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Process Design and Techno-ECONOMIC Evaluation of a Decarbonized Cement Production Process Using Carbon Capture and Utilization

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Abstract: To address a decarbonized cement production process (DCPP), a calcium looping process is connected to an industrial cement production process (CPP) for capturing CO₂ by 93.5–96%. Since the captured CO₂ purity is up to 99.9 wt%, the carbon capture and utilization (CCU) process is connected to generate the additional products of urea and methanol. An integration of DCPP and CCU, named the DCPP-based polygeneration system, is being developed for three scenarios. To meet the power demand for producing high-purity hydrogen and oxygen, Scenario 1 adopts water electrolysis and the full green electricity grid; Scenario 2 adopts the Cu-Cl thermochemical cycle and the partial green electricity grid; and Scenario 3 adopts water electrolysis and the heat recovery steam generator (HRSG). Through the techno-economic analysis and comparisons, the CO₂ avoided costs of three scenarios are estimated between 16.53 and 21.42 USD/ton, which are lower than the conventional DCPP of around 40 USD/ton. It is due to the fact that the polygeneration scheme could reduce the LCOP (levelized cost of producing 1 ton of clinker) due to the production of valorized products. It is noted that Scenario 2 is superior to other scenarios since the RenE2P cost in Scenario 2 is lower than it is in Scenario 1 and the captured CO₂ rate in Scenario 2 is lower than it is in Scenario 3.

Keywords: calcium-looping; carbon capture and utilization; cement production process; economics

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1. Introduction

The cement production process was energy- and carbon-intensive, accounting for approximately 7% of global CO₂ emissions. To meet the European regulations, such as a legal obligation to reduce EU emissions by at least 55% by 2030, the price of carbon contracts on the EU Emissions Trading Scheme (ETS) has hit \$106.57 (€100) per tonne [1]. The recirculation of CO₂ technology for capturing CO₂ from the cement process could create a value chain where the cost of capturing pure carbon is quite high [2]. Several different carbon-capture technologies have been used in the cement industry, where calcium looping (CaL) is a promising technology for capturing CO₂ from the flue gas and achieving 90% CO₂ capture efficiency by recycling deactivated CaO sorbent reinserted into the precalciner and mixing with the raw material of the kiln [3]. A study showed that the CaL system has significant technical and economic advantages compared to the gas-liquid absorption case using alkanolamine (MDEA) as a chemical solvent due to lower capital and operational costs as well as lower CO₂ avoidance costs [4]. A study showed that the CaL technology was superior to gas-liquid absorption using MDEA for post-combustion capture configuration due to a lower carbon footprint and better economic indicators [5]. Through the process design and integration of methanation of carbon dioxide and the CaL process, the simulation showed that this integrated process produces 1 ton of methane with a molar fraction of nearly 91% by consuming 344–370 GJ [6].

The commercialization of CaL has not reached commercial-scale demonstration in the cement sector yet. The main challenges included that the CaO-based adsorbent should maintain its high sorbent activity during long-term cycling and that an air separation unit (ASU) for the oxyfuel combustion in the calciner was necessary [7]. A pilot test of CaL for a cement plant showed that the large limestone makeup flow was used in the calciner to keep the Sorbent activity [8]. An experimental study showed that the carbonation temperature, the CO₂ concentration for CaO-based adsorbent, and the reactor type affected the adsorption efficiency [9]. For high sorbent make-up flows in a 200 kW calcium looping pilot plant, the CO₂ capture efficiencies are up to 98% in the carbonator at a carbonation temperature of around 600 °C [10].

A carbon capture and utilization (CCU) technology using concrete wastes such as alkali wastes could capture a portion of the CO₂ emitted from the cement kiln flue gas to produce recarbonate [11]. This study claimed that the cement plant usually emits much more CO₂ than can be utilized below 10% in a single CO₂ utilization plant, such as in the production of ethanol or food-grade CO₂ [12]. A study showed that the CaL process integrated with coal-based power plants or cement production processes could enhance industrial symbiosis and reduce cost by adding the production of value-added products such as methanol, polymers, and acetic acid [13]. Although the CaL process played an important role in the decarbonization of cement plants, the promising chemical candidate for mitigation of CO₂ by chemical conversion dominated environmental impacts and costs. A study showed that the high CO₂ content (11–17 vol%) of flue gas from fluid catalytic cracking has great economic potential for methanol production due to methane and hydrogen as byproducts [14].

Regarding the economic comparisons of the decarbonization options for a cement production process, it shows that the oxy-combustion CO₂ capture is superior to the chemical scrubbing system for post-combustion CO₂ capture due to its higher carbon capture rate and lower CO₂ avoided cost [15]. A similar study showed that the cost of oxy-combustion CO₂ capture in the cement production process was effectively reduced due to the generation of hydrogen products and byproduct oxygen via the electrolysis of water [16]. For the economic evaluation of the polygeneration system for olefins from industrial off-gas such as coke oven gas or hydrogen, coke oven gas is more competitive than hydrogen due to the feed price [17]. The CaL cluster treating the flue gas from multiple industrial emitters could reduce the cost of capturing CO₂ by connecting a cluster of industrial sites with significant heat demands with a decarbonized cement production process using the CaL system [18].

In this paper, the decarbonized cement production process (DCPP) using an integration of a CPP and a CaL process is developed. The process design and simulation of the DCPP in Aspen Plus® are shown in Section 2. The DCPP not only produces the clinker but also releases high-purity and high-temperature CO₂. To drive a circular economy, DCPP-based polygeneration systems using three types of carbon capture and utilization (CCU) are proposed, which are described in Section 3. Regarding the market evaluations of potential chemical products in Table 1, it shows that methanol as the fuel demand and urea as the fertilizer demand are quite high in Taiwan, and the high-purity CO₂ demand in the world will be up to 230 million tons per year. Moreover, the economic evaluations of three scenarios of DCPP-based polygeneration systems in terms of capital expenditure (CAPEX), operating expense (OPEX), and CO₂ avoided cost are described in Section 4.

Table 1. Comparisons of methanol, urea, and CO₂.

	Methanol	Urea	CO ₂ (99.9 wt%)
Selling price (USD/ton)	310	303	11.3 [19]
Average demand (ton/yr)	450.9 × 10 ⁶ in Taiwan [20]	0.1 × 10 ⁶ in Taiwan [21]	230 × 10 ⁶ in the world [22]
Application	Fuel	Fertilizer	Urea; Food; Enhanced oil recovery (EOR)

2. Decarbonized Cement Production Process

2.1. Cement Production Process

This case study of the cement production process (CPP) is based on the configuration of the cement plant at Taiwan Cement Ltd., located in Hualien, Taiwan. Figure 1 describes the CPP as consisting of three major processes. The first is two five-stage cyclone preheaters, which are composed of ten cyclones (C1, C2, . . . , C10) in total. The cyclone preheater is the countercurrent heat exchanger that recovers the waste heat of flue gas from the pre-calciner and heats up two sets of raw materials as well. The second is the pre-calciner with the calcium carbonate decomposition reaction.

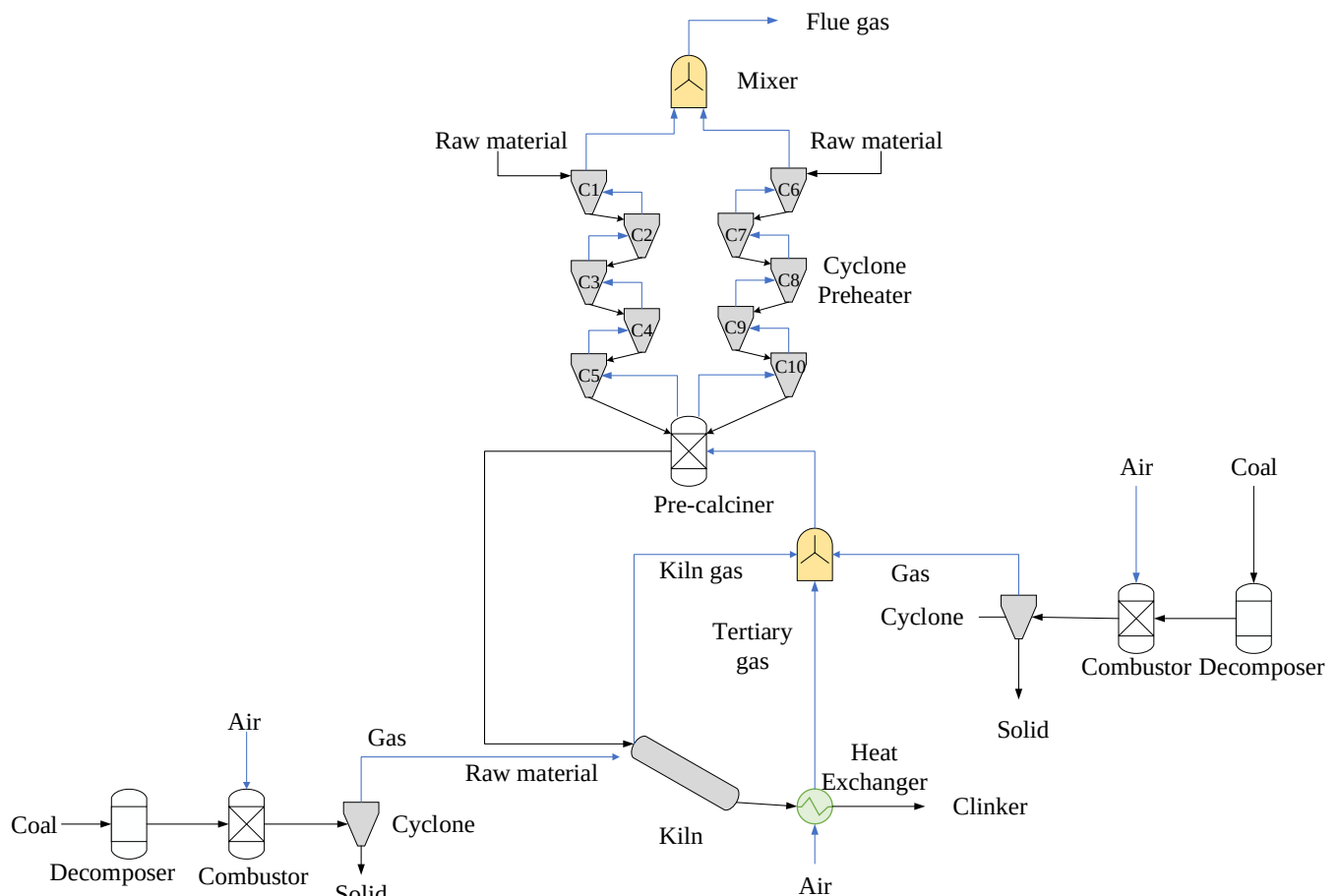


Figure 1. Cement production process.

It is part of the calcining work of a cement rotary kiln. The third is the cement rotary kiln to produce the clinker. Since the operating temperatures of the pre-calciner and cement rotary kiln are around 900 °C and 1250 °C, respectively [23], two coal combustion units are used to meet the heat demands of the pre-calciner and cement rotary kiln. Notably, the outlet product of the kiln is reduced to 100 °C by using an air cooler and the flue gas from the top of the cyclone preheaters (C1 and C6), which are operated at 370 °C.

Regarding the process simulation of the CPP in Aspen Plus[®], first, the compositions of coal and raw materials in Table 2 are slightly modified as compared to the coal and raw materials for the cement plant in Taiwan Cement Ltd., where the amounts of CaO, Al₂O₃, SiO₂, and Fe₂O₃ meet the specifications of hydraulic modulus, silica ratio, and alumina ratio [23]. Second, the reactions in the Aspen Plus module of the kiln are shown in Table 3. The simulation results, such as the outlet flowrates and their compositions of clinker and flue gas, can be found in Table 2. Notably, the compositions of the flue gas are validated

according to the real data from Taiwan Cement Ltd., which are shown in Table S1 in the Supplementary Materials.

Table 2. Parameters of the cement production process.

Coal Compositions			
Proximate analysis		wt%	
Moisture			4.0
Volatiles			6.5
Fixed carbon			74.85
Ash			16.85
Ultimate analysis		wt%	
C			74.85
H			3.25
N			0.98
S			0.38
O			1.82
			16.85
Raw materials		ton/day	13,440
CaO			9072.0
Al ₂ O ₃			672.0
SiO ₂			3306.2
Fe ₂ O ₃			389.8
Coal for pre-calciner		ton/day	531.3
Coal for kiln		ton/day	434.7
Air for pre-calciner		ton/day	5769
Air for kiln		ton/day	3462.1
Flue gas		ton/day	16730.2
N ₂		wt%	55
CO ₂		wt%	26.1
H ₂ O		wt%	12.1
O ₂		wt%	6.4%
Clinker		ton/day	9578.8
C ₂ S		wt%	25.5
C ₃ A		wt%	7.9
C ₃ S		wt%	48.4
C ₄ AF		wt%	9.46

Table 3. Operating conditions and specifications of process units in the DCPD-based polygeneration system.

Process unit: Aspen Plus module and specification
CPP [23] Pre-calciner: RStoic module Temperature = 900 °C; Pressure = 1 bar (1) $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ with 100% conversion Kiln: RStoic module Temperature = 1250 °C; Pressure = 1 bar (2) $\text{CaO} + \text{SiO}_2 \rightarrow 2\text{CaO} \cdot \text{SiO}_2$ (C₂S) with 27% conversion (3) $\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (C₃A) with 8% conversion (4) $\text{CaO} + \text{SiO}_2 \rightarrow 3\text{CaO} \cdot \text{SiO}_2$ (C₃S) with 58% conversion (5) $4\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (C₄AF) with 4% conversion
CaL process [24] Carbonator: RStoic module Temperature = 650 °C; Pressure = 1 bar $\text{CO}_2 + \text{CaO} \rightarrow \text{CaCO}_3$ with 90% conversion Calciner: RStoic module Temperature = 940 °C; Pressure = 1 bar $\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$ with 100% conversion

Table 3. Cont.

Process unit: Aspen Plus module and specification
Ammonia synthesis reactor [25]: RPlug module Temperature = 300 °C; Pressure = 200 bar; $H_2/N_2 = 3$ $r_{NH_3} = 1.8 \times 10^6 \exp\left(\frac{-20.5}{RT}\right) P^{1.59}_{H_2} P^{0.82}_{N_2}$
Urea synthesis reactor [26]: RPlug module Temperature = 200 °C; Pressure = 100 bar; $NH_3/CO_2 = 4$ $R_{urea} = 2.5 \times 10^8 \exp\left(\frac{-94.5}{RT}\right) \times C_T \times \left(X_{H_2NCOO^-} - \frac{1}{K_{NH_3}} \frac{X_{NH_2CONH_2} X_{H_2O}}{K_{NH_4^+}}\right)$
Methanol synthesis reactor [27]: RPlug module Temperature = 250 °C; Pressure = 50 bar; $H_2/CO_2 = 3$; Cu/ZnO/Al ₂ O ₃ catalyst; Catalyst density = 1775 kg/m ³ ; Fixed bed porosity = 0.5 $r_{CH_3OH} = \frac{k_1 P_{CO_2} P_{H_2} - k_6 P_{H_2O} P_{CH_3OH} P_{H_2}^2}{(1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O})^3}$ $r_{RWGS} = \frac{k_5 P_{CO_2} - k_7 P_{H_2O} P_{CO} P_{H_2}^{-1}}{1 + k_2 P_{H_2O} P_{H_2}^{-1} + k_3 P_{H_2}^{0.5} + k_4 P_{H_2O}}$
Three-step Cu-Cl cycle [28]: RStoic module Temperature = 430 °C; Pressure = 1 bar Hydrolysis reaction: $2CuCl_{2(aq)} + H_2O_{(g)} \rightarrow 2CuOCl_{2(s)} + 2HCl_{(g)}$ with 100% conversion Oxygen reaction: $CuOCl_{2(s)} \rightarrow 2CuCl_{(l)} + 0.5O_{2(g)}$ with 100% conversion Electrochemical reaction: $2CuCl_{(l)} + HCl_{(l)} \rightarrow 2CuCl_{2(aq)} + H_{2(g)}$ with 100% conversion

2.2. Calcium-Looping Process

Referring to the previous work for the simulation of the calcium-looping (CaL) process [29], the CaL process is built by Aspen Plus® and shown in Figure 2. The CaL process is composed of two individual reactors, a carbonator and a calciner, and two cyclones. The flue gas (F_{flue1}) and active CaO are fed into the carbonator to carry out the following exothermic reaction at a temperature of around 650 °C.

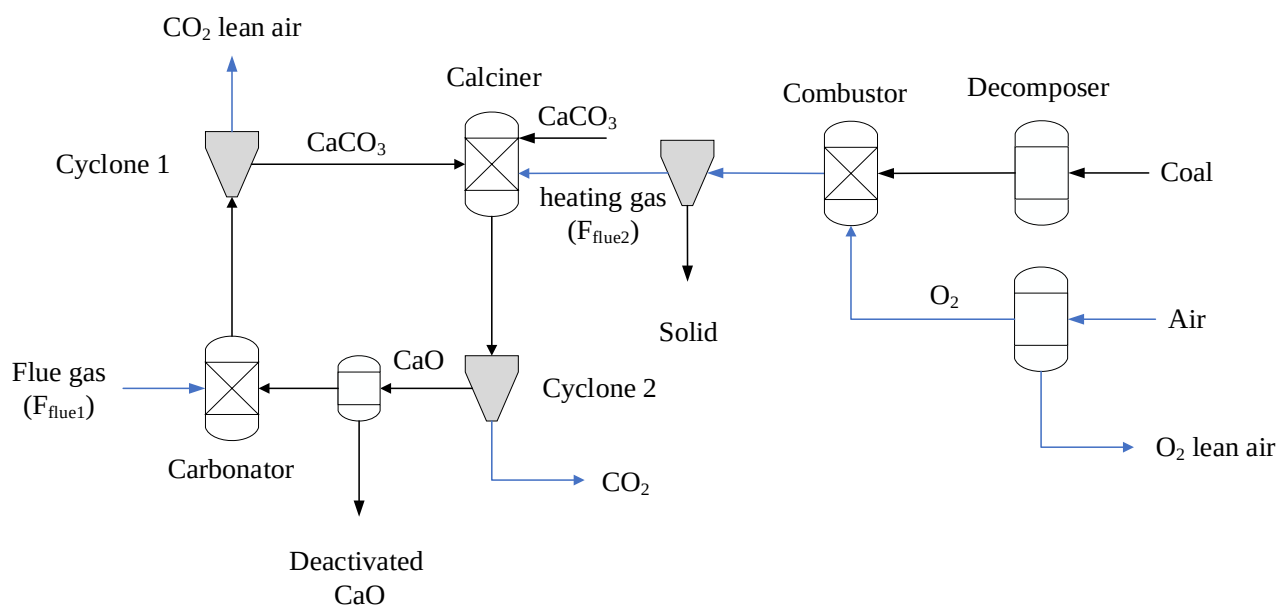


Figure 2. Calcium-looping process.

In the carbonator, the solid product of $CaCO_3$ is delivered to the calciner by conveyor, and the CO_2 -lean gas (tail gas) is emitted into the air after cyclone 1. In the calciner,

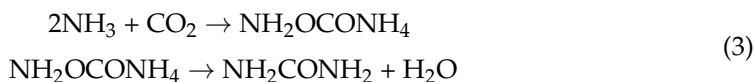
the calcium carbonate decomposition reaction described in Equation (1) is carried out at a temperature of around 940 °C; notably, the solid product of CaO flows back to the carbonator by conveyor, and the high-purity CO₂ gas is easily produced after cyclone 2. The oxyfuel coal combustion is used to provide the heating source for the high-temperature heating gas (F_{flue2}). The deactivated CaO is removed and the fresh CaCO₃ is added to maintain the stable operation of the calciner.

3. DCP-PP-Based Polygeneration System

3.1. Carbon Capture and Utilization

The decarbonized cement production process (DCPP) is an integration of the CPP and CaL processes. Based on the prescribed operating conditions and inlet flowrates of the DCP-PP in Tables 2 and 3, the emitted gases from the DCP-PP include the tail gas at 940 °C from the carbonator, the high-purity CO₂ at 650 °C from the calciner, and the pure N₂ gas from the air separation unit (ASU). To address carbon capture and utilization (CCU), these gases are converted to chemicals through the following processes:

1. Ammonia synthesis reactor (ASR): N₂ and H₂ are synthesized to produce NH₃ in the Haber process. Based on the operating conditions and kinetics of the ASR in Table 3, Figure 3a shows that the ASR model by using the RPlug reactor module in Aspen Plus[®] is validated due to the acceptable curve fitting of experimental data as shown in Table S1 in the Supplementary Materials [30].
2. Urea synthesis reactor (USR): Urea is produced through the following reactions:



where CO₂ and NH₃ are supplied from the calciner in the CaL process and the ASR, respectively. Based on the operating conditions and kinetics of the USR in Table 3, Figure 3b shows that the USR model by using the RPlug reactor module in Aspen Plus[®] is validated due to the acceptable curve fitting of experimental data as shown in Table S1 in the Supplementary Materials [26].

3. Methanol synthesis reactor (MSR): Methanol production from CO₂ is achieved through a catalytic process in the gas phase assuming that the following CO₂ hydrogenation is the only desired reaction [27].



The reactants CO₂ and H₂ are supplied from the calciner in the CaL process and the hydrogen production process, respectively. Based on the operating conditions, specifications for catalyst, and kinetics of the MSR in Table 3, Figure 3c shows that the MSR model by using the RPlug reactor module in Aspen Plus[®] is validated due to the acceptable curve fitting of experimental data as shown in Table S1 in the Supplementary Materials.

According to the above reactions for producing ammonia, urea, and methanol, a large amount of hydrogen is required. To address the more efficient and clean hydrogen production process, the polymer electrolysis membrane (PEM), water electrolysis, and the Cu-Cl thermochemical cycle are illustrated. PEM electrolysis usually has a higher energy efficiency (80–90%) as well as a larger hydrogen production rate than alkaline electrolysis [31]. Referring to the modeling of a PEM electrolyzer [32], the mathematical models of the PEM water electrolysis in Table S2 and the corresponding Simulink block diagram in Figure S1 can be found in the Supplementary Materials. The Cu-Cl thermochemical cycle is another option for hydrogen production by using the thermochemical method for water splitting. It is validated that the three-step Cu-Cl thermochemical cycle with prescribed reactions in Table 3 could reduce the electricity demand by using an electrochemical reactor in place of the PEM water electrolysis [33]. Based on the previous work [28], the simulation of a three-step Cu-Cl thermochemical cycle could be achieved in Aspen Plus[®].

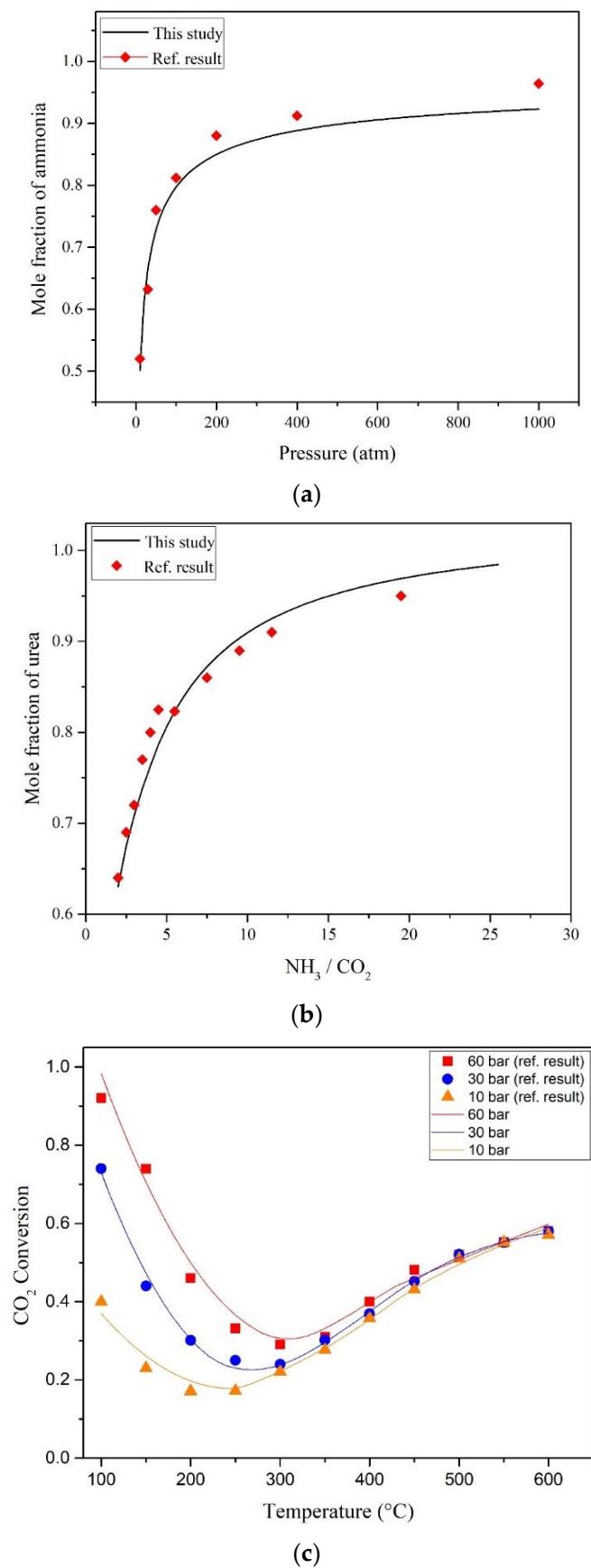


Figure 3. Model validation: reactions of (a) ammonia synthesis, (b) urea synthesis, and (c) methanol synthesis.

3.2. Process Integration

Regarding the integration of the DCP and CCU, three types of DCP-based polygeneration systems are proposed, which are shown in Figures 4–6, respectively. Integration of a renewable energy source to the power grid named RenE2P is treated as “the green electricity grid” which is the uninterruptible power supply for the cold/heat utilities, compressors, ASU, and water electrolysis.

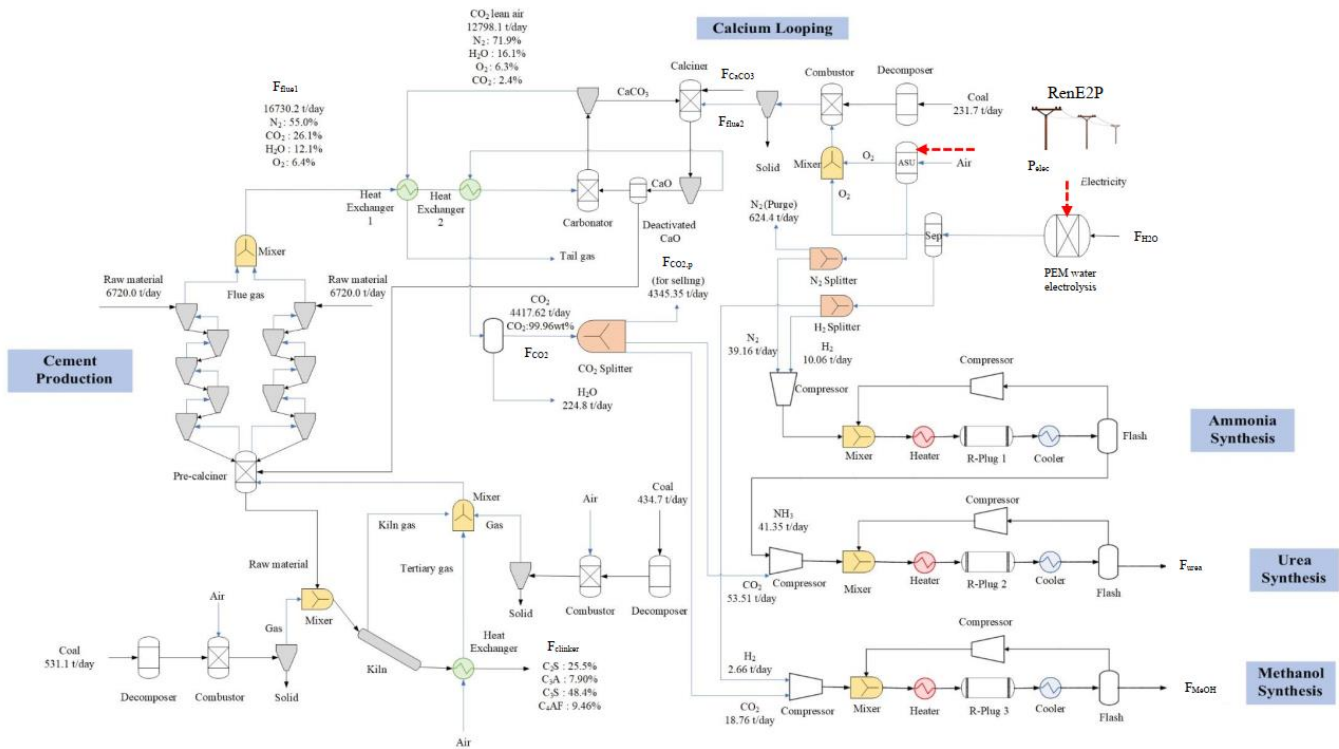


Figure 4. Scenario 1: DCP-based polygeneration system using PEM water electrolysis.

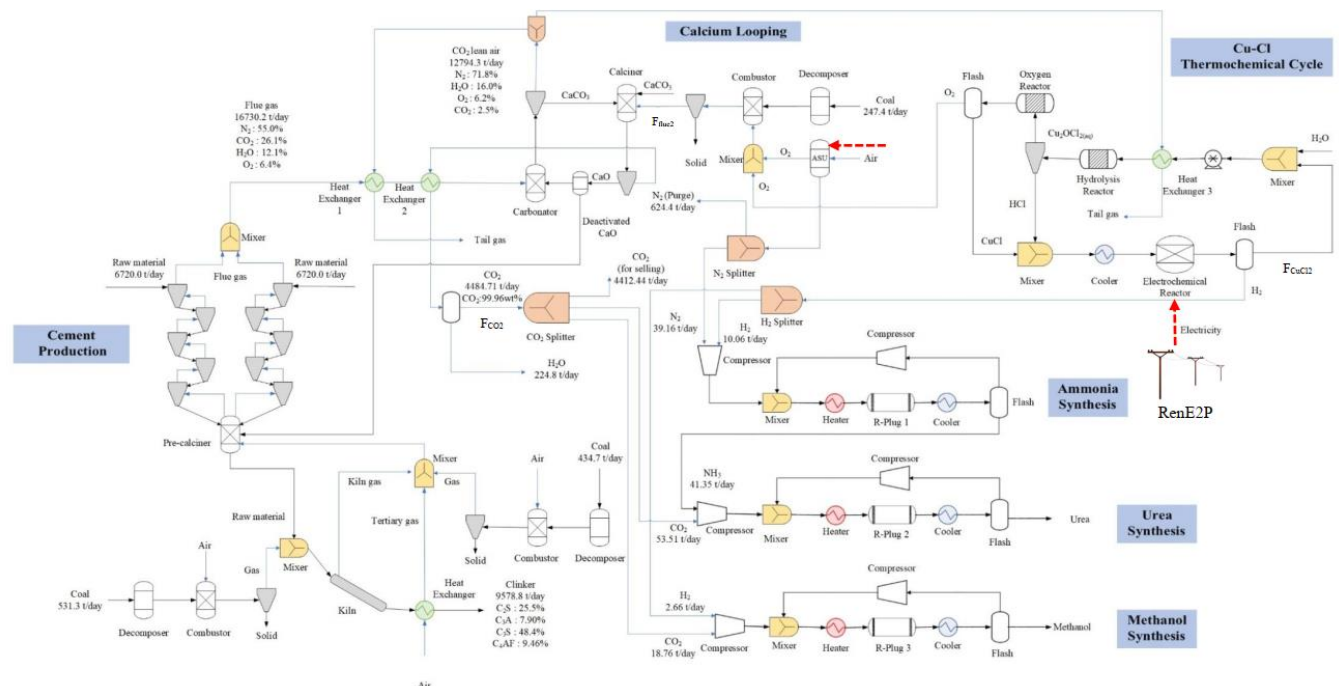


Figure 5. Scenario 2: DCP-based polygeneration system using the Cu-Cl thermochemical cycle.

is consumed, 94% of N₂ is not consumed, and 100% of CO₂-lean gas (tail gas) from the carbonator is emitted into the air.

The CaL process plays an important role in producing high-purity CO₂ for the CCU, so the corresponding CO₂ capture efficiency is expressed by

$$\text{CO}_2 \text{ capture efficiency} = \frac{F_{\text{CO}_2} \times w_{\text{CO}_2}}{F_{\text{fuel1}} \times w_{\text{fuel1,CO}_2} + F_{\text{fuel2}} \times w_{\text{fuel2,CO}_2}} \times 100\% \quad (5)$$

where F_{CO_2} is the outlet tail gas flowrate from the calciner, F_{fuel1} is the inlet flue gas flowrate of the carbonator, and F_{fuel2} is the inlet heating gas flow of the calciner. w_{CO_2} , $w_{\text{fuel1,CO}_2}$, and, $w_{\text{fuel2,CO}_2}$ represent the CO₂ concentrations of the inlet/outlet flows of tail gas, flue gas, and heating gas, respectively. Table 4 shows the comparisons of three scenarios in terms of captured CO₂ rate and CO₂ capture efficiency. The captured CO₂ rate, i.e., CO₂ gas from the calciner (ton/day), in Scenario 3 is higher than in other scenarios due to the coal and air flowrates in the CaL in Scenario 3 being higher than in other scenarios, so it implies that the CO₂ capture efficiency in Scenario 3 is lower than in other scenarios. The Cu-Cl thermochemical cycle added in Scenario 2 increases the heat demand by recovering the waste heat of tail gas from the CaL process, so that the consumption of coal and CaCO₃ for the CaL process increases. The HRSG added in Scenario 3 meets the power demand of the PEM water electrolysis, so it indirectly increases the consumption of coal and CaCO₃ for the CaL process. Regarding total CO₂ emissions evaluations, Figures 4–6 show that the CO₂ emissions of Scenarios 1–3 are 179.83 tons/day, 217.71 tons/day, and 280.04 tons/day, respectively, according to the flowrates of tail gas with prescribed CO₂ concentrations. As compared to the CO₂ emissions of the CPP of 4366.9 tons/day according to the flue gas (F_{flue1}) with 26.1% CO₂, it is validated that the CaL process could capture CO₂ of F_{flue1} by 93.5~96%.

Table 4. Main parameters of Scenarios 1–3 in terms of the calcium looping process.

		Scenario 1	Scenario 2	Scenario 3
Coal	ton/day	231.7	247.4	283.1
Air	ton/day	840	870	1026
CaCO ₃	ton/day	204.0	218	250
CO ₂ gas from calciner	ton/day	4417.62	4484.71	4652.02
CO ₂	wt%	99.96	99.96	99.96
N ₂ -rich gas from carbonator	ton/day	12798.1	12794.3	12822.2
N ₂	wt%	71.9	71.8	71.8
H ₂ O	wt%	16.1	16.0	16.2
O ₂	wt%	6.3	6.2	6.4
CO ₂	wt%	2.4	2.5	3.0
CO ₂ capture efficiency	%	91.7	92.1	90.8

4. Economics

4.1. Cost Estimation

The economic evaluation of DCP-based polygeneration systems such as Scenario 1, Scenario 2, and Scenario 3 in terms of capital expenditure (CAPEX) and operating expenditure (OPEX) is addressed as follows:

- CAPEX: The equipment cost of the DCP-based polygeneration systems is based on the prescribed cost functions in Table 5, which provide the cost information for the scale-up. Notably, the input parameters of cost functions, including the heat transfer areas for the heat exchanger (A_{HX}), the different flowrates for the compressor (F_{inlet}), the load duty of the pump (W_{pump}), chemical reactors, kilns, cyclones, ASU, Cu-Cl thermochemical cycles, and PEM water electrolysis, can be found by Aspen Plus simulation. Moreover, the total equipment costs of Scenarios 1–3 named C_{S1} , C_{S2} , C_{S3} as the summation of the cost functions of process units and the corresponding total

- investment costs of Scenarios 1–3 named TIC_{S1} , TIC_{S2} , and TIC_{S3} as 105% of total equipment costs are shown in Table 5.
- ii. OPEX: The annual costs for labor, maintenance, insurance, raw materials of the CCP and CaL, fuel (coal), and chemicals (H_2O , $CuCl_2$) are shown in Table 6, in which these values and the evaluations are related to the illustrated literature. Notably, the purchasing/selling prices of materials/products and the carbon tax are quoted on the internet. The calculation of the number of laborers for the CCP and CCU is based on a specific correlation formula.

Table 5. CAPEX estimations of DCCP-based polygeneration system.

Equipment Unit	
Pre- or calciner (including Coal combustion unit)	$C_{calciner} = 4.6 \times 10^7 \left[0.15 \left(\frac{V_{Calc}}{1150.5 \text{ m}^3} \right)^{0.67} + \left(\frac{V_{Carb}}{1150.5 \text{ m}^3} \right)^{0.67} \right]$
Cement rotary kiln (including Coal combustion unit) [34]	$C_{cement} = 9.5 \times 10^7 \left(\frac{F_{clinker} \left[\frac{\text{ton}}{\text{day}} \right]}{4000} \right)^{0.64}$
Cyclone	$C_{cyclone} = 17,640 \times \left(\frac{F_{gas}}{4.7 \frac{\text{m}^3}{s}} \right)^{0.66}$
Air Separation unit (ASU)	$C_{ASU} = 58,252,320 \times \left(\frac{F_{O_2, Cal}}{3900.1 \frac{\text{kmol}}{\text{hr}}} \right)^{0.5}$
Calcium looping	$C_{CaL} = 4.6 \times 10^7 \left[0.85 \left(\frac{Q_{Calc}}{534 \text{ MW}} \right)^{0.9} + 0.15 \left(\frac{V_{Calc}}{1150.5 \text{ m}^3} \right)^{0.67} + \left(\frac{V_{Carb}}{1150.5 \text{ m}^3} \right)^{0.67} \right]$
Heat exchanger	$C_{HEX} = 130 \times \left(\frac{A_{HX}}{0.093 \text{ m}^2} \right)^{0.78}$
Cu-Cl thermochemical cycle	$C_{cu-cl} = 1.64 \times 10^8 \times \left(\frac{F_{H_2}}{100 \text{ ton/day}} \right)^{0.75}$
PEM water electrolysis	$C_{PEM} = 9.3 \times 10^7 \times \left(\frac{F_{H_2}}{100 \text{ ton/day}} \right)^{0.65}$
Steam turbine	$C_{ST} = 6000 \times \dot{W}_{ST}^{0.7}$
Compressor	$C_{comp} = \frac{71.7 \times F_{inlet}}{0.92 - \eta_{comp}} \times \pi_{comp} \times \ln(\pi_{comp})$ F_{inlet} : mass flow rate (kg/s) π_{comp} : pressure ratio η_{comp} : compressor isentropic efficiency (0.85)
Pump	$C_{pump} = 1120 \times \dot{W}_{pump}^{0.78}$
Condenser	$C_{cond} = 8000 \times \left(\frac{A_{cond}}{100} \right)^{0.6}$ A_{cond} : heat transfer area (m^2)
Ammonia synthesis reactor	$C_{NH_3} = 10^8 \times \left(\frac{F_{NH_3}}{1000 \text{ ton/day}} \right)^{0.58}$
Methanol synthesis reactor	$C_{MeOH} = 7 \times 10^9 \times \left(\frac{F_{methanol}}{54,794.5 \text{ ton/day}} \right)^{0.78}$
Urea synthesis reactor	$C_{urea} = 7.5 \times 10^6 \times \left(\frac{F_{urea}}{200 \text{ ton/day}} \right)^{0.64}$
CCP	$C_{CCP} = C_{cement} + C_{calciner} + 10 C_{cyclone}$
CaL process	$C_{CaL} = 2 \times C_{cyclone} + C_{carbonator} + C_{calciner}$
HRSG	$C_{HRSG} = 8 \times C_{HEX} + 3 \times C_{ST} + C_{pump}$
Ammonia synthesis process (ASP)	$C_{ASP} = C_{NH_3} + 2 \times C_{comp}$
Urea synthesis process (USP)	$C_{USP} = C_{urea} + 2 \times C_{comp}$
Methanol synthesis process (MSP)	$C_{MSP} = C_{MeOH} + 2 \times C_{comp}$
CCU of Scenario 1	$C_{CCU, S1} = C_{PEM} + C_{ASP} + C_{USP} + C_{MSP}$
CCU of Scenario 2	$C_{CCU, S2} = C_{cu-cl} + C_{ASP} + C_{USP} + C_{MSP}$

Table 5. Cont.

Equipment Unit	
CCU of Scenario 3	$C_{CCU,S3} = C_{HRSG} + C_{ASP} + C_{USP} + C_{MSP}$
Total equipment cost of Scenario 1	$C_{S1} = C_{CPP} + C_{CaL} + C_{ASU} + C_{CCU,S1}$
Total equipment cost of Scenario 2	$C_{S2} = C_{CPP} + C_{CaL} + C_{ASU} + C_{CCU,S2}$
Total equipment cost of Scenario 3	$C_{S3} = C_{CPP} + C_{CaL} + C_{ASU} + C_{CCU,S3}$
Fees (land, auxiliary devices, and site preparation, etc.)	$5\% \times C_{S1}, 5\% \times C_{S2}, 5\% \times C_{S3}$
Total investment costs (TIC) of Scenarios 1–3	$TIC_{S1} = 105\% \times C_{S2}, TIC_{S2} = 105\% \times C_{S2}, TIC_{S3} = 105\% \times C_{S3}$

Table 6. Economic conditions and assumptions.

Coal (C_{coal})	USD/ton	77.12
Raw materials of CPP ($C_{feed,CCP}$)	USD/ton	5.92
$CaCO_3$ (C_{CaCO3})	USD/ton	10
H_2O (C_{H2O})	USD/m ³	0.74
$CuCl_2$ (C_{CuCl2})	USD/ton	25,000
RenE2P (C_{elec})	USD/kWh	0.17
CO ₂ (99.9wt%) selling price (S_{CO2})	USD/ton	11.3
Methanol selling price (S_{MeOH})	USD/ton	310
Urea selling price (S_{urea})	USD/ton	303
Cement selling price (S_{cement})	USD/ton	80
Carbon tax (C_{CO2})	USD/ton	55
Annual payment per labor	USD/yr	20,000
Annual maintenance and insurance costs of the CPP	USD/yr	$5.25\% \times C_{CPP}$
Annual maintenance, labor, and insurance costs of the CaL	USD/yr	$12\% \times C_{CaL}$
Annual maintenance and insurance costs of the CCU	USD/yr	$5.25\% \times C_{CCU,S1},$ $5.25\% \times C_{CCU,S2},$ $5.25\% \times C_{CCU,S3}$
Discount rate	%	6
Annual working day	hr	300
Construction time	yr	3
Total plant life	yr	17

$$N_O = \left(6.29 + 31.7N_{solid}^2 + 0.23N_{fluid}\right)^{0.5} \quad (6)$$

where N_O is the number of operators per shift, N_{solid} is the number of processing steps involving the handling of particulate solids, and N_{fluid} is the number of non-particulate processing steps regarding compression, heating, cooling, mixing, and reaction. The operating shifts are 900 shifts per year by 300 days/year $\times$ 3 shifts/day, and the operating shifts are 215 shifts by 43 weeks/year $\times$ 5 shifts/week. The number of shifts needed in the plant N_S was calculated by

$$N_S = \frac{\frac{365 \text{ days}}{\text{year}} \times \frac{3 \text{ shift}}{\text{day}}}{\frac{43 \text{ weeks}}{\text{year}} \times \frac{5 \text{ shift}}{\text{week}}} \quad (7)$$

and the total number of laborers N_{tot} for the CPP and CCU is shown by

$$N_{tot} = N_O \times N_S \quad (8)$$

The OPEX estimations of Scenarios 1–3 are shown as follows.

$$\begin{aligned} \text{Scenario 1 : } OPEX_{S1} = & (C_{coal} \times F_{coal} + C_{feed,CCP} \times F_{feed,CCP} + C_{CaCO3} \times F_{CaCO3} \\ & + C_{H2O} \times F_{H2O} + C_{elect} \times P_{elec}) \times 300 + N_{tot} \times 20,000 \\ & + 5.25\% \times C_{CPP} + 12\% \times C_{CaL} + 5.25\% \times C_{CCU,S1} \end{aligned} \quad (9)$$

$$\text{Scenario 2 : } OPEX_{S2} = (C_{coal} \times F_{coal} + C_{feed, CPP} \times F_{feed, CPP} + C_{CaCO3} \times F_{CaCO3} + C_{CuCl2} \times F_{CuCl2} + C_{H2O} \times F_{H2O} + C_{elec} \times P_{elec}) \times 300 + N_{tot} \times 20,000 + 5.25\% \times C_{CPP} + 12\% \times C_{CaL} + 5.25\% \times C_{CCU, S2} \quad (10)$$

$$\text{Scenario 3 : } OPEX_{S3} = (C_{coal} \times F_{coal} + C_{feed, CPP} \times F_{feed, CPP} + C_{CaCO3} \times F_{CaCO3} + C_{H2O} \times F_{H2O} + C_{elec} \times P_{elec}) \times 300 + N_{tot} \times 20,000 + 5.25\% \times C_{CPP} + 12\% \times C_{CaL} + 5.25\% \times C_{CCU, S3} \quad (11)$$

where the flowrates of the raw materials of CPP, CaCO₃, H₂O, and ChCl₂ are $F_{feed, CPP}$, F_{CaCO3} , F_{H2O} , and F_{CuCl2} , respectively, and the purchased prices of the raw materials and fuel (coal) of CPP, CaCO₃, H₂O, and ChCl₂ are $C_{feed, CPP}$, C_{coal} , C_{CaCO3} , C_{H2O} , and C_{CuCl2} , respectively.

4.2. Economic Evaluation

The economic models of Scenarios 1–3 named S1, S2, and S3 are described by the following cash flow,

$$CF|_{i,t+3} = (S_{MeOH} \times F_{MeOH} + S_{urea} \times F_{urea} + S_{CO2} \times F_{CO2,p} + S_{cement} \times F_{clinker}) \times 300|_{t+3} - (OPEX_i + C_{CO2} \times (F_{CO2} \times w_{CO2}) \times 300)|_{t+3} - TIC_{i,t}, \quad i = \{S1, S2, S3\}, \quad t = 1, 2, \dots, 14 \quad (12)$$

For three-year construction, it is assumed that $TIC_{i,1} = 0.4 \times TIC_i$, $TIC_{i,2} = 0.3 \times TIC_i$, and $TIC_{i,3} = 0.3 \times TIC_i$. Moreover, the internal rate of return (IRR) is obtained by solving the following equation:

$$\sum_{t=1}^{17} \frac{CF|_{i,t}}{(1+r)^t} = 0, \quad i = \{S1, S2, S3\} \quad (13)$$

where r is the discount rate.

To address the economics of the CCP with/without the use of CaL and CCU, the CO₂ avoided cost is described as

$$CO_2 \text{ avoided cost}|_i = \frac{LCOP_{CaL+CCU,i} - LCOP_{ref}}{CO_{2tot, ref} - CO_{2tot, CaL+CCU,i}} \left(\frac{\$}{ton} \right), \quad i = \{S1, S2, S3\} \quad (14)$$

where $LCOP_{CaL+CCU}$ and $LCOP_{ref}$ represent the levelized cost of producing 1 ton of clinker from the CCP with/without the use of CaL and CCU, respectively. Similarly, $CO_{2tot, CaL+CCU}$ and $CO_{2tot, ref}$ represent the CO₂ emission intensity of producing 1 ton of clinker from the CCP with/without the use of CaL and CCU, respectively.

$$LCOP_{CaL+CCU,i} = \sum_{t=1}^{17} \frac{CF|_{i,t}}{(1+r)^t} / \sum_{t=4}^{17} \frac{P_{clinker}|_t}{(1+r)^t}, \quad i = \{S1, S2, S3\} \quad (15)$$

where $P_{clinker}(\text{ton/yr}) = F_{clinker} \times 300$.

According to the above economic evaluations of Scenarios 1–3, the corresponding economic comparisons in terms of CO₂ avoided cost and economic indicators (IRR and payback period) are shown in Table 7. Referring to some literature for the cost analysis of the CPP with the use of the CaL process, the CO₂ avoided cost was around 40 USD/ton [35,36]. It is noted that the CO₂ avoided costs of three scenarios of DCCP-based polygeneration systems are between 16.53 and 21.42 USD/ton. It is validated that the CCU method could effectively reduce the LCOP due to producing multiple products. Scenario 1 has a lower CO₂ avoided cost due to a lower captured CO₂ rate from the calciner, but it consumes more green energy (RenE2P) to do the CCU, such that its IRR is lower than other scenarios, and Scenario 3 has a higher CO₂ avoided cost due to a higher captured CO₂ rate from the calciner, but its IRR is higher than Scenario 1 due to HRSG in place of RenE2P. The IRR and the payback period of Scenario 2 are superior to other scenarios since the RenE2P cost in

Scenario 2 is lower than it is in Scenario 1 and the captured CO₂ rate in Scenario 2 is lower than it is in Scenario 3. Notably, the IRR of the DCCP is lower than the IRR of the CPP by 5.7%, at least since the CAPEX and OPEX of the CaL process increase the total cost of the DCCP. Finally,

Table 7. Economic evaluations of Scenarios 1–3.

	CPP	Scenario 1	Scenario 2	Scenario 3
CO ₂ avoided cost (\$/ton)	--	16.53	18.92	21.42
IRR (%)	23.87%	20.49%	22.51%	22.21%
Payback period (year)	6.05	6.60	6.26	6.30

5. Conclusions

Three types of the DCCP-based polygeneration system have the same products (clinker, methanol, and urea), but the power sources and hydrogen production processes are different. In Scenario 1, the PEM water electrolysis requires an expensive green electricity grid. In Scenario 2, the Cu-Cl thermochemical cycle in place of the PEM water electrolysis can effectively decrease the green electricity grid supply, although the CAPEX of the Cu-Cl thermochemical cycle is higher than the PEM water electrolysis. In Scenario 3, the HRSG system fully replaces the electricity grid but indirectly increases the OPEX of the CaL process, such that its CO₂ avoided cost is higher than in other scenarios. From the cement market viewpoint, the CPP is superior to the DCCP if the carbon tax is below 55 USD/ton. From a circular economy perspective, the DCCP-based polygeneration system is superior to DCCP due to its ability to produce valorized products. For the future study, the more valorized chemical products would be addressed to enhance the economics of the DCCP-based polygeneration system.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11072043/s1>. Figure S1: Flowchart of PEM water electrolysis with Simulink; Table S1: Experimental data in the processes of kiln, NH₃, urea, MeOH; Table S2: Mathematical models of PEM water electrolysis

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Nomenclature

ASR	Ammonia synthesis reactor
ASU	Air separation unit
CAPEX	Capital expenditure
CCU	Carbon capture and utilization
CaL	Calcium looping
CPP	Cement production process
DCCP	Decarbonized cement production process
HRSG	Heat recovery steam generator
IRR	Internal rate of return
LCOP	Levelised cost of producing 1 ton clinker
MSR	Methanol synthesis reactor

OPEX	Operating expense
PEM	Polymer electrolysis membrane
USR	Urea synthesis reactor
WGS	Water gas shift
PSA	Pressure swing adsorption
RenE2P	Renewable energy source for power grid
TIC	Total investment cost
C_{S1}, C_{S2}, C_{S3}	The summation of the cost functions of process units in Scenarios 1–3
N_{tot}	The total number of labors
N_S	The number of shifts needed in the plant
N_O	The number of operators per shift

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