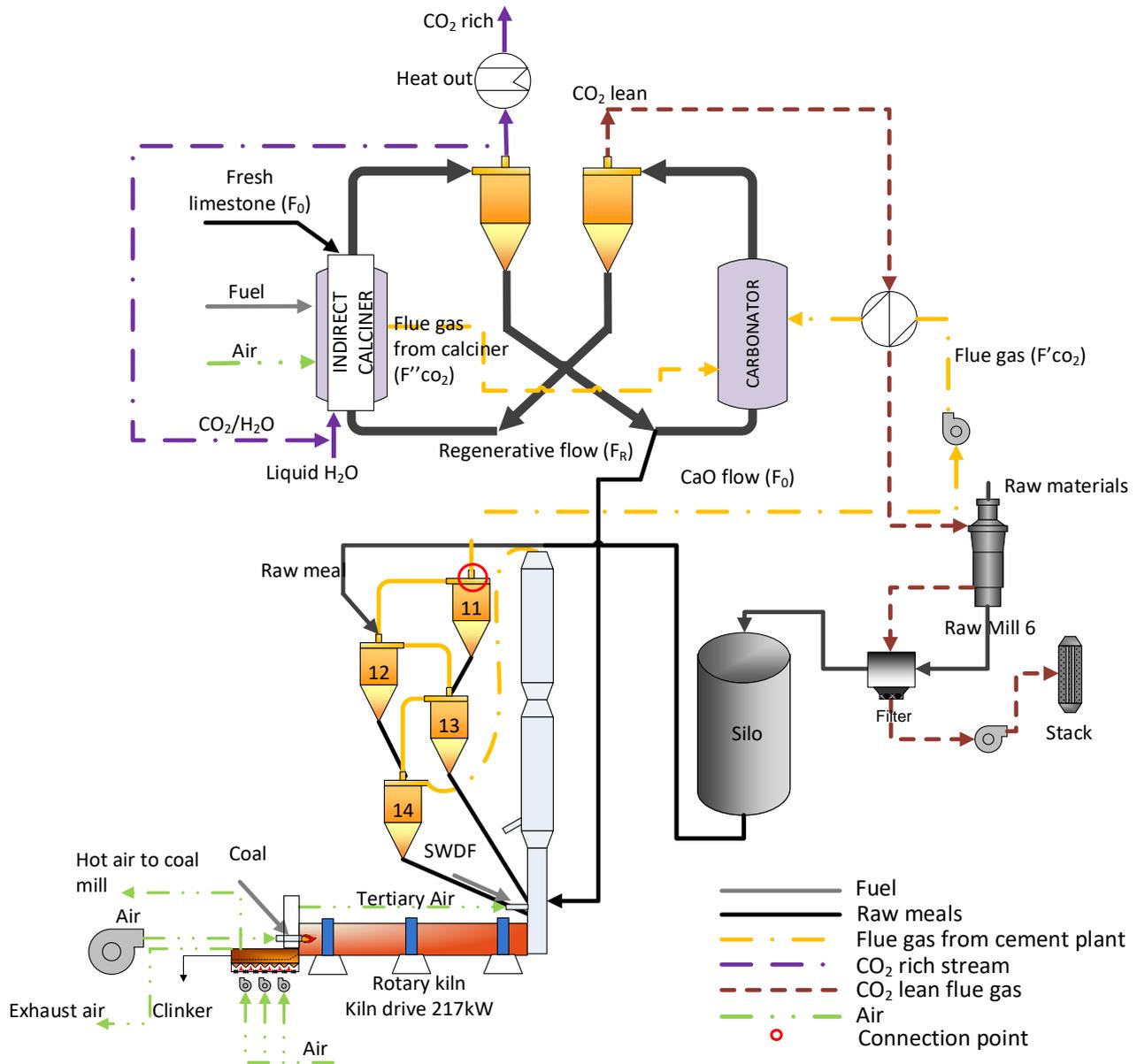
Figure 19: Schematic diagram of the tail-end integration of IH-CCL with minor interruption to the existing cement production

Full integration

The full integration, as shown Figure 20, is achieved by combining the indirect-heated calciner with the pre-calciner in the cement plant. The existing four-stage pre-heaters are separated, with pre-heaters 13 and 14 connected with the indirect-heated calciner for CO_2 stripping and pre-heaters 11 and 12 modified as a carbonator for CO_2 capture. The indirect-heated calciner needs to be separated from the rotary kiln to allow solid transportation only. The flue gas from the rotary kiln is fed into the indirect-heated calciner to heat up the solids and then enters the carbonator for decarbonisation, together with the flue gas resulting from SWDF combustion. The CO_2 lean flue gas is sent to the raw mills to pre-heat the raw meals. Due to the high temperature of flue gas from the kiln and the exothermic carbonation reaction, the flue gas will be cooled down with heat recovery

for steam generation. Carbonated solid flow is then sent to the calciner for regeneration. The CaO flow from the calciner is partly fed to the kiln for clinker production and partly to the carbonator for cyclic CO_2 capture. Obviously, this configuration requires significant modifications to the existing pre-heaters, but it should not require as much additional footprint as the other two configurations would.
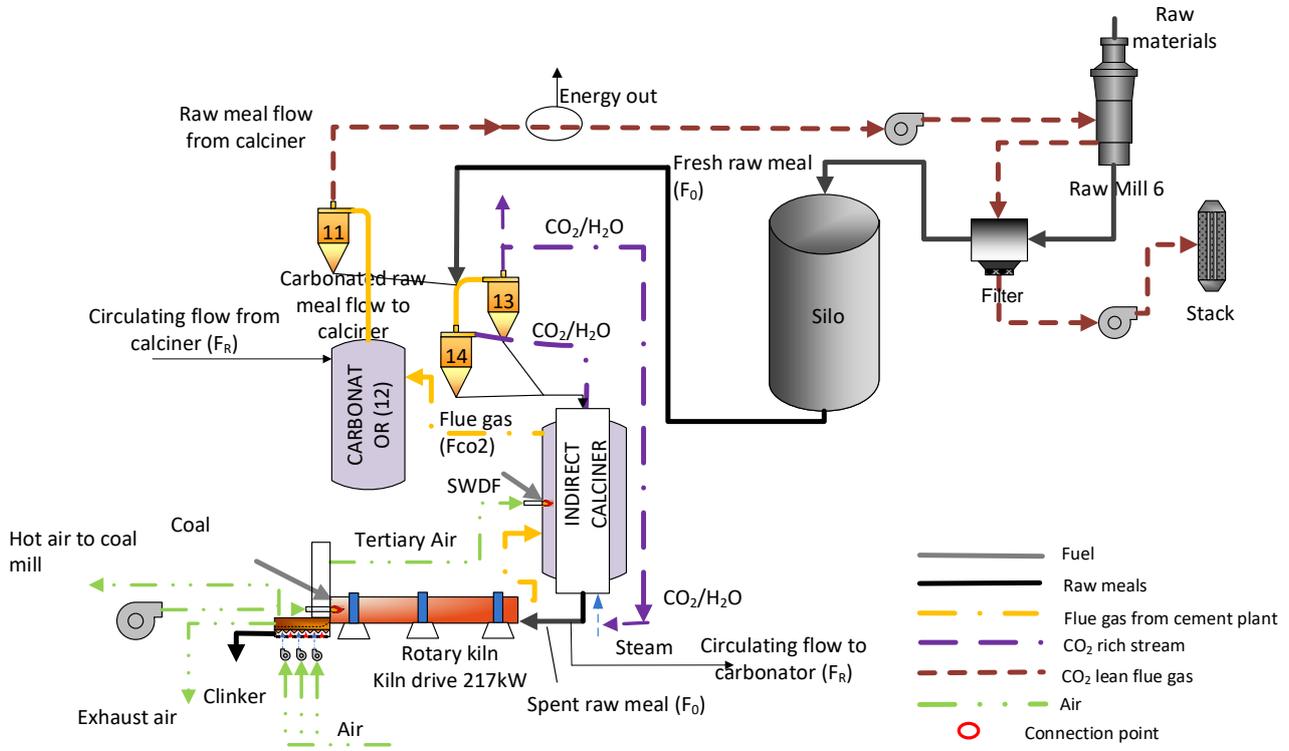
Figure 20: Schematic diagram of the full integration of IH-CCL by modifying the existing cement production

The configurations of tail-end integration and full integration are the cases most studied in the literature.[58, 87, 89, 92] The studies are all based on the European BAT, which uses a kiln system with five-stage pre-heaters, a pre-calciner and a rotary kiln. For the tail-end integration, the dust loading in the flue gas is usually omitted. Also, previous studies usually include the kiln system instead of the whole cement production process, which is considered in this project.

4.1.3   Boundary conditions and analysis methods

Process simulations of these three integration configurations were carried out with the boundary conditions and assumptions summarised in Table 12. A heat recovery steam generation (HRSG) system was applied in the process simulation. The amount of electricity was calculated by multiplying the amount of thermal heat absorbed by the HRSG system with the steam turbine efficiency. The electric consumption of the CO_2 compression process was calculated from the electric consumption per tonne of CO_2 compressed. As discussed above, the reference cement plant was also simulated and validated against the operating data. The electric consumption associated with raw material preparation, cement and fuel grinding, and clinker production was estimated with the assumptions adapted from the literature.[93] Also, it should be noted that the available waste heat from the existing cement plant was re-used as far as possible to save energy consumption.

To quantify the emission abatement and energy performance of these various integration configurations, a number of key performance indices (KPIs) were used to calculate the captured CO_2,

direct and indirect CO_2 emissions, and primary energy consumptions of the reference plant with and without CO_2 capture.

The overall CO_2 capture efficiency (CCE) was calculated as the ratio between the CO_2 capture $m_{CO2,capt}$ and the total CO_2 generated in the process $m_{CO2,gen}$:

$$CCE = \frac{m_{co2,capt}}{m_{co2,gen}}$$
(2)

Table 12: Boundary conditions and assumptions for process simulation

Item	Unit	Value
Clinker production process		
Clinker production	t/h	183.9
Clinker/cement factor	Kg clk/kg cem	0.88
Primary and transport air to rotary kiln	Nm^3/t clk	254.4
Primary and transport air temperature	ºC	1000
Tertiary air to pre-calciner	Nm^3/t clk	473
Tertiary air temperature	ºC	1000
Hot air to coal mill	Nm^3/t clk	82.2
Temperature of hot air to coal mill	ºC	600
Exhaust air	Nm^3/t clk	1009.5
Temperature of exhaust air	ºC	320
Rotary kiln gas outlet temperature	ºC	950
Clinker discharge temperature	ºC	60
Raw meals temperature after raw mills	ºC	70
Dust loading in flue gas	% of raw meal	8[a]
CCL process		
Carbonator temperature	ºC	650
Carbonator pressure	Bar	1
Carbonated fraction	%	80
Combustor temperature	ºC	1050
Combustor pressure	Bar	1
Excessive air	%	15
Calciner temperature	ºC	850
Calciner pressure	Bar	1
Steam fraction in calciner	%	60
Decomposition rate	%	100
Electric consumption in cement plants[93]		
Crushing and grinding of raw materials	kWh/t raw materials	35
Clinker production including fans, materials conveying, rotary kiln operation	kWh/t clk	36
Cement grinding	kWh/t cem	57
Coal grinding	kWh/t coal	14
Others		
Steam cycle efficiency[90]	%	25-35
Electric consumption for CO_2 compression [94]	kWh/t CO_2	100
Electricity generation efficiency (η_{el})[b]	% HHV	35
Specific CO_2 emissions of electric power (e_{el})[b]	Kg/kWh	973
a: this is only considered in the tail-end integration case		
b: this is based on the subcritical coal-fired power plant[95]		

The total CO_2 included direct CO_2 generated by fuel combustion and from limestone decomposition in the integrated processes, but not CO_2 generated indirectly by power consumption.

Equivalent CO_2 emissions ($e_{clk,eq}$) were computed with Eq. (3) as the sum of the direct emissions from the cement kiln (e_{clk}) and the indirect emissions associated with the electricity imported from the electric grid ($P_{e,clk}$) and on the specific CO_2 emissions of electric power (e_{el}). $P_{el,clk}$ is the specific power consumption, which is negative when power is consumed and positive when it is generated:

$$e_{clk,eq} = e_{clk} + P_{el,clk} e_{el} \qquad (3)$$

e_{clk} can be calculated from:

$$e_{clk} = \frac{m_{co2,emit}}{m_{clk}} \qquad (4)$$

Where $m_{co2,emit}$ is the CO_2 emitted from the cement plant stack and m_{clk} is the clinker production.

Primary energy consumption ($q_{clk,eq}$) is to assess the impact of retrofit on the energy performance, and was then calculated as:

$$q_{clk,eq} = q_{clk} + q_{el,clk} \qquad (5)$$

Where q_{clk} is the direct specific primary energy consumption while $q_{el,clk}$ is the indirect specific primary energy consumption. They were calculated through:

$$q_{clk} = \frac{m_{fuel} HHV_{fuel}}{m_{clk}} \qquad (6)$$

$$q_{el,clk} = \frac{P_{e,clk}}{\eta_{el}} \qquad (7)$$

In order to compare different technologies from an energy and environmental point of view, the SPECCA (Specific Primary Energy Consumption for CO_2 Avoided) index can be used.[58, 90, 95, 96] The SPECCA index is defined by the following equation, quantifying the increased equivalent fuel consumption to avoid the emission of CO_2 in a cement kiln with CO_2 capture with respect to a reference cement kiln without capture:

$$SPECCA = \frac{q_{clk,eq} - q_{clk,eq,ref}}{e_{clk,eq,ref} - e_{clk,eq}} \qquad (8)$$

4.1.4 Process simulation results and discussion

The main results of the mass and energy balances are presented in Table 13. In general, all the integration cases resulted in an increased fuel consumption and thus thermal input compared to the reference cement plant with no CO_2 capture. The full integration case had the lowest increase (2.45MW$_{HHV}$/t clk), which is about three times that of the reference value (0.81MW$_{HHV}$/t clk). This is followed by the significant increases of the tail-end integration (4.59MW$_{HHV}$/t clk) and the downstream integration (4.6MW$_{HHV}$/t clk). This can be attributed to the fact that in the full integration a significant portion of the energy required for $CaCO_3$ decomposition in the calciner was contributed by the flue gas at ~1,000°C from the rotary kiln.

In all cases, the fuel input to the rotary kiln was almost the same, as the integration cases had little impact on the energy balance of the rotary kiln. Compared to the reference cement plant, the fuel input to the pre-calciner in the downstream and tail-end integration cases decreased dramatically by 59.4%. This is because both integration cases have a high integration level of 50%, meaning that about 50% of CaO required in the clinker production comes from the IH-CCL process and thus the heat required for limestone decomposition in the pre-calciner was significantly reduced. In the full integration case, the pre-calciner coincided with the indirect-heated calciner where about 80% the total fuel input was consumed.

The overall CO_2 capture efficiency (CCE), calculated as per the Eq. (2), was slightly higher in the downstream and tail-end integration case (83.63% and 83.8%). The slight reduction in the CCE in

the full integration case owes to the lower F_R/F_{CO2} (0.77 vs 1.48). It is expected that the increase in the molar rate of the re-circulating solid flow would increase the overall CCE, though the energy balance in the indirect-heated calciner needs to be re-established.

Table 13: Main results of the mass and energy balances of these three integrated CCL and cement plant and the ref cement plant

Parameters	Ref plant	Downstream integration	Tail-end integration	Full integration
F_R/F_{CO2}	--	1.47	1.48	0.77
F_0/F_{CO2}	--	0.13	0.13	0.73
Clinker production, t/h	176.1	198.7	197.7	178.9
CO_2 from cement kiln flue gas, kmol/t clk	22.93	10.44	10.35	8.40
CO_2 from fuel combustion in CCL, kmol/t clk	--	30.58	30.54	--
CO_2 from make-up limestone in CCL, kmol/t clk	--	5.24	5.20	13.22
Total CO_2 captured, kmol/t clk	--	38.69	38.62	24.68
CO_2 capture efficiency (CCE), %	--	83.63	83.8	79.01
Fuel in rotary kiln, MW_{HHV}/t clk	0.49	0.43	0.42	0.45
Fuel in pre-calciner, MW_{HHV}/t clk	0.32	0.13	0.13	--
Fuel in indirect-heated calciner, MW_{HHV}/t clk	--	4.04	4.04	2.00
Direct specific primary energy consumption (q_{clk}), MJ_{HHV}/t clk	0.82	4.60	4.59	2.45
Power balance, MW_e				
Electric output		200.9[a]	244.35[a]	45.97[b]
Pump	-3.86	-10.83	-10.68	-4.83
Electric for fuel grinding	-0.36	-1.89	-1.88	-0.87
Electric for raw materials preparation	-9.75	-9.27	-9.23	-9.75
Electric for clinker production	-6.34	-7.15	-7.12	-6.44
CO_2 compression	--	-33.83	-33.59	-19.43
Net electric	-20.30	137.93	181.86	4.65
a: the thermal efficiency of steam cycle is assumed at 35%. b: the thermal efficiency of steam cycle is assumed at 25%.				

A general result shown in Table 13 is that the higher the thermal input was in the IH-CCL system, the higher the electricity was generated by the steam cycle. Therefore, the downstream and tail-end integration cases produced the highest electricity (200.9MW_e and 244.35MW_e) based on the steam cycle thermal efficiency of 35%. This electricity output overcame the electric consumption mainly associated with the following components in order: CO_2 compression (33.83 MW_e and 33.59 MW_e), the pump (10.83 MW_e and 10.68 MW_e), raw material preparation (9.27 MW_e and 9.23 MW_e), and clinker production (7.15 MW_e and 7.12 MW_e). Due to the significantly higher fuel consumption in the indirect-heated calciner, the electric consumption (1.89 MW_e and 1.88 MW_e) for fuel grinding in the downstream and tail-end integration cases were a lot higher than that in the full integration case (0.87 MW_e) and the reference cement plant (0.36 MW_e). The fuel grinding, however, still consumed the least electricity. As a result, the downstream and tail-end integration cases had a large net electricity output of 137.93 MW_e and 181.86 MW_e. In contrast, the full integration case has a lower electricity output of 45.97 MW_e based on the steam cycle thermal efficiency of 25%. As described in Section 4.1.1, the selection of the steam cycle efficiency considered the temperature profile of the heat available and the thermal input.[90] A sensitivity analysis to the steam cycle efficiency was performed in Section 4.4. After subtracting the electric consumption for CO_2 compression (19.43 MW_e), raw material preparation (9.75 MW_e), clinker production (6.44 MW_e),

and pump (4.83 MW$_e$), the net electricity generation for this case came down to 4.65 MW$_e$. It can be clearly seen that the integration of IH-CCL process with cement production becomes a co-producer of cement and electricity. The electricity output not only compensates the electric consumption of the whole integrated plant, the remaining can be exported to the electricity grid.

It should be noted that most of the results for the downstream integration and tail-end integration were very close, except the electricity output (200.9MW$_e$ vs 244.35MW$_e$) and the net power (137.93 MW$_e$ vs 181.86 MW$_e$). The difference is mainly caused by the fact that the tail-end integration case treated flue gas from the pre-heater tower instead of from the raw mills, saving a significant amount of heat that can be used for generating steam for the steam cycle.

The KPIs of these three integrated cases and the reference cement plant are presented in Table 14. Negative indirect CO_2 emissions were obtained in all three cases, due to the net electric export. In the downstream and tail-end integration cases, the indirect CO_2 emissions (-0.68 t CO_2/t clk and -0.9 t CO_2/t clk) were negative and significantly higher than the direct CO_2 emissions (both 0.35 t CO_2/t clk) at the cement kiln stack, leading to negative equivalent CO_2 emissions (-0.32 t CO_2/t clk and -0.54 t CO_2/t clk). Due to less electricity generated in the full integration case, its equivalent CO_2 emissions were positive (0.26t CO_2/t clk). On the other hand, the direct specific primary energy consumptions in the downstream integration and tail-end integration cases (16,558.1 MJ/t clk and 16,512.8 MJ/t clk) were significantly higher than that in the full integration case (5,474.48 MJ/t clk) and the reference plant (1,088.75 MJ/t clk). Owing to the net electricity export, the indirect specific primary energy consumptions in all three integration cases were negative, relatively to that in the reference plant.

The best SPECCA was obtained for the full integration case (1,396.71 MJ/t clk), followed by the tail-end integration (2,264.18 MJ/t clk) and downstream integration (4,124.32 MJ/t clk). Although the downstream and tail-end integration cases had much larger indirect specific primary energy consumption than the full integration case, they also had much higher direct specific primary energy consumptions, leading to higher SPECCA. The SPECCAs for the tail-end integration was lower than the downstream integration case, due to higher electricity output. It should be noted that the SPECCAs obtained for the tail-end integration and full integration of IH-CCL were significantly lower than that of Oxy-CCL integration cases (3,170-4,420 MJ$_{LHV}$/t clk),[58] implying a potential to significantly reduce the energy consumption for CO_2 capture.

Table 14 Key performance indices of these three integrated CCL and cement plant and the ref cement plant

KPIs	Ref plant	Downstream integration	Tail-end integration	Full integration
Direct CO_2 emissions at stack (e_{clk}), t CO_2/t clk	1.01	0.35	0.35	0.29
Indirect CO_2 emissions ($e_{clk,el}$), t CO_2/t clk	0.11	-0.68	-0.9	-0.03
Equivalent CO_2 emissions ($e_{clk, eq}$), t CO_2/t clk	1.12	-0.32	-0.54	0.26
Direct specific primary energy consumption (q_{clk}), MJ/t clk	2,943.69	16,558.10	16,512.8	5,474.48
Indirect specific primary energy consumption ($q_{clk,el}$), MJ/t clk	1,088.75	-6,576.21	-8,714.56	-244.25
Equivalent primary energy consumption($q_{clk,eq}$) ,MJ/t clk	4,032.44	9,981.9	7,798.23	5,230.23
SPECCA, MJ/t clk	--	4,124.32	2,264.18	1,396.71

4.2 Retrofitability assessment

The general criteria below were identified and discussed here to qualitatively assess the overall retrofitability of the three integration cases taking into account the site investigation and technical assessment results.

- Impact on the existing cement plant;
- Major equipment and modifications required;
- Flue gas pre-treatments;
- Footprint;
- Additional resources required;
- Operating experience and potential challenges; and
- Emission limits.

The assessment of each criterion against the three integration configurations is presented in Table 15, and is elaborated in more detail in the following section.

4.2.1 Impact on the cement production operation

The downstream integration involves a standalone IH-CCL plant taking flue gas from the cement plant raw mill. Therefore, no major modification is required to the existing cement plant and thus no production stop is expected. The tail-end integration takes flue gas from the pre-heater stages, thus requiring rerouting the flue gas to the new IH-CCL plant for CO_2 capture. This causes minor impact on the cement plant operation due to the short production stop required for the flue gas rerouting. In contrast, the full integration case results in significant modifications to the pre-heater stages and pre-calciner as they need to be replaced with a carbonator, an indirect-heated calciner and associated cyclones. The cement plant has to stop for a long period for the modification.

On the other hand, the downstream integration and tail-end integration cases should have negligible impact on the clinker quality, as the kiln system remains unchanged. The full integration case involves significant modifications to the pre-heaters, which however may impact the clinker quality due to changes in gas atmosphere, temperature and/or other conditions.

4.2.2 Major new equipment and modifications required

Additional major equipment and construction required in the integrated processes are identified, as presented in Table 15. Both the downstream integration and tail-end integration cases require a standalone IH-CCL plant that can be installed close to the existing rotary kiln or further away. The flue gas from the cement plant can be routed to the IH-CCL plant via insulated ducts. In the tail-end integration case, the insulated duct may be larger, and a high temperature rated blower is required due to higher flue gas temperatures. Based on the technical feasibility study results (see Section 4.1), the overall fuel consumption in these two integrated processes are significantly increased. As a result, the volume flow rate of the flue gas is expected to be significantly larger than the existing cement plant. Therefore, a new coal grinding plant and a separate dust filter are required. The full integration case has significant modifications required to replace the existing pre-heater stages and pre-calciner. This means a new tower structure is required to support the new fluidised beds and associated cyclones. Due to the fact that >90% of raw meals have a particle size of <90µm, the conventional fluidised beds that usually accommodate solid particles of a few hundred microns may not be suitable. The entrained flow fluidised beds have been proposed as one solution to fully integrate with the cement manufacture process.[58, 95, 97] As the full integration case requires much

less fuel than the other two cases, the existing coal grinding facilities and dust filter/ESP may be sufficient.

In all integration cases, the common auxiliaries include the HRSG system, the steam turbine unit and power generator for heat recovery, and a CO_2 compression unit for CO_2 compression for subsequent transportation. In comparison to the conventional Oxy-CCL process, the energy- and capital-intensive ASU and CO_2 purification unit (CPU) are therefore avoided.

4.2.3 Flue gas pre-treatments

It is expected that the flue gas pre-treatment for the IH-CCL process is much less than other PCC technologies, as the sorbent is quite tolerant to other substances in flue gas (e.g. SO_2, moisture etc.). In both the downstream and tail-end integration cases, the flue gas only needs to be pre-heated to 650^oC for subsequent carbonation. To this end, a gas-gas heat exchanger is required. However, it should be noted that in the tail-end integration case, the flue gas exiting the pre-heater contains a significant amount of raw meals (~8 % of the mass flow rate of raw meals). The raw meals may need to be removed to avoid dust clogging and deposition in the downstream heat exchanger. The full integration case is configured into the existing kiln system, no flue gas pre-treatment is required.

4.2.4 Footprint

In the downstream integration and tail-end integration cases, the IH-CCL plant is erected not only for CO_2 capture but also for significant power generation. The IH-CCL plant involves a HRSG system, steam turbine and power generator, and CO_2 compression unit, resulting in significant footprint. Fortunately, the standalone IH-CCL plant can be installed further away from the cement plant if the available space is limited. In contrast, the full integration case requires less footprint as the IH-CCL plant will be integrated with the existing cement plant. Also due to the significantly lower power output, the size of the required steam cycle will be a lot smaller. It is expected that the footprint of the full integration case is half less than that of the downstream and tail-end configurations. But the auxiliary systems, such as HRSG system, steam turbine and power generator, and CO_2 compression unit should sit close to the kiln system. Nevertheless, based on the site survey of the reference cement plant, the site space should not be a limiting factor for the retrofit.

4.2.5 Additional resources required

Unlike other PCC technologies, the CCL process uses calcium carbonate that is environmentally benign. The handling, transportation and disposal of limestone are familiar to the operators. However, steam is required in the CCL process to recover heat. Also, the downstream CO_2 compression is new to the operators. The handling of steam, operation of new auxiliaries including the steam turbine and CPU are different skill set to the operators.

Table 15: Retrofitability assessment of the integrated IH-CCL and cement plant

	Downstream integration	Tail-end integration	Full integration
Impact on existing cement plant operation	- No major modification required to the existing cement plant - Negligible impact on the cement kiln operation - Negligible impact on clinker quality	- Rerouting of the flue gas required - A short production stop is required for the rerouting; - Minor impact on cement kiln operation; - Negligible impact on clinker quality	- Significant modifications to the pre-heaters and pre-calciner; - A long production stop is required for the modification; - Possible adverse impact on clinker quality
Major new equipment/construction required	- A standalone CCL plant; - A new fuel grinding plant - An insulated duct to connect the CCL plant and existing cement plant; - A heat recovery steam generation system (HRSG); - A steam turbine unit and power generator CO_2 compression unit - A separate dust filter	- A standalone CCL plant; - A new fuel grinding plant - An insulated duct with a high temperature rated blower to connect the CCL plant and existing cement plant; - A heat recovery steam generation system (HRSG); - A steam turbine unit and power generator CO_2 compression unit - A separate dust filter	- Existing pre-heater stages and pre-calciner to be removed; - An integrated CCL (entrained flow fluidised beds) and new pre-heating cyclones; - A new tower structure; - A heat recovery steam generation system (HRSG); - A steam turbine unit and power generator CO_2 compression unit
Pre-treatment of flue gas	Gas pre-heating required	- Gas pre-heating required - Optional dust removal	N/A
Footprint	Significant footprint including existing cement plant, the new CCL plant, the new turbine house for the steam turbine unit and electric generator, the CO_2 compression unit, and the dust filter	Significant footprint including existing cement plant, the new CCL plant, the new turbine house for the steam turbine unit and electric generator, the CO_2 compression unit, and the dust filter	Smaller footprint (possibly less than half of the footprint for the other two cases) including existing cement plant, the new turbine house for the steam turbine unit and electric generator, and the CO_2 compression unit
Additional resources required	A large amount of steam	A large amount of steam	A considerable amount of steam
Operating experience and potential challenges	- Low TRL and scarce operational experience; - Dust in gas streams poses challenges to the operability of heat exchangers.	- Low TRL and scarce operational experience; - Dust in gas streams poses challenges to the operability of heat exchangers.	- Low TRL and scarce operational experience; - Impact on clinker quality to be assessed.
Emission limits	Additional dust removal required	Additional dust removal required	No extra action required

4.2.6 Operating experience and potential challenges

Although the conventional Oxy-CCL process has been demonstrated through a number of pilot-scale CCL plants for applications in coal-fired power plants, the IH-CCL process has gained very limited operating experience with a very low TRL. Also, the downstream integration and tail-end integration cases requires at least one heat exchanger for pre-heating the incoming flue gas. The dust loaded in the CO_2-lean flue gas may cause operational problems, such as dust deposition and clogging. In the full integration process, the operational experience on the entrained flow fluidised beds is also scarce. More R&D is required to gain operational experience and increase the TRL of IH-CCL.

4.2.7 Emission limits

Based on the technical assessment results, the emissions of SO_2 and NO_X are similar to the current emission level and thus require no desulphurisation and DeNox unit. The heavy metals are not included in the simulation, but their emissions are expected to sit within the emission limits. This is because air-fired combustion is employed in the IH-CCL process, the same as the existing cement process. However, while dust emissions may be an issue, they can be mitigated through additional dedusting systems. Clearly the volume flow rate of flue gas from the integrated cement process will increase substantially due to the large fuel input. The existing dust filter/ESP may not be able to handle such a large flow rate. Additional dust filter/ESP may be required to meet the dust emission limit. Therefore, an additional dust filter has been included in the following economic analysis.

4.3 Preliminary economic analysis

A preliminary economic analysis was performed based on the process simulation results and the major equipment identified through the retrofitability assessment, to gain a high level of understanding of the costs of retrofitting the IH-CCL plant into the existing cement plant, including the capital investment costs, the total operational costs, and associated specific cost of CO_2 avoided.

4.3.1 Method for cost estimation and analysis

All costs presented in this project are in AUD. Where necessary, prices obtained from the literature were converted to AUD. Assumptions for the cost estimation are summarised in Table 16. As mentioned above, space availability for the additional units was not analysed. No carbon tax was considered.

Total plant cost (*TPC*) of each item was estimated with Eq. (9), by increasing the total direct costs (*TDC*) by the indirect cost factor (*INCF*), the owner's cost factor (*OCF*) and the project contingencies factor (*CF_{project}*). Total direct costs are estimated with Eq.(9), as the sum of the equipment cost (*EC*), the installation cost (*IC*), increased by process contingency factor (*CF_{process}*).

$$TPC = TDC\ (1 + INCF + OCF + CF_{project}) \tag{9}$$

$$TDC = (EC + IC)\ (1 + CF_{process}) \tag{10}$$

To estimate the equipment cost (*EC*), functions as summarised in Table 17 for each major equipment were used. The equipment costs were correlated in terms of a base cost multiplied by a ratio of sizes raised to the scaling factor "n", as shown in Eq. (11)

$$Cost_2 = Cost_{ref}(size_2/size_{ref})^n \tag{11}$$

Two different process contingency factors were assumed for the different items, expressed as percentage of the installed equipment cost. The first process contingency factor depends on the maturity of the technology, i.e. on its technology readiness level (TRL). For the downstream and tail-end CCL plant where the typical fluidised bed carbonator can be used (TRL=6), the process contingencies were assumed equal to 20%. The cost of indirect-heated calciner was estimated based on a fluidised calciner plus an air-fired combustor. Due to the low TRL, process contingencies of 60% were assumed. The process contingency of 25% was assumed for the new tower structure required in the full integration case. For the CO_2 compression unit, process contingencies were equal to 20%. The second process contingency factor depends on the level of detail of the equipment list used to estimate the equipment cost. It was assumed equal to 12% of the installed equipment cost and has was applied only to the CCL reactors and the CO_2 compression unit. The Opex including variable costs and fixed costs were calculated based on the assumptions made in Table 17.[58, 90] Overall, the cost estimation should belongs to EPRI Category I, which is similar to AACE Class 5/4.[98]

Table 16 Assumptions for the economic analysis

General	
Currency	AUD$
Plant capacity factor, %	85
Discount rate, %	10
Recovery period, years	25
Capital Recovery Factor	0.11
Construction time for cement kiln, years	2
Construction time for CCL plant, years	3
Capex	
Process contingencies of CCL plant (maturity), %(EC+IC)	see Table 17
Process contingencies of CCL plant (level of detail of equipment list), %(EC+IC)	see Table 17
Indirect costs factor (INCF), %TDC	14
Owner's costs factor (OCF), %TDC	7
Project contingencies factor (CFproject), %TDC	27
Variable Opex	
Raw meal price, $/t	6
Coal, $/GJ_{HHV}	3
Electricity, $/MWh_e	80
Fixed Opex	
Insurance and local tax, % TPC/year	2
Maintenance cost, % TPC/year	2.5
Number of employees in cement kiln	130
Number of employees in CCL plant	50/60/20[a]
Labour cost, $/year	140,000
Maintenance labour, % of maintenance cost	40
Administrative and support labour, % of O&M labour cost	30
a: number of employees for downstream, tail-end and full integration cases are 50, 60, and 20 respectively	

Two economic indices were employed here to evaluate the economic performance of the cement production with the CCL processes.

- Cost of clinker (CoC)

The cost of clinker (*CoC*) was evaluated by summing the contributions of the investment cost C_{inv}, converted into a yearly constant annualised flow through a Capital Carrying Charge factor, of the fuel cost C_{fuel}, of the raw material costs C_{RM}, of the electricity cost C_{el}, of the other O&M cost $C_{O\&M}$, all referred to the ton of clinker produced (i.e. as $/t clk). In the case where the cement plant is characterised by a net power export, revenues for electricity export to the grid (i.e. negative costs) has been considered. The calculation is shown in Eq. (12)

$$CoC = C_{inv} + C_{fuel} + C_{RM} + C_{el} + C_{O\&M} \tag{12}$$

- Cost of CO_2 avoided (CCA)

The cost of CO_2 avoided was calculated with Eq (13), comparing the cost of clinker and the equivalent specific emissions of the cement plant with and without CO_2 capture.

$$CCA = \frac{CoC - CoC_{ref}}{e_{clk,eq,ref} - e_{clk,eq}} \tag{13}$$

$e_{clk,eq}$ includes the direct and indirect CO_2 emissions and can be calculated through the Eq. (2) for the reference plant with and without CO_2 capture.

4.3.2 Results of cost estimation and discussions

The breakdown of the total plant cost of the three integrated IH-CCL plants is presented in Table 18. In the downstream integration and tail-end integration cases, more than 70% of the cost of the IH-CCL plant (76.22% and 74.27%) was due to the fluidised bed carbonator and indirect-heated calciner. The high fuel consumption in the calciner and the significant thermal energy that needs to be transferred away from the carbonator to recover the energy input necessitates larger size of reactors and thus higher Capex. Following the reactors, the Capex in the downstream and tail-end integration cases were associated with the HRSG system (4.3% and 5.13%), the steam turbine, electric generator and auxiliaries (5.8% and 6.94%), CO_2 compression unit (5.88% and 5.82%), dust filter (2.53% and 2.46%), and the fuel grinding plant (3.41% and 3.37%). In the full integration case, the Capex cost for the reactor system was significantly lower (39.97% of the total IH-CCL plant cost). The HRSG system, steam turbine, power generator and auxiliaries also presented lower shares (1.67% and 2.26%). On the other hand, the cost of the new tower structure partially offset the advantage of the cost of the reactors, leading to a share of 36.24% of the total IH-CCL plant cost. The tower structure cost was assumed to be proportional to the weight of the equipment to be supported. In this project, the weight of 600 tonne was used for the estimation. After the reactor system and tower structure, with an overall Capex share of 78.21% of the total CCL plant, the largest cost in the full integration was associated with the CO_2 compression unit (15.37% of the total IH-CCL plant).

As a result of the high Capex for the reactors, a total IH-CCL plant cost of 1,087.68 and 1,093.75 M$ were obtained for the downstream integration and tail-end integration cases, respectively. For the full integration case, a significantly lower total IH-CCL plant cost of 293.66 M$ was obtained.

Table 17: Calculation assumptions for the capital costs of cement plant integrated with CCL process

Item	EC function, M$[b]	Installation cost factor, % of EC	Process contingencies factor (maturity), % of (EC+IC)	Process contingencies factor (level of detail of equipment list), % of (EC+IC)	Ref
Limestone grinding plant	$EC = 2.184 \times (\frac{m_{rawmeal}[tph]}{30})^{0.67}$	0	0	5	58, 96
Coal grinding plant	$EC = 40 \times (\frac{m_{rawcoal}[tph]}{227})^{0.67}$	240	0	5	99
Fluidised bed carbonator	$EC = 0.365 \times Q[MWth] + 6.434$	110	20	12	58, 96
Fluidised bed indirect-heated calciner[a]	$EC = 0.324 \times (Q[MW])^{0.65}$	107	60	12	58, 96
Entrained flow carbonator	$EC = 0.144 \times (V_{in}[\frac{m^3}{s}])^{0.5}$	0 (included in EC of tower structure)	60	12	58, 96
Entrained flow calciner	$EC = 0.0882 \times (V_{out}[\frac{m^3}{s}])^{0.5}$	0 (included in EC of tower structure)	60	12	58, 96
Air-fired combustor	$EC = 1.98 \times (\frac{Q[MWth]}{10})^{0.67}$	150	60	12	100
Preheater stages[c]	$EC = 6.69 \times 10^{-9}(D_{cycl}[mm])^2 + 4.614 \times 10^{-6}(D_{cycl}[mm]) + 0.027$	166	0	5	58, 96
Kiln riser	$EC = 0.141 \times (V_{out}[\frac{m^3}{s}])^{0.5}$	206	0	5	58
Insulated ducts	$EC = 0.0454 \times (V_{out}[\frac{m^3}{s}])^{0.5}$	240	0	5	58, 96
Tower structure	$EC = 58.8 \times (\frac{M[ton]}{670})$	0 (included in EC 40%)	25	5	58
Heat recovery system for steam generation	$EC = 74.59 \times (\frac{MW[net]}{473.6})^{0.67}$	0	0	5	101
Steam turbine, electric generator and auxiliaries	$EC = 56.62 \times (\frac{MW[net]}{200})^{0.67}$	0	0	5	102
Dehydration unit	$EC = 3.36 \times (\frac{m_{co2,capt}[kg/s]}{205.86})^{0.6}$	0	0	5	102
CO$_2$ compression	$EC = 18.77 \times (\frac{P_{com}[MW]}{13})^{0.67}$	0	20	12	58, 96, 102
Dust filter	$EC = 17.15 \times (\frac{m_{flue\,gas}[kmol/h]}{35720})^{0.67}$	0	0	0	103

Others (including fans, pumps, heat exchangers, feed water preheaters etc)[d]

a: the sum of the following items: (i) the cost of the refractory lined reactor, (ii) the cost of cyclone and (iii) the cost of fuel handling equipment

b: the cost is converted to Aud$ based on the exchange rate of €/ $ AUD=1.68, USD$/AUD$=1.55

c: three pre-heater cyclones are considered in this project

d: the TPC of other equipment is estimated to be 5% of the total TPC

Table 18: Breakdown of the total plant cost (TPC) of the integrated IH-CCL plants

	Downstream integration	Tail-end integration	Full integration
CCL plant cost, M$ (% of total CCL plant)			
Fuel grinding plant	37.06 (3.41)	36.89 (3.37)	--
Fluidised bed carbonator	470.09 (43.22)	470.09 (42.98)	--
Fluidised bed indirect-heated calciner[a]	358.95 (33)	342.27 (31.29)	--
Entrained flow carbonator	--	--	8.50 (2.96)
Entrained flow calciner[a]	--	--	85.48 (29.8)
Preheater stages[b]	--	--	26.41 (9.21)
Insulated ducts	2.42 (0.2)	3.96 (0.36)	--
Tower structure	--	--	103.96 (36.24)
Heat recovery steam generation (HRSG) system	46.62 (4.3)	56.09 (5.13)	4.78 (1.67)
Steam turbine, electric generator and auxiliaries	63.06 (5.8)	75.86 (6.94)	6.47 (2.26)
Dehydration unit	3 (0.28)	2.98 (0.27)	2.15 (0.75)
CO_2 compression unit	63.95 (5.88)	63.65 (5.82)	44.10 (15.37)
Dust filter	27.54 (2.53)	26.94 (2.46)	--
Others (including fans, pumps, heat exchangers, feed water preheaters etc)	15.00 (1.38)	15.00 (1.37)	5.00 (1.74)
Total CCL plant, M$	1,087.68	1,093.75	293.66
Reference cement plant, M$	463	463	463
Total plant cost (TPC), M$	1,550.68	1,556.75	756.66
a: the cost is a sum of costs for the calciner and air-combustor; b: the cost includes a kiln riser and 3 pre-heater stages			

The breakdown of the cost of clinker for the cement plant with and without IH-CCL plant is presented in Table 19. The clinker cost for the reference cement plant without CO_2 capture was estimated at 119.19$/t, which was about 9% higher than the estimation of IEA[104]. Capex, variable Opex and fixed Opex contributed with a similar share to the total cost of clinker. In comparison, the downstream integration and tail-end integration cases showed much higher clinker costs (235.78 and 216.78$/t). This can be attributed to the significantly higher Capex (153.93 and 151.17$/t) and fixed Opex (82.53 and 81.66$/t), although their variable Opex (3.34 and -16.05$/t) were the lowest due to the revenues from the net electric power. The full integration case had a total clinker cost of 175.69$/t, the lowest among all the integration cases. In all the integration cases, the highest contribution to the cost of clinker was derived from the capital expenditure.

Table 19: Breakdown of the cost of clinker (CoC) for the cement plant with and without CCL plant

	Ref cement plant	Downstream integration	Tail-end integration	Full integration
Raw meal price, $/t clk	9.49	8.00	8.00	9.34
Fuel, $/t clk	10.74	50.87	49.54	16.42
Electricity, $/t clk	17.24	-55.53	-73.59	-2.06
Variable opex, $/t clk	**_37.47_**	**_3.34_**	**_-16.05_**	**_23.7_**
Insurance and local tax, $/t clk	9.26	20.96	21.15	11.29
Maintenance, $/t clk	11.58	26.20	26.44	14.11
Labour, $/t clk	21.98	35.37	34.07	26.13
Fixed opex, $/t clk	**_42.82_**	**_82.53_**	**_81.66_**	**_51.53_**
Cement plant, $/t clk	38.90	34.48	34.65	38.29
CCL plant, $/t clk	--	115.45	116.52	62.16
Capex, $/t clk	**_38.9_**	**_153.93_**	**_151.17_**	**_98.45_**
Cost of clinker (CoC), $/t clk	**_119.19_**	**_235.78_**	**_216.78_**	**_175.69_**

The breakdown of the cost of CO_2 avoided for all the integration cases is presented in Table 20. The lowest CCA of 58.68$/t was obtained for the tail-end integration, followed by 65.88$/t for the full integration case and 80.83$/t for the downstream integration case. In all cases, the variable Opex were negative due to the net power export, which partially compensated for the increased Capex. The tail-end integration case showed much less CCA than the downstream integration case, mainly due to its higher net electric export and lower Capex.

Table 20: Breakdown of the estimated cost of CO_2 avoided (CCA) for the integrated cement plant with CCL plant

	Downstream integration	Tail-end integration	Full integration
Variable Opex, $/t CO₂	-23.67	-32.18	-16.06
Fixed Opex, $/t CO₂	27.53	23.36	10.16
Capex, $/t CO₂	76.96	67.50	71.78
Cost of CO₂ avoided (CCA), $/t CO₂	80.83	58.68	65.88

4.4 Sensitivity analysis

To understand the uncertainty and the dependency of some assumptions, the sensitivities of the CCA to the following parameters were evaluated in various ranges as below. The results are presented in Figure 21.

- Discount rate: +/-30% of the reference value;

- Power cost: +/-50% of reference value;

- Fuel cost: +/-50% of reference value;

- Process contingencies ($CF_{process}$): +/-50% of reference values; and

- Steam cycle efficiency: 20-40%
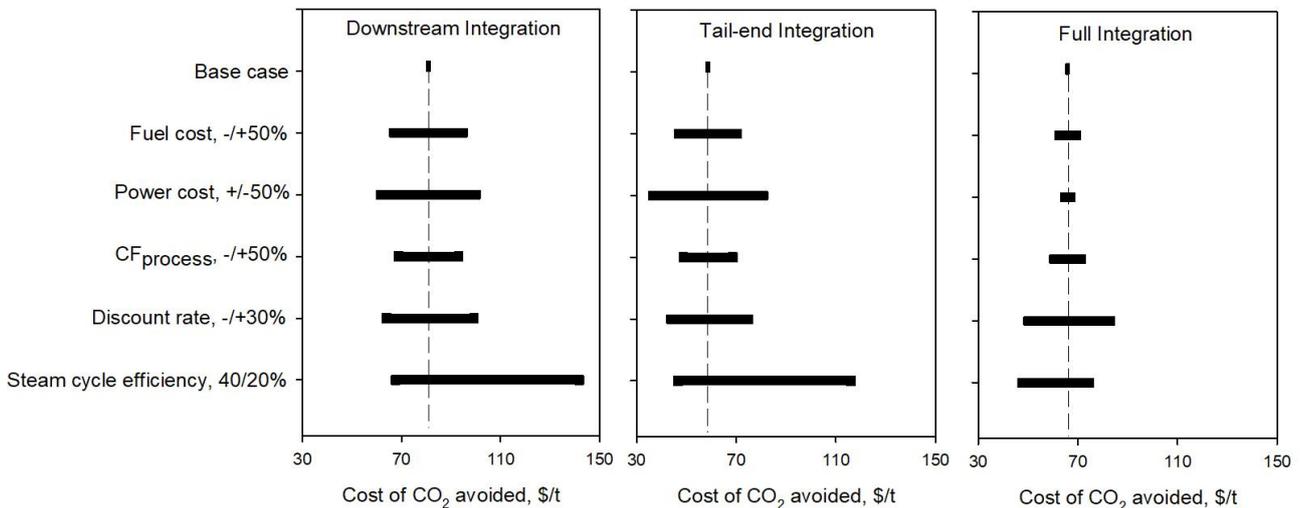
Figure 21: Sensitivities of the CCA relative to the base cases

As discussed in the previous sections, the steam cycle efficiencies for the base cases of the three configurations were assumed based on the thermal input and temperature profile of the heat available. The sensitivity analysis on the steam cycle efficiency in the range of 20-40%, as shown in Figure 21, shows that the steam cycle efficiency has the largest impact on the CCA of the downstream and tail-end configurations. When the steam cycle efficiency increases from 20% to 40%, the CCAs of the downstream and tail-end configurations reduce from 141.8$/t to 67.5$/t and

from 116$/t to 46.5$/t, respectively. The impact of the steam cycle efficiency on the CCA of the full integration case is much less noticeable, due to the much lower thermal input to the HRSC. The CCA of the full integration case reduces from 74.5$/t with the steam cycle efficiency of 20% to 47.5$/t for the efficiency of 40%.

After the steam cycle efficiency, the power cost has the largest impact on the CCAs of the downstream and tail-end configurations, due to the significant net electric export. In contrast, the power cost has the least impact on the CCA of the full integration case. As all three configurations are exporting electricity to the grid, they can benefit from higher electricity price. An increase of the electricity price by 50% leads to the CCA reductions of 37.6% for the tail-end configuration, 23.8% for the downstream configuration, and 1.8% for the full integration.

The discount rate is the most influential parameter on the CCA for the full integration, but the second most influential for the downstream and tail-end configurations. A reduction of the discount rate by 30% leads to the CCA reductions of 21% for the tail-end configuration, 25.8% for the downstream configuration, and 25% for the full integration.

The fuel cost is also an important parameter influencing the CCA. In general, the CCA is negatively affected by an increase of the fuel price compared with the reference cement kiln, due to the higher fuel consumption in all configurations. An increase of the fuel price by 50% leads to the CCA increases of 17.2% for the tail-end configuration, 19.9% for the downstream configuration, and 5% for the full integration.

$CF_{process}$ were varied in ±50% of the reference values assumed in Table 16. The variation of $CF_{process}$ leads to CCA variations of ±14.9% for the tail-end configuration, ±16.8% for the downstream configuration, the ±8.3% for the full integration.

4.5 Comparison with other CO_2 capture technologies

The cost of CO_2 avoided (CCA) of the IH-CCL process integrated with cement production was compared with other CO_2 capture technologies that have been studied for CO_2 capture in the cement industry. These CO_2 capture technologies have been reviewed in Chapter 2, including the chemical absorption using MEA and chilled ammonia process (CAP), oxyfuel combustion, membraned-based CO_2 capture, and Oxy-CCL process. Similarly, the Oxy-CCL process can be configured with the cement plant as a tail-end or a fully integrated plant. The CO_2 capture efficiency (CCE) and CCA of these technologies from the literature has been summarised in Table 21, with the origin currency converted to AUD where necessary. It should be noted that the productivity and labour costs will likely vary significantly between jurisdictions. And the costs include CO_2 capture and compression. The mean costs of these technologies and the CCA of the IH-CCL processes are shown in Figure 22, with error bars if applicable covering the complete cost range as summarised in Table 21.

In general, the highest mean cost is associated to the chemical absorption using MEA (117.78 $/t) and CAP (109.9$/t). The cost of MEA fluctuates in a wide range of 71.93-182.6 $/t, depending on the solvent used and the source of steam. Following the chemical absorption, the mean cost of membrane-assisted CO_2 capture technology is 102.8 $/t. The CCA of the Oxy-CCL process is 100.54 $/t for the tail-end configuration and 97.28 $/t for the full integration. Among these CO_2 capture technologies that are studied for the cement industry, oxy-fuel combustion seems to possess the lowest CCA (65.45 $/t). However, the oxy-fuel combustion technology usually presents a relatively lower CO_2 capture efficiency (66.7%) while the Oxy-CCL process shows the highest CO_2 capture

efficiency (93-95%). Also, oxy-fuel combustion requires extensive retrofitting to the kiln system. Owing to its relatively lower CCA, the oxy-fuel combustion technology may suite more to greenfield cement plants.

In comparison with the cost data from the literature, the IH-CCL process being studied in this project has a significant potential to bring down the CO_2 avoidance cost. In particular, the calculated CCA (58.68$/t) of the IH-CCL tail-end configuration is the lowest among all the technologies. The tail-end configuration also has very minor impact to the existing cement kiln system as discussed above. The IH-CCL full integration case shows a slightly higher CCA of 65.88$/t, which is comparable to that of oxy-fuel combustion and still a lot lower than other CO_2 capture technologies. Although the full integration also requires significant modifications to the existing pre-heater stages and pre-calciner, the rotary kiln remains unchanged.

Table 21: Summary of the cost of CO_2 capture technologies from the literature for the cement industry

Author	Year	Origin currency	Ref plant size, clinker production, t/h	CO_2 capture efficiency (CCE), %	CO_2 avoided cost[a], $/$CO_2$
Amine scrubbing (MEA)					
Voldsund et al [105]	2018	Euro	120.7	90	133.1
Barker et al[104]	2009	Euro	115.4	74.4	178.3
Ho et al[106]	2008	AUD	126.8	89.5	76
Summers et al[107]	2014	USD	125.9	95	148.3
IEAGHG[10]	2008	Euro	115.4	74.1	98.9
IEAGHG[15]	2013	Euro	125	Unknown	108-182.6
Atsonios et al[102]	2015	Euro	164.9	Unknown	117.96
Hana Gerbelova et al[103]	2017	Euro	230	86.6	71.93
Chilled ammonia process (CAP)					
Voldsund et al[105]	2018	Euro	120.7	90	109.9
Oxyfuel combustion (Oxy)					
Voldsund et al[105]	2018	Euro	120.7	90	70.38
Barker et al[104]	2009	Euro	115.4	60	66.73
ECRA Phase II[9]	2009	Euro	125	60	59.43
Kuramochi et al[108]	2012	Euro	126.8	Unknown	73.04
Zhou et al[109]	2016	USD	208.3	62	77.5
IEAGHG[10]	2008	Euro	115.4	61.2	56.94
IEAGHG[15]	2013	Euro	125	Unknown	66.4-83
Hana Gerbelova et al[103]	2017	Euro	230	67	61.72
Membrane-assisted CO_2 capture (MAC)					
Voldsund et al[105]	2018	Euro	120.7	90	138.6
Barker et al	2018	USD	126.8	80	67[b]
Oxy-CCL Tail-end integration (Oxy-CCL Tail)					
Voldsund et al[105]	2018	Euro	120.7	94%	86.98[c]
Atsonios et al[102]	2015	Euro	164.9	93	114.1[d]
Oxy-CCL Full integration (Oxy-CCL Full)					
Voldsund et al[105]	2018	Euro	120.7	95	97.28
a: the currency is converted to AUD when necessary, based on Euro/AUD=1.66, USD/AUD=1.55					
b: this is the CO_2 capture cost					
c: this is for integration level of 50%					
d: this is for integration level of 8%					
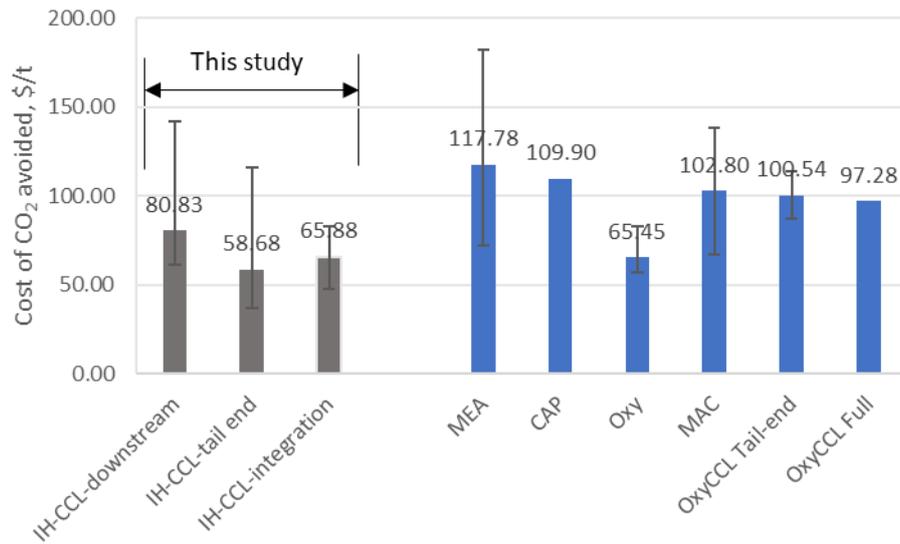
Figure 22 Comparison of estimated cost of CO₂ avoided for CO₂ capture technologies in the cement industry. Costs for other CO₂ capture technologies from the literature are presented on their mean values with error bars covering the complete cost range as summarised in Table 21. Error bars for the three IH-CCL configurations in this study are based on the sensitivity analysis

5 Conclusions and recommendation

5.1 Conclusions

The project studies the retrofit of a novel IH-CCL process into an existing cement plant for deep CO_2 emissions reduction at competitive costs. The IH-CCL process is based on the reversible reaction between CaO and CO_2 and is more compatible with cement production than other PCC technologies, as the spent materials can be re-used for clinker production. Nationally, there has been no research on retrofitting existing cement plants with calcium looping in an industrial setting.

The project include technology surveys to better understand the latest technological development in reducing carbon emissions from the cement sector, site investigation to collect relevant technical information and understand its current operation, and techno-economic feasibility assessment to understand the technical retrofitability, economic viability and potential CO_2 emissions reduction.

In the techno-economic assessment, the novel IH-CCL process was then retrofitted into a reference cement plant through three different integration configurations, including the downstream integration, tail-end integration and the full integration. The reference cement plant is based on a dry process with 4 stages of pre-heaters, a pre-calciner and a rotary kiln with a clinker production of 184 t/h. A snapshot of the techno-economic assessment results is shown in the table below.

	Ref plant	Downstream integration	Tail-end integration	Full integration
SPECCA, MJ/t clk	--	4,124.32	2,264.18	1,396.71
Cost of clinker (CoC), $/t clk	119.19	235.78	216.78	175.69
Cost of CO_2 avoided (CCA), $/t CO_2	--	80.83	58.68	65.88

The best SPECCA was obtained for the full integration case (1,396.71 MJ/t clk), followed by the tail-end integration (2,264.18 MJ/t clk) and downstream integration (4,124.32 MJ/t clk). The retrofit of IH-CCL resulted in significant increases in the calculated CoC from 119.19$/t for the reference plant without CO_2 capture to 175.69$/t for full integration, 216.78$/t for tail-end integration, and 235.78$/t for downstream integration. The significant increases are mainly attributed to the high Capex, which seems a common problem for all CO_2 capture technologies. Among all integration configurations, the IH-CCL tail-end configuration has the lowest CCA of 58.68$/t and the full integration case shows a slightly higher CCA of 65.88$/t. The downstream integration configuration has the highest CCA of 80.83$/t. Compared with other PCC technologies, the IH-CCL tail-end and full integration configurations have a potential to significantly improve the commercial viability of CO_2 capture from cement production.

The retrofitability of these three integration configurations was also qualitatively assessed through six criteria based on the technical assessment results. Although the downstream and tail-end configurations are expected to have much larger footprint than the full integration case, all the three configurations should be able to fit in the existing reference plant based on the site investigation. Also, both the downstream and tail-end configurations involve a standalone IH-CCL plant with very minor impact on the existing cement plant and negligible impact on the clinker quality. In contrast, the full integration case requires significant modifications to the existing kiln system, and the impact on the clinker quality is currently unclear due to changes in the gas atmosphere and temperatures. Moreover, additional dust removal may be required for the downstream and tail-end configurations due to the high fuel consumption. Lastly, the handling of steam, operation of new auxiliaries

including the steam cycle and CO_2 compression unit are required in all cases and are different skill set to the operators.

The economic index relies on assumptions related to the discount rate, electricity price, fuel price, process contingencies and steam cycle efficiency, etc. A sensitivity analysis of the CCA was performed, showing a strong dependency on all variables for both the downstream and tail-end configurations. In comparison, the CCA for the full integration configuration was more sensitive to the discount rate and steam cycle efficiency than the other variables.

In summary, the IH-CCL tail-end integration is recommended for retrofitting to existing cement plants due to the lowest CCA and very minor impact on the existing cement manufacture process. The full integration case offers the lowest SPECCA and clinker cost, indicating the potential to minimise the energy consumption for CO_2 capture. But this option requires significant modifications to the existing pre-heaters and tower structure, and a long stop of cement production for the modifications. For this reason, the full integration case may better suit greenfield cement plants.

5.2 Recommendations

For the first time the IH-CCL technology is investigated for CO_2 capture in the Australian cement industry. Based on the techno-economic assessment, the novel IH-CCL technology can be retrofitted to an existing cement plant for deeply cutting CO_2 emissions in a cost competitive manner. To further progress the IH-CCL technology, the following R&D is recommended:

- Fundamental R&D

    The IH-CCL technology eliminates the need of an energy-intensive ASU but needs larger size of reactors due to the higher fuel consumption. As a result, the Capex represents the largest share of the total plant cost. Therefore, a thorough thermodynamic analysis is required to minimise the fuel consumption and ultimately the Capex.

    On the other hand, it is still unclear at this stage that how the retrofit might impact the clinker quality, particularly in the full integration case due to changes in gas atmosphere, temperature and/or other conditions. Some lab-scale experimental work should be carried out to understand the impact and identify the work required to ensure the clinker quality.

- Pilot-scale prototype unit demonstration

    Although the Oxy-CCL process has been demonstrated through a number of pilot-scale plants, the operational experience associated with IH-CCL is scarce and its TRL is low. A pilot-scale IH-CCL prototype unit needs to be erected to gain engineering and operational experience to reduce the high Capex for the future deployment in the cement industry. The pilot-scale IH-CCL prototype unit also needs to be demonstrated at a cement plant using real flue gas.

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Appendices

List of publications arising from the project

N/a

List of all staff that have been engaged on the project and any associated academic/professional qualifications obtained.

Project team	Academic/professional qualifications
Jon Yin	• PhD in Mechanical Engineering • Master of Engineering in Thermal & Power Engineering • Bachelor of Engineering in Thermal & Power Engineering
Chaoen Li	• PhD in Physical Chemistry • Master of Computer • Master of Engineering in Applied Organic Chemistry • Bachelor of Science in Organic Chemistry
Shi Su	• Doctor of Engineering in Thermal Energy • PhD in Chemical Engineering • Bachelor of Engineering in Thermal Energy
Xin Xiang Yu	• Master of Engineering in Power Machinery • Bachelor of Engineering in Mechanical Engineering
Gabriel Paicu	• Bachelor in Chemical Engineering, specialised in cement, glass and ceramics

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: Research Scientist

Name: Junjun (Jon) Yin

Date: 23/09/2020

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