

CARBON-CLOSURE SIZING OF A CALCIUM LOOPING TO UREA RETROFIT FOR A NIGERIAN CEMENT KILN: OXY-FUEL AND SORBENT MAKE-UP CARBON AS UREA FEEDSTOCK

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ABSTRACT

Cement manufacture accounts for about half of Nigeria's in-scope industrial carbon dioxide emissions, yet the country remains a net importer of nitrogen fertiliser, and its inland kilns lie far from any prospective geological storage. Carbon capture and utilisation is therefore the only near-term decarbonisation route available to them. This work develops, in Aspen Plus V12.1, an integrated calcium looping (CaL) capture and CO₂-stripping urea synthesis complex retrofitted to the Ashaka cement plant, Gombe State, and introduces a carbon-closure framework for sizing such retrofits. The framework recognises that the carbon delivered by a CaL island to a utilisation plant is not restricted to the CO₂ abstracted from the kiln flue gas: calcination of the sorbent make-up and oxy-fuel combustion in the calciner deliver additional CO₂ into the same purified product stream at no incremental separation duty. A dimensionless closure factor Λ and a slipstream-sizing equation are derived and applied. For a 2.4% flue-gas slipstream (120.2 t d⁻¹) the island delivers 36.6 t d⁻¹ of 99.2 wt% CO₂, of which 31.5% is endogenous, exactly matching the stoichiometric requirement of a 50 t d⁻¹ urea plant ($\Lambda = 1.00$); sizing on captured flue-gas carbon alone would have oversized the slipstream by 46%. The high-pressure loop, modelled with SR-POLAR, attains 66.4% per-pass conversion at 190 °C, 150 bar and N/C = 3.0 with 0.62 wt% biuret. Integration of the carbonator and carbamate-condenser exotherms supplies the evaporation duty and reduces net thermal demand by 23.4% to 3.95 GJ t⁻¹ urea. The levelised cost of urea is US\$577 t⁻¹ at an ammonia price of US\$450 t⁻¹, falling to US\$492 t⁻¹ on domestically sourced ammonia, against an import parity of US\$580 t⁻¹.

Keywords: Ammonium carbamate, Aspen Plus, Calcium looping, Carbon capture and utilisation, Green urea, Process integration

1 INTRODUCTION

The cement industry is responsible for approximately 7% of global anthropogenic carbon dioxide emissions, of which about two-thirds arise from the calcination of limestone and are therefore irreducible by fuel switching or efficiency measures alone [1]. Nigeria is the largest cement producer in Africa, and industry accounts for 16% of the emissions covered by the national Energy Transition Plan, roughly half of which are attributable to cement [2, 3]. Unlike the coastal petrochemical corridor, however, the major Nigerian kilns are located in the interior, hundreds of kilometres from the depleted fields and saline aquifers of the Niger Delta that constitute the country's only mapped storage capacity [4]. Pipeline transport for a single inland kiln is not economically defensible, so for these plants

the practical decarbonisation option is not capture and storage but capture and utilisation, in which the captured carbon is converted into a product that carries the cost of its own separation. Urea is the natural candidate. It is the only large-tonnage chemical whose synthesis consumes CO₂ stoichiometrically, its market in Nigeria is import-dependent, and the fertiliser it provides addresses a food-security deficit in the same north-eastern states in which the kilns operate. Recent studies have examined this pairing in several jurisdictions: Kashyap et al. [5] assessed monoethanolamine (MEA) capture from thirty-two Indian cement plants feeding green urea synthesis; Shrestha et al. [6] evaluated piperazine absorption at the Hetauda cement plant coupled to surplus Nepalese hydropower; Asgharian et al. [7] performed a techno-economic analysis of MEA capture from a Danish cement plant integrated with electrolytic ammonia; and Zecca et al. [8] examined an analogous symbiosis between steelmaking and urea production. Every one of these studies employs a solvent-based capture step. Calcium looping offers a materially different proposition for a cement host. The sorbent is the same limestone the plant already quarries, the spent purge is a partly calcined raw meal that can be returned to the clinker line, and the carbonator exotherm is released at 650-700 °C, a temperature at which it can raise process steam rather than being rejected to cooling water [9, 10, 11]. The technology has been demonstrated to TRL7 in the 1.7 MWth La Pereda pilot, where capture efficiencies approaching 99% have been reported [12], and at 30 kWth under cement flue-gas conditions, where an apparent carbonation rate constant of 0.36 s⁻¹ was measured [13]. Techno-economic assessments of tail-end and integrated CaL for cement plants place the cost of CO₂ avoided between about 52 and 59 € t⁻¹, competitive with amine scrubbing and with a substantially smaller thermal penalty [14, 15, 16]. A feature of the CaL island that has attracted little attention in the utilisation literature is the composition of its product stream. Because the calciner is fired under oxy-fuel conditions and is charged continuously with fresh limestone to offset sorbent deactivation, the purified gas leaving the calciner contains carbon from three distinct sources: the CO₂ abstracted from the kiln flue gas, the CO₂ released by calcination of the make-up, and the CO₂ produced by combustion of the calciner fuel. In a capture-and-storage application the latter two are treated as parasitic, since they enlarge the compression and storage duty. In a capture-and-utilisation application they are not parasitic at all: they are feedstock, delivered into the same purified, compressed stream at no incremental separation cost. Any sizing calculation that equates the utilisation plant's carbon demand with the flue-gas carbon captured will therefore oversize the capture island, the slipstream duct, the sorbent inventory and the associated capital. This paper formalises that observation. The specific objectives are (i) to derive a carbon-closure framework, comprising a closure factor and a slipstream-sizing equation, that allocates all carbon sources in a CaL island to the stoichiometric demand of a downstream utilisation plant; (ii) to develop a complete Aspen Plus V12.1 model of a CaL island coupled to a CO₂-stripping urea loop sized for 50 t d⁻¹ of prilled urea at the Ashaka cement plant; (iii) to establish the optimum operating window through sensitivity analysis and to quantify the benefit of heat integration; and (iv) to assess the levelised cost of urea against Nigerian import parity and to identify the variable that governs viability. To the authors' knowledge this is the first assessment of a calcium looping-to-urea complex for any sub-Saharan African cement plant, and the first to treat calciner-endogenous carbon explicitly as a design variable.

2 PROCESS DESCRIPTION AND MODELLING

2.1 Reference plant and design basis

The Ashaka cement plant in Gombe State operates a dry-process rotary kiln of nominal 1.0 Mt y⁻¹ clinker capacity, discharging approximately 5000 t d⁻¹ of flue gas containing 22.5 wt% CO₂. A slipstream is drawn downstream of the existing bag filter and conditioned before entering the carbonator. The design basis for the integrated complex is summarised in Table 1. An operating availability of 8000 h y⁻¹ is assumed throughout, consistent with a modular plant subject to the availability of the host kiln. [2, 3, 14, 16].

Table 1. Design basis for the integrated calcium looping-urea complex

Parameter	Value	Unit	Remark
Kiln flue gas (total)	5000	t d ⁻¹	Host plant, 1.0 Mt y ⁻¹ clinker
CO ₂ in flue gas	22.5	wt%	After bag filter
Slipstream fraction, ϕ	2.4	%	Design value, Eq. (11)
Slipstream flow	120.2	t d ⁻¹	To carbonator
Carbonator temperature / pressure	675 / 1.2	°C / bar	RGibbs, equilibrium
Calciner temperature / pressure	925 / 1.0	°C / bar	Oxy-fuel, RGibbs
Limestone make-up	6.7	t d ⁻¹	5% of circulating solids
Calciner fuel (natural gas)	3.2	t d ⁻¹	Oxy-fired with 95% O ₂
Urea production	50.0	t d ⁻¹	99.7 wt%, 8000 h y ⁻¹
Reactor temperature / pressure	190 / 150	°C / bar	RPlug, $\tau = 25$ min
NH ₃ /CO ₂ molar ratio, N/C	3.0	-	Reactor inlet basis
H ₂ O/CO ₂ molar ratio	0.4	-	Reactor inlet basis
Ammonia feed purity	99.5	wt%	Imported or domestic

2.2 Carbon-closure framework

The stoichiometry of urea synthesis fixes the carbon demand of the utilisation plant. Writing the target product rate as a mass flow of prilled urea of specified purity, the stoichiometric carbon dioxide demand is [17, 18].

$$\dot{m}_{\text{CO}_2, \text{st}} = \frac{M_{\text{CO}_2} w_U \dot{m}_U}{M_U \eta_U} \quad (1)$$

where M_i is the molar mass of species i , w_U the urea mass fraction in the product and η_U the carbon utilisation efficiency of the synthesis loop, which approaches unity when all unconverted carbamate is recovered and recycled. The carbon supplied by the calcium looping island is the sum of three terms. Carbon dioxide is abstracted from the flue-gas slipstream in the carbonator according to

$$E_c = 1 - \frac{F_{\text{CO}_2, \text{out}}}{F_{\text{CO}_2, \text{in}}} \quad (2)$$

carbon dioxide is released by calcination of the limestone make-up charged to maintain sorbent activity, and further carbon dioxide is generated by oxy-fuel combustion of the calciner fuel. Since the calciner operates on oxygen rather than air, all three streams leave the calciner as a single high-concentration gas which is dried, purified and compressed together. The total carbon delivered to the utilisation plant is therefore;

$$\dot{m}_{\text{CO}_2, \text{sup}} = \eta_p \left[E_c y_{\text{CO}_2} \dot{m}_{\text{fg}} + \frac{M_{\text{CO}_2}}{M_{\text{CaCO}_3}} \dot{m}_{\text{mk}} + \frac{M_{\text{CO}_2}}{M_f} v_f \dot{m}_f \right] \quad (3)$$

in which η_p is the fractional recovery of the purification and compression train, y_{CO_2} the mass fraction of carbon dioxide in the flue gas, and v_f the number of moles of carbon dioxide produced per mole of fuel burned. The dimensionless carbon-closure factor is defined as the ratio of supply to stoichiometric demand,

$$\Lambda = \frac{\dot{m}_{\text{CO}_2, \text{sup}}}{\dot{m}_{\text{CO}_2, \text{st}}} \quad (4)$$

A closure factor of unity denotes an exactly carbon-balanced complex, in which the capture island is sized to deliver precisely the carbon the synthesis loop can fix. Values below unity leave the urea plant carbon-starved and its capacity is then supply-limited; values above unity represent capital committed to carbon that must be vented or stored. It is convenient to express the fraction of the delivered carbon that originates inside the capture island rather than in the kiln flue gas.

$$\theta = \frac{(M_{\text{CO}_2}/M_{\text{CaCO}_3}) \dot{m}_{\text{mk}} + (M_{\text{CO}_2}/M_f) v_f \dot{m}_f}{\dot{m}_{\text{CO}_2, \text{sup}} / \eta_p} \quad (5)$$

Setting $\Lambda = 1$ in Eq. (4) and solving for the slipstream gives the sizing equation that is the principal design result of this framework.

$$\dot{m}_{fg} = \frac{\dot{m}_{CO_2, st}/\eta_p - (M_{CO_2}/M_{CaCO_3})\dot{m}_{mk} - (M_{CO_2}/M_f)v_f\dot{m}_f}{E_{cyCO_2}} \quad (6)$$

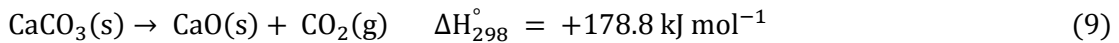
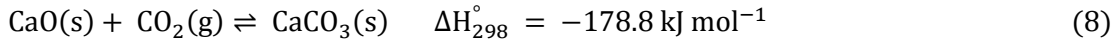
and the corresponding slipstream fraction of the host kiln is

$$\varphi = \frac{\dot{m}_{fg}}{\dot{m}_{fg, tot}} \quad (7)$$

Equations (1) to (7) are solved simultaneously with the flowsheet because the make-up and fuel terms themselves scale with the slipstream; convergence is obtained in three to four outer iterations.

2.3 Calcium looping island

The carbonation and calcination reactions are.



with oxy-fuel combustion in the calciner supplying the calcination enthalpy.



Both reactors are represented as RGibbs blocks operating at chemical equilibrium, an assumption justified at the high sorbent activity and long residence times characteristic of cement-plant service [11, 13]. Progressive loss of sorbent carrying capacity through pore closure and sintering is described by the Grasa-Abanades deactivation expression.

$$X_N = \frac{1}{\frac{1}{1-X_r} + kN} + X_r \quad (11)$$

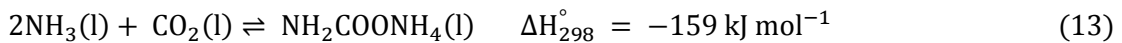
where X_N is the CaO conversion attainable in cycle N , X_r the residual conversion and k the deactivation constant [19]. The average carrying capacity of the circulating inventory under a continuous make-up is obtained by weighting Eq. (11) over the age distribution of the particles.

$$X_{ave} = \sum_{N=1}^{\infty} r_N X_N, \quad r_N = \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \quad (12)$$

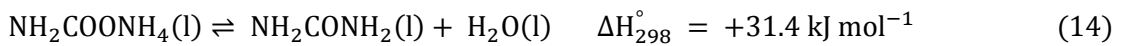
with F_0 the make-up and F_R the circulation molar flow of calcium. Three-stage intercooled compression (MCompr) with interstage knock-out raises the purified gas to the 150bar required by the synthesis loop, using the Peng-Robinson equation of state with Boston-Mathias modification.

2.4 Urea synthesis loop

Urea is formed in two consecutive steps. Ammonia and carbon dioxide react exothermically in the liquid phase to give ammonium carbamate.



which then dehydrates endothermically to urea in the rate-controlling step.



The principal side reaction is the condensation of two urea molecules to biuret, which is phytotoxic above about 1 wt% and is therefore the constraint that bounds reactor temperature from above.



The reactor is modelled as an RPlug block with the dehydration rate expressed as a reversible second-order liquid-phase reaction.

$$r_U = k_f \left(C_C - \frac{C_U C_W}{K_{eq}} \right) \quad (16)$$

and biuret formation as second order in urea, $r_B = k_B C_U^2$. Per-pass conversion is defined on the carbon fed to the reactor.

$$X_U = \frac{\dot{n}_{\text{urea}}}{\dot{n}_{\text{CO}_2, \text{in}}} \quad (17)$$

The loop follows total recycle CO₂ stripping practice. The carbamate condenser CC-101 is a HeatX block coupled to an RGibbs block; the reactor R-101 is an RPlug block with sieve trays; the falling-film stripper ST-101 is a ten-stage RadFrac block without condenser or reboiler, using carbon dioxide as stripping gas; the high-pressure scrubber SC-101 is a five-stage RadFrac block; the low-pressure decomposers F-101 and F-102 and the vacuum evaporators EV-101 and EV-102 are Flash2 blocks; the process-condensate hydrolyser HY-101 is an RCSTR block. The flowsheet, stream numbering and solution sequence are shown in Figure 1.

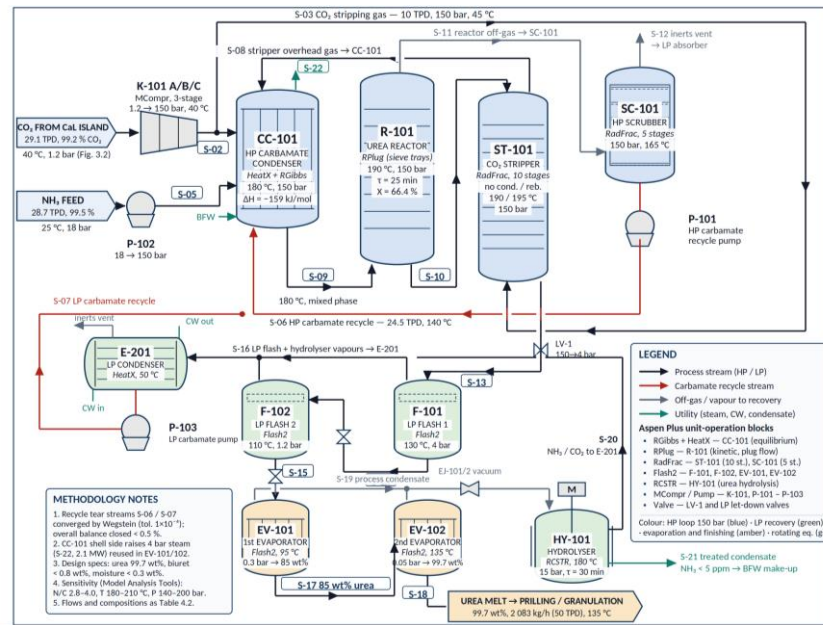


Figure 1. Aspen Plus V12.1 process flowsheet of the calcium looping-to-urea complex, showing the high-pressure synthesis loop, the low-pressure recovery and finishing train, and stream numbering

2.5 Thermodynamics and solution strategy

Property method selection follows the phase behaviour of each section. SR-POLAR is used throughout the high-pressure loop because it reproduces vapour-liquid equilibrium in the NH₃-CO₂-urea-H₂O system at 150 bar and 190 °C, where strong association and the presence of ionic carbamate defeat cubic equations of state. NRTL-RK is applied below 5bar in the low-pressure recovery and evaporation section, and Peng-Robinson with the Boston-Mathias alpha function is used for carbon dioxide compression [20, 21]. The recycle tears are placed on the high-pressure carbamate recycle S-06 and the low-pressure carbamate recycle S-07 and are converged by the Wegstein method under the criterion.

$$\frac{|x^{k+1} - x^k|}{|x^k|} \leq 1 \times 10^{-4} \quad (18)$$

with the additional requirement that the overall mass balance close to better than 0.5%. Design specifications enforce 99.7 wt% urea, biuret below 0.8 wt% and moisture below 0.3 wt% in the product by manipulating the evaporator pressures and the stripping-gas split.

2.6 Economic model

Capital cost is estimated by the factored method on a modular basis with a Nigerian location factor of 1.15 and is levelised using the capital recovery factor.

$$\text{CRF} = \frac{i(1+i)^n}{(1+i)^n - 1} \quad (19)$$

at a discount rate i of 12% over a plant life n of 15 years. The levelised cost of urea is

$$LCOU = \frac{CRF \times CAPEX + OPEX}{m_{U,a}} \quad (20)$$

where $m_{U,a}$ is the annual urea output. The carbon dioxide utilised is credited on the stoichiometric carbon fixed in the product, net of the carbon introduced by combustion of the calciner fuel.

3 RESULTS AND DISCUSSION

3.1 Carbon closure of the capture island

Application of Eqs. (1) to (7) to the 50 t d⁻¹ target gives a stoichiometric carbon dioxide demand of 36.53 t d⁻¹, equivalent to 830 kmol d⁻¹ of carbon, together with an ammonia demand of 28.3 t d⁻¹ and a co-produced water flow of 14.9 t d⁻¹. The three contributions to supply are compared with this demand in Figure 2(a) and tabulated in Table 2. Capture of 94.5% of the 27.0 t d⁻¹ of carbon dioxide contained in the 120.2 t d⁻¹ slipstream yields 25.6 t d⁻¹; calcination of the 6.7 t d⁻¹ limestone make-up contributes a further 2.9 t d⁻¹; and oxy-fuel combustion of 3.2 t d⁻¹ of natural gas contributes 8.8 t d⁻¹. After a purification and compression recovery of 98% the island delivers 36.6 t d⁻¹ of carbon dioxide at 99.2 wt% purity, giving a closure factor of 1.00. The endogenous fraction defined by Eq. (5) is 31.5%. Nearly one third of the carbon feeding the urea plant therefore never passed through the carbonator, and would in a capture-and-storage application have been counted as an energy penalty rather than as a product. The design consequence is quantified in Figure 2(b): had the slipstream been sized on captured flue-gas carbon alone, 175.2 t d⁻¹ of flue gas, or 3.5% of the kiln, would have been required to reach the same urea capacity, an oversizing of 46% in duct, cyclone, carbonator and solids-handling capacity. Conversely, at fixed slipstream the endogenous term raises attainable urea capacity from 34.3 to 50.0 t d⁻¹. This is a systematic advantage of oxy-fired looping capture over solvent capture in utilisation service, and it does not appear in the studies that have paired amine or piperazine capture with urea synthesis [5, 6, 7], in which combustion carbon is external to the capture system and cannot be recovered into the product stream.

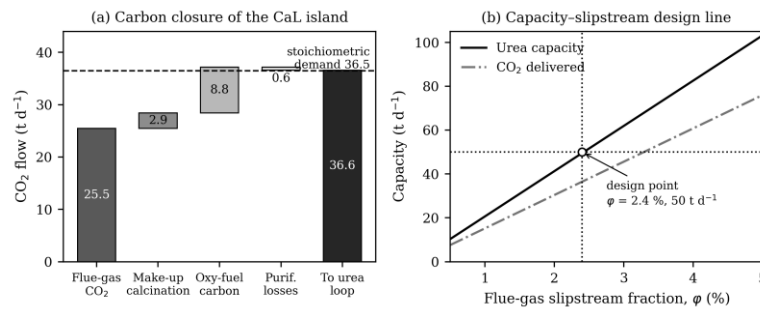


Figure 2. Carbon closure of the calcium looping island: (a) contributions of flue-gas, make-up calcination and oxy-fuel carbon to the delivered CO₂ compared with the stoichiometric demand of a 50 t d⁻¹ urea plant; (b) urea capacity and delivered CO₂ as functions of the flue-gas slipstream fraction, Eq. (6)

Table 2. Carbon closure of the calcium looping island at the design slipstream ($\phi = 2.4\%$)

Carbon source	Flow (t d ⁻¹)	Share (%)	Basis
Flue-gas CO ₂ captured	25.6	68.5	27.0 t d ⁻¹ inlet at $E_c = 0.945$
Calcination of limestone make-up	2.9	7.9	6.7 t d ⁻¹ CaCO ₃
Oxy-fuel combustion in calciner	8.8	23.6	3.2 t d ⁻¹ CH ₄
Gross carbon available	37.3	100.0	Calciner off-gas
Purification and compression losses	-0.7	-1.9	$\eta_p = 0.98$
CO ₂ delivered to urea loop	36.6	98.1	99.2 wt% purity, 150 bar
Stoichiometric demand, Eq. (1)	36.5	-	50.0 t d ⁻¹ at 99.7 wt%
Closure factor, Λ	1.00	-	Eq. (4)
Endogenous fraction, θ	31.5	-	Eq. (5)

3.2 Capture performance

The carbonator attains 94.5% capture at 675 °C and 1.2 bar with a total solid's circulation of 205 t d⁻¹, of which 98.5 t d⁻¹ is active calcium oxide. The cyclone separates 99.5% of the solids and the lean gas returned to the stack carries 1.5 t d⁻¹ of residual carbon dioxide, a slip of 1.8%. The calciner achieves 98.5% calcination at 925 °C on 12.5 t d⁻¹ of 95% oxygen. Specific energy consumption of the capture section is 2.45 GJ per tonne of carbon dioxide, some 30% below the 3.5 to 4.0 GJ t⁻¹ typical of monoethanolamine scrubbing of cement flue gas, because the carbonator exotherm is recovered as 4 bar steam rather than rejected. The 0.8 t d⁻¹ of calcium sulphate formed by sulphation of the sorbent leaves with the purge, which is returned to the clinker line as partly calcined raw meal and therefore incurs no disposal cost, an option unavailable to solvent systems and one of the standing arguments for looping capture at a cement host [14, 16]. The overall validation of these performance metrics against literature and pilot data is summarised in Table 5.

3.3 Urea loop performance

At the optimum of 190 °C, 150 bar, N/C = 3.0 and H₂O/C = 0.4 the plug-flow reactor achieves 66.4% per-pass conversion of carbon dioxide to urea in a residence time of 25 min, within the 65 to 68% band reported for industrial carbon dioxide stripping technology [17, 18]. The corresponding stream summary is given in Table 3. Reactor effluent of 128.1 t d⁻¹ contains 38.9 wt% urea; the falling-film stripper decomposes 82.3% of the unconverted carbamate against 10 t d⁻¹ of stripping gas and returns the released ammonia and carbon dioxide to the condenser, while the high-pressure scrubber recovers 98.5% of the ammonia and carbon dioxide leaving in the reactor off-gas. The low-pressure decomposers at 4 and 1.2 bar remove a further 95.4% of the residual carbamate, and the two vacuum evaporators concentrate the solution from 68 wt% to 99.7 wt% urea, with 0.62 wt% biuret and 0.25 wt% moisture in the melt delivered to prilling.

Table 3. Stream summary of the high-pressure synthesis loop at the optimum (190°C, 150bar, N/C = 3.0)

Stream	CO ₂ feed	NH ₃ feed	Reactor effluent	Stripper bottoms	Urea melt
Mass flow (t d ⁻¹)	36.6	28.4	128.1	84.1	50.0
Temperature (°C)	40	25	190	195	135
Pressure (bar)	150	150	150	150	0.05
Urea (wt%)	0	0	38.9	59.3	99.7
Carbamate (wt%)	0	0	25.7	6.9	0
NH ₃ (wt%)	0	99.5	16.6	7.6	0.03
CO ₂ (wt%)	99.2	0	0	0	0
H ₂ O (wt%)	0.8	0.5	18.7	26.2	0.25
Biuret (wt%)	0	0	0.12	0.45	0.62

3.4 Sensitivity analysis

The response of the synthesis loop to the two variables that define the operating window is shown in Figure 3. Raising the ammonia-to-carbon ratio from 2.8 to 4.0 increases per-pass conversion from 61.2 to 68.7% by displacing the dehydration equilibrium of Eq. (14), but the carbamate recycle rises by 74% and with it the condenser duty and the compression load on the recycle pump. The marginal conversion gain collapses above N/C = 3.0, which captures 85% of the available improvement for 30% of the recycle penalty, and 3.0 is therefore selected. Reactor temperature produces a steeper conversion response, from 58.4% at 180°C to 70.1% at 210°C, but biuret formation, being second order in urea and strongly activated, rises from 0.45 to 1.65 wt%. The 0.8 wt% product specification is breached above 195°C, so the optimum is bounded from above by product quality rather than by equilibrium, and 190°C is retained with a 5 °C margin. Pressure was varied between 140 and 200 bar and returned only 6.1% additional conversion for a 94% increase in compression power, confirming 150 bar as the economic optimum.

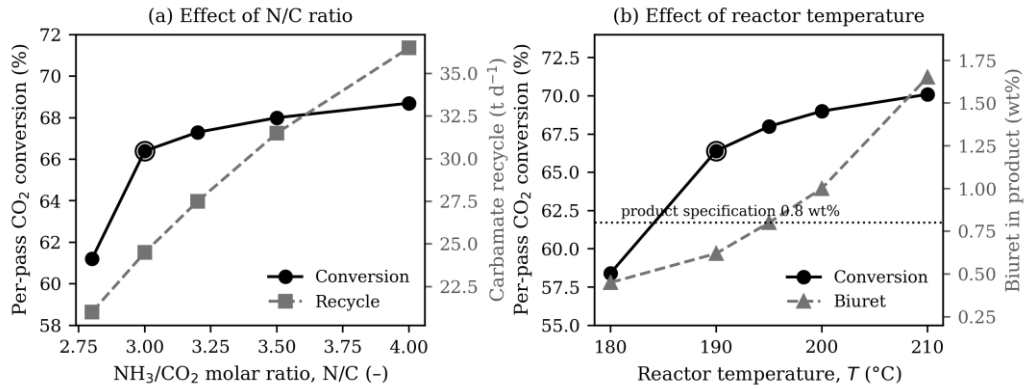


Figure 3. Sensitivity of the synthesis loop: (a) effect of NH_3/CO_2 molar ratio on per-pass conversion and carbamate recycle at 190°C and 150bar; (b) effect of reactor temperature on conversion and biuret content at N/C = 3.0 and 150bar. Circles mark the selected optimum

The capture island exhibits the equilibrium-kinetic trade-off characteristic of calcium looping, Figure 4(a). Below 675°C the carbonation rate limits conversion within the available residence time; above it the reverse reaction of Eq. (8) becomes significant and sintering accelerates, so that average calcium oxide conversion falls from 81 to 64% across the range while capture efficiency peaks at 94.5%. Cyclic deactivation, Figure 4(b), stabilises at about 75.5% after twenty cycles at the 5% make-up rate, at which point the make-up and the purge to the clinker line are in balance. It should be noted that the residual conversion implied by this simulation is markedly higher than the 7 to 10% commonly fitted to natural limestones in power-plant service [19, 22]; the discrepancy reflects the high make-up ratio permitted when the purge has a productive destination in the adjacent kiln, and warrants experimental confirmation on Ashaka limestone.

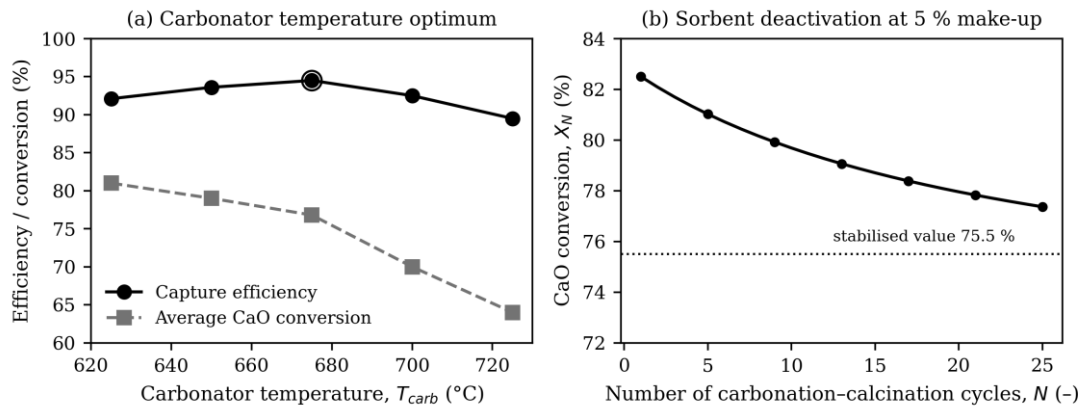


Figure 4. Sensitivity of the capture island: (a) carbonator temperature against capture efficiency and average CaO conversion; (b) sorbent deactivation over twenty-five carbonation-calcination cycles at 5% make-up, fitted to Eq. (11)

Table 4. Summary of the sensitivity analysis

Variable and range	Response	Constraint or trade-off	Selected value
N/C, 2.8-4.0	Conversion 61.2 $\rightarrow$ 68.7%	Recycle +74%, biuret +46%	3.0
Reactor T , 180-210 $^{\circ}\text{C}$	Conversion 58.4 $\rightarrow$ 70.1%	Biuret 0.45 $\rightarrow$ 1.65 wt%, specification breached above 195 $^{\circ}\text{C}$	190 $^{\circ}\text{C}$
Reactor P , 140-200 bar	Conversion 64.1 $\rightarrow$ 68.0%	Compression power 0.68 $\rightarrow$ 1.32 MW	150 bar
Carbonator T , 625-725 $^{\circ}\text{C}$	Capture 92.1 $\rightarrow$ 94.5 $\rightarrow$ 89.5%	CaO conversion 81 $\rightarrow$ 64% by sintering	675 $^{\circ}\text{C}$
Cycles, 1-25	CaO conversion 82.5 $\rightarrow$ 74.8%	Make-up cost against purge credit	5% make-up

3.5 Heat integration

Two large exotherms are available at useful temperature. The carbonator releases 2.1 MW at 675 °C and the carbamate condenser a further duty at 180 °C, both of which are raised as 4 bar saturated steam and returned to the evaporation train. Specific steam consumption falls to 0.42 t per tonne of urea against the 0.5 to 0.6 t t⁻¹ typical of conventional total-recycle plants. Net thermal demand for the integrated complex is 6.43 MW compared with 8.4 MW without integration, a saving of 23.4%, corresponding to a specific energy consumption of 3.95 GJ per tonne of urea. This is the principal thermodynamic argument for coupling looping capture to urea synthesis rather than to storage: the high-temperature exotherm that is a liability in a capture-only plant becomes the utility supply of the utilisation plant. [9, 10, 14].

3.6 Model validation

Table 5 compares the simulation against pilot and industrial data. The capture island agrees to within 0.5 percentage points of the 30 kW_{th} cement-conditions pilot and reproduces the apparent carbonation rate constant of 0.36 s⁻¹ measured in that facility [13], while the delivered purity is slightly below the 99.9% reported at La Pereda [12] because a single dehydration stage is specified here. Per-pass conversion and biuret content fall inside the industrial ranges for carbon dioxide stripping technology, and the specific energy of the urea section lies within 1.1% of industrial practice. Agreement of this quality across two coupled islands supports the use of the model for scale-up, subject to the sorbent caveat noted in Section 3.4.

Table 5. Validation of the model against pilot-scale and industrial data

Parameter	This study	Reference value	Deviation	Source
CO ₂ capture efficiency	94.5%	93.5-96%, 30 kW _{th} pilot	+0.5%	[13]
Carbonation rate constant	0.36 s ⁻¹	0.36 s ⁻¹ measured	0%	[13]
CO ₂ purity after compression	99.2 wt%	99.9%, La Pereda 1.7 MW _{th}	-0.7%	[12]
Specific capture energy	2.45 GJ t ⁻¹	2.3-2.6 GJ t ⁻¹	+2.1%	[12, 14]
Urea per-pass conversion	66.4%	65-68% industrial	within range	[17, 18]
Biuret at optimum	0.62 wt%	0.6-0.9 wt% industrial	within range	[18]
Specific energy, urea section	1.82 GJ t ⁻¹	1.75-1.95 GJ t ⁻¹	+1.1%	[18]
Levelised cost of urea	US\$577 t ⁻¹	US\$465 t ⁻¹ (India, MEA)	+24%	[5]

3.7 Techno-economics and strategic implications

Capital cost of the modular complex is estimated at US\$18.5 million, distributed between the capture island (US\$7.2 million), the synthesis island (US\$8.1 million) and utilities (US\$3.2 million). Annual operating cost is US\$6.90 million, of which ammonia at US\$450 t⁻¹ accounts for US\$4.26 million, or 62%. At 8000 h y⁻¹ the plant produces 16 650 t of urea, and Eqs. (19) and (20) give a levelised cost of US\$577 t⁻¹ against a Nigerian import parity of about US\$580 t⁻¹. The margin at the reference ammonia price is therefore slender, and the result is best read as a statement about ammonia rather than about capture: rearranging Eq. (20) at the import parity gives a break-even ammonia price of US\$454 t⁻¹, and procurement of ammonia at the US\$300 t⁻¹ achievable from domestic gas-based capacity reduces the levelised cost to US\$492 t⁻¹, a margin of US\$88 t⁻¹. A carbon credit of US\$30 per tonne on the 12 190 t y⁻¹ of carbon dioxide fixed in the product contributes a further US\$22 t⁻¹. The strategic reading is that the capture step is not the obstacle. Carbon from the kiln is effectively free at the point of capture, and the closure analysis of Section 3.1 shows that nearly a third of the carbon requirement is met by the capture island's own combustion and calcination without any additional flue gas being processed. What determines viability is the price of the nitrogen. This inverts the emphasis of the existing literature, in which capture cost dominates [5, 6], and it points to co-location with Nigerian ammonia capacity, or to captive ammonia synthesis, as the decisive variable for deployment. On the output side, 16 650 t y⁻¹ of urea would fertilise some 185 000 ha at a 90 kg ha⁻¹ dose, or reach roughly 66 000 smallholders at a 50 kg ha⁻¹ starter dose, in the same north-eastern states where the host kiln operates and where cereal deficits are most acute [23].

4 CONCLUSIONS

An integrated calcium looping and carbon dioxide stripping urea complex has been modelled in Aspen Plus V12.1 for the Ashaka cement plant, and a carbon-closure framework has been developed for sizing capture-and-utilisation retrofits. The principal conclusions are as follows. (1) The carbon delivered by an oxy-fired calcium looping island to a utilisation plant exceeds the carbon abstracted from the host flue gas. At the Ashaka design point 31.5% of the 36.6 t d⁻¹ delivered to the urea loop originates in calcination of the sorbent make-up and in oxy-fuel combustion within the calciner. (2) Sizing on this basis gives a closure factor of unity at a flue-gas slipstream of 2.4%, whereas sizing on captured flue-gas carbon alone would have required 3.5% and oversized the capture island by 46%. The sizing equation, Eq. (6), is general to any oxy-fired looping capture plant feeding a stoichiometric utilisation process. (3) The synthesis loop attains 66.4% per-pass conversion at 190 °C, 150 bar and N/C = 3.0, delivering 50.0 t d⁻¹ of 99.7 wt% urea at 0.62 wt% biuret. The optimum is bounded from above by biuret formation rather than by equilibrium. (4) Recovery of the carbonator and carbamate-condenser exotherms as 4 bar steam supplies the evaporation duty, cutting net thermal demand by 23.4% to 3.95 GJ per tonne of urea and specific steam consumption to 0.42 t t⁻¹. (5) The levelised cost of urea is US\$577 t⁻¹ at an ammonia price of US\$450 t⁻¹ and US\$492 t⁻¹ on domestic ammonia, against an import parity of US\$580 t⁻¹. Viability is governed by the ammonia price, with a break-even value of US\$454 t⁻¹, and not by the cost of capture. Experimental determination of the cyclic carrying capacity of Ashaka limestone under cement-plant flue-gas conditions, and dynamic modelling of the coupling between an intermittent kiln and a continuous synthesis loop, are recommended as the next steps.

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NOMENCLATURE

C_i	Molar concentration of species i , kmol m^{-3}
E_c	Carbonator CO_2 capture efficiency, -
F_0	Sorbent make-up molar flow of calcium, kmol h^{-1}
F_R	Sorbent circulation molar flow of calcium, kmol h^{-1}
i	Discount rate, -
k	Sorbent deactivation constant, -
k_f	Forward rate constant of carbamate dehydration, $\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$
K_{eq}	Equilibrium constant of carbamate dehydration, -
M_i	Molar mass of species i , kg kmol^{-1}
m_i	Mass flow rate of stream i , t d^{-1}
n	Plant economic life, years
N	Number of carbonation-calcination cycles, -
r_N	Age-distribution weighting of particles at cycle N , -
r_U	Rate of urea formation, $\text{kmol m}^{-3} \text{s}^{-1}$
T	Temperature, $^{\circ}\text{C}$
w_U	Urea mass fraction in product, -
X_N	CaO conversion at cycle N , -
X_r	Residual CaO conversion, -
X_U	Per-pass conversion of CO_2 to urea, -
y_{CO_2}	CO_2 mass fraction in flue gas, -

GREEK SYMBOLS

ΔH°_{298}	Standard enthalpy of reaction at 298 K, kJ mol^{-1}
η_p	Recovery of the purification and compression train, -
η_U	Carbon utilisation efficiency of the synthesis loop, -
θ	Endogenous carbon fraction, -
$\mathcal{A}$	Carbon-closure factor, -
ν_f	Moles of CO_2 per mole of fuel combusted, -
τ	Reactor residence time, min
φ	Flue-gas slipstream fraction, -

ABBREVIATIONS

<i>CaL</i>	Calcium looping
<i>CAPEX</i>	Capital expenditure
<i>CCU</i>	Carbon capture and utilisation
<i>CRF</i>	Capital recovery factor
<i>HP</i>	High pressure
<i>LCOU</i>	Levelised cost of urea
<i>LP</i>	Low pressure
<i>MEA</i>	Monoethanolamine
<i>N/C</i>	Ammonia-to-carbon dioxide molar ratio
<i>OPEX</i>	Operating expenditure
<i>SR-POLAR</i>	Schwartzentruber-Renon polar equation of state
<i>TRL</i>	Technology readiness level