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Decarbonization of Fossil Energy-intensive Industrial Processes using Innovative Calcium Looping Technology

Calin-Cristian Cormos [a,*], Ana-Maria Cormos [a], Letitia Petrescu [a], Cristian Dinca [b]

[a] Babes – Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos, Postal code: RO-400028, Cluj – Napoca, Romania
[b] Politehnica University, Faculty of Power Engineering, 313 Splaiul Independentei, Postal code: RO-060042, Bucharest, Romania
cormos@chem.ubbcluj.ro

Mitigation of fossil carbon dioxide emissions from the main industrial sectors is a key element in the fight against global warming and climate change. In this respect, the main fossil energy-intensive processes (e.g., heat and power generation, cement, iron and steel, chemical applications etc.) are to be decarbonized for the future low-carbon economy. This paper is evaluating the post-combustion carbon capture based on innovative Calcium Looping (CaL) technology to be applied for decarbonization of various fossil-based industrial applications e.g., power generation, cement, iron and steel production. As illustrative cases, relevant industrial size systems are considered (e.g., 1,000 MW power plants, 4 Mt/year steel mills, 1 Mt/year cement plants). As benchmarks, similar processes without carbon capture as well as ones using chemical gas-liquid absorption for carbon capture are considered to assess the energy penalty for decarbonization. The decarbonized systems have 90 % carbon capture rate. As assessment tools a wide range of process systems engineering elements are used as follow: mathematical modelling and simulation using ChemCAD software, model validation based on experimental data, thermal integration analysis using pinch method for optimization of overall energy efficiency, technical and environmental evaluation to quantify the key performance indicators. As the results show, the innovative calcium looping technology for post-combustion carbon capture has significant advantages in comparison to the chemical gas-liquid absorption in term of higher overall plant energy efficiency (by about 2 net energy efficiency percentage points), lower CO_2 capture energy penalty (7 - 8 vs. 10 net energy efficiency percentage points), reduced specific CO_2 emissions etc.

1. Introduction

Reduction of fossil CO_2 emissions from the main industrial sectors represents today a factor of paramount importance in the attempt to control global warming and climate change (Metz et al., 2005). In medium to long term, the energy-intensive processes such as power, cement, iron and steel, chemical are to be fundamentally changed in respect to the future low-carbon economy (EU, 2014). Reduction of fossil CO_2 emissions can be done by various approaches: increasing the utilization of renewable energy sources (e.g., solar, wind, biomass), improving the energy efficiency along the whole chain from production, transportation and utilization and deployment of Carbon Capture, Utilization and Storage (CCUS) technologies. Each of these methods can be applied (with some process restrictions) for decarbonization of industrial sectors e.g., the renewable energy sources are prone to be used for low-carbon power generation since the carbon capture, utilization and storage is to be used for other industrial processes where renewables are more difficult to be implemented (for instance, chemical and petrochemical systems, cement, iron and steel production, pulp and paper etc.).
This work is assessing the key elements of post-combustion decarbonization using innovative calcium looping method applied to relevant industrial systems e.g., 1000 MW power plants (Astolfi et al., 2019), 4 Mt/year iron and steel mills (IEAGHG, 2013), 1 Mt/year cement plants (IEAGHG, 2008). The innovative calcium looping decarbonization technology has promising advantages in terms of reduced energy and cost penalties for CO_2 capture, higher overall energy efficiency coupled with the ability to integrate the spent sorbent within the evaluated processes e.g., flue gas desulfurization, cement and steel plants etc. (Fennell and Anthony, 2015).

The targeted decarbonized industrial-size concepts were assessed using process modelling and simulation tools being subject of detailed thermal integration using Pinch analysis - see Klemeš, 2013. The main mass and energy balances were used further to calculate the key performance indexes. To benchmark the CaL decarbonization technology, reactive gas-liquid absorption by alkanolamines was used (Sanchez et al., 2014). As relevant novelty aspects of this work, one can mentioned: quantification of decarbonization process impact to various relevant fossil-intensive industrial applications and developing an integrated evaluation methodology using process engineering tools for innovative calcium looping-based CO_2 capture method.

2. Process description, model assumptions and thermal integration aspects

The innovative calcium looping CO_2 capture technology is using a solid sorbent (either natural or synthetic) in a carbonation – calcination cycle. The main chemical reaction of CaL cycle is the following one:

$$CaO \quad + \quad CO_2 \quad \leftrightarrow \quad CaCO_3 \qquad \Delta H_r^0 = -178\ kJ/mol \tag{1}$$

The conceptual design of calcium looping cycle (see Figure 1) involves two separate circulated fluidised bed reactors: the carbonation reactor in which the flue gases containing CO_2 react with calcium oxide to form calcium carbonate and the calcination reactor in which the reaction is reversed to regenerate the sorbent and release captured CO_2. Since the calcium carbonate decomposition is exothermic, additional heat input is to be provided to the calcination reactor. Most commonly, this is done via oxy-fuel combustion (Astolfi et al., 2019).

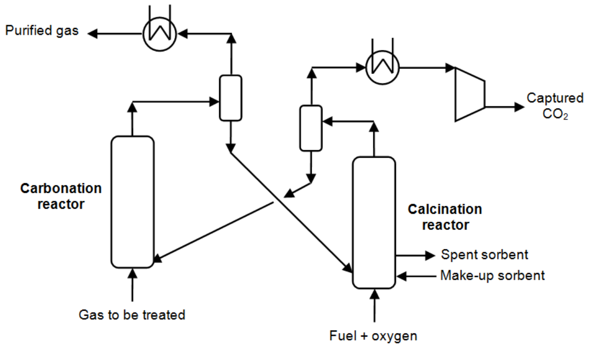

Figure 1: Conceptual design of calcium looping cycle for post-combustion CO_2 capture

One of the key issues in CO_2 capture systems represent the energy consumption for capture which reduces the overall efficiency of decarbonized system. For reactive gas-liquid absorption, the CO_2 capture energy penalty is about 3 GJ/t which turns into about 10 net efficiency percentage points on overall decarbonized power plant compared to the correspondent non-carbon capture design (Sanchez et al., 2014). In case of CaL technology, relevant process characteristics of this method reduce the CO_2 capture energy penalty to about 7 net percentage points. This positive reduction lays in the fact that operational temperature for CaL reactors are high enough (e.g., carbonation reactor 500 – 650 °C, calcination reactor 850 – 1,000 °C) to enhance high temperature heat recovery. For this reason, the detailed thermal integration analysis of CaL cycle is used to optimize the overall energy efficiency (Klemeš, 2013). As illustrative example, Figure 2 presents the Composite Curves of CaL cycle integrated into a 1,000 MW fossil-based power plant.

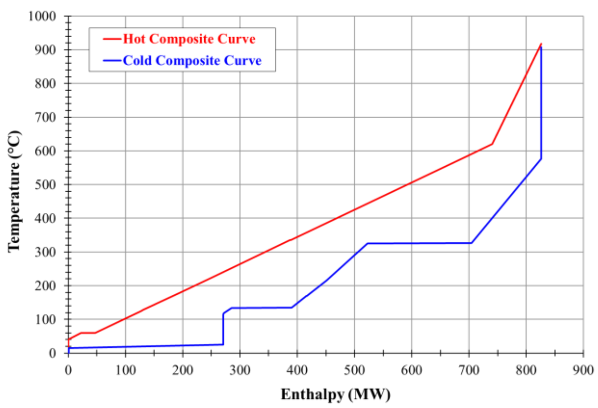

Figure 2: Composite Curves of calcium looping cycle integrated with 1,000 MW power plant

Table 1 shows the most relevant design characteristics of the industrial-size power generation, cement and steel production processes assessed for decarbonization as well as for the calcium looping cycle. The benchmark cases without carbon capture and with carbon capture using reactive gas-liquid absorption were used to quantify the CO_2 capture energy penalty.

Table 1: Design characteristics

Plant sub-system	Design specifications
Fossil fuel compositions and thermal properties	*Coal* Composition (% wt. dry): 72.30 % carbon, 4.11 % hydrogen, 1.69 % nitrogen, 7.45 % oxygen, 0.56 % sulphur, 13.89 % ash; Moisture: 8 %; Lower heating value (as received conditions): 25.17 MJ/kg *Natural gas* Composition: 89 % methane, 7 % ethane, 1 % propane, 0.1 % butanes, 0.01 % pentanes, 2 % carbon dioxide, 0.89 % nitrogen; Lower heating value: 46.73 MJ/kg
Super-critical power plant	Steam cycle characteristics: (290 bar / 582 ^{o}C) with two reheats (75 bar / 580 ^{o}C and 20 bar / 580 ^{o}C) with 1,000 MW net power output Flue gas denitrification unit with 95 % NO_x removal efficiency Flue gas desulphurisation unit with 98-99 % SO_x removal efficiency
Cement plant	Production capacity: 1 Mt/y cement Flue gas denitrification unit with 95 % NO_x removal efficiency Flue gas desulphurisation unit with 98-99 % SO_x removal efficiency
Integrated iron & steel plant	Production capacity: 4 Mt/y hot rolled coil (HRC) CO_2 capture from steam plant, hot stoves, lime kilns and coke ovens Heat and power block: Subcritical steam boiler (169 bar / 565 ^{o}C) with steam reheat (40 bar / 565 ^{o}C) / Combined cycle (HP 100 bar / MP 25 bar / LP 9 bar with MP reheat)
Calcium looping unit	Sorbent: calcium-based sorbent (limestone) Carbonation reactor: 550 - 600 ^{o}C / Calcination reactor: 850 – 1,000 ^{o}C CO_2 capture rate: 90 %
Air separation unit	Oxygen purity (% vol.): 95 % O_2, 2 % N_2, 3 % Ar Ancillary power consumption: 200 kWh/t O_2
CO_2 processing unit	Delivery pressure: 120 bar Compressor efficiency: 85 % TEG (Tri-ethylene-glycol) dehydration unit CO_2 quality specification (vol. %): >95 % CO_2, <2,000 ppm CO, <250 ppm H_2O, <100 ppm H_2S, <4 % non-condensable gases
Heat recovery & steam cycle	Steam turbine efficiency: 85 % Steam wetness ex. steam turbine: max. 10 % Minimum approach temperature: $\Delta T_{min.}$ = 10 ^{o}C

3. Results and discussions

The fossil-based energy-intensive industrial applications coupled with post-combustion CO_2 capture by calcium looping were simulated using ChemCAD. The developed models were validated with experimental data. As illustrative example, Figure 3 presents the experimental vs. simulation results for calcium looping cycle (Cormos, 2020). One can noticed that there is a good correlation between data. The simulation results where then employed for quantification of key performance indexes such as fuel consumption, ancillary power consumption, overall energy efficiency, carbon capture rate, specific CO_2 emissions etc.

3.1 Coal-based super-critical power plants

A conventional power plant size of 1,000 MW net power was considered in three operational scenarios: Case 1.a without carbon capture, Case 1.b with post-combustion CO_2 capture using a calcium looping cycle and Case 1.c with post-combustion CO_2 capture using MEA-based gas-liquid absorption. For the benchmark cases 1.a and 1.c, own modelling and simulation analysis (Cormos, 2020) as well as relevant literature sources were used (IEAGHG, 2006; NETL, 2015). Table 2 shows the key performance indicators for super-critical pulverized coal power plants in both scenarios with and without carbon capture.

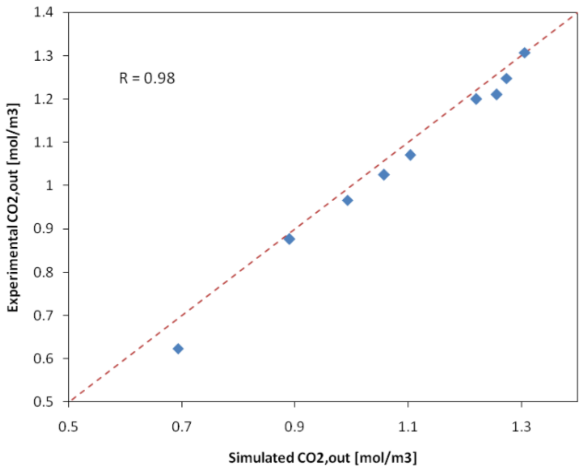

Figure 3: Validation of the calcium looping cycle model

Table 2: Key performance indicators for coal-based power plants

Plant indicator	Units	Case 1.a	Case 1.b	Case 1.c
Input coal flowrate	t/h	330.05	397.83	418.45
Coal lower calorific value	MJ/kg		25.17	
Input coal thermal energy	MW_{th}	2,307.60	2,781.50	2,925.66
Gross power output	MW_e	1,057.81	1,193.64	1,138.15
Ancillary consumption	MW_e	57.81	193.64	138.15
Net power output	MW_e	1,000.00	1,000.00	1,000.00
Net electrical efficiency	%	43.33	35.95	34.18
CO_2 capture rate	%	0.00	90.00	90.00
Specific CO_2 emissions	kg/MWh	801.75	78.12	90.05

One can noticed from results presented in Table 2 that decarbonization of power generation induces a significant reduction of overall energy efficiency from about 43 % in a non-carbon capture scenario to about 34 – 36 % in a scenario with 90 % carbon capture rate. The CO_2 capture energy penalty is about 7.4 % for the calcium looping system in comparison to about 9.2 % for reactive gas-liquid absorption system. The environmental benefit is clear by a significant reduction of the specific CO_2 emissions. The calcium looping cycle shows improved performances in comparison to the MEA-based gas-liquid absorption cycle. The difference between overall net power plant efficiencies is about 1.8 percentage points in favour of CaL cycle, this is mainly due to high temperature heat recovery potential of looping cycle. An additional technological advantage of calcium looping cycle is that the spent sorbent can be used for process desulfurization either in a wet unit to treat the flue gases before CO_2 capture or directly usage in the boiler.

The calcium looping cycle can also be used as CO_2 capture system in a pre-combustion configuration being used also for enhancing the water gas shift (WGS) reaction. In this case, the CaL unit is integrated either in reforming or gasification power plants. As the results show (Cormos et al., 2018), the pre-combustion CO_2 capture using a CaL cycle has an energy penalty of about 6 – 7 net percentage points.

3.2 Cement plants

A conventional cement plant size of 1 Mt/year was considered in three operational scenarios: Case 2.a without carbon capture, Case 2.b with post-combustion CO_2 capture using a calcium looping cycle and Case 2.c with post-combustion CO_2 capture using a MEA-based gas-liquid absorption cycle.

For the benchmark cases 2.a and 2.c, own modelling and simulation analysis (Cormos and Cormos, 2017) as well as relevant literature sources were used (IEAGHG, 2008). Table 3 shows the key performance indicators for cement plants in both scenarios with and without carbon capture. For ancillary heat and power consumption, the decarbonized cement plants have to be provided with a coal-based combustion unit. This fact has as consequence a certain amount of excess power that can be exported to the grid lowering the overall cement plant specific CO_2 emissions.

Table 3: Key performance indicators for cement plants

Plant indicator	Units	Case 2.a	Case 2.b	Case 2.c
Input coal flowrate (for decarbonized designs)	t/h	-	22.12	33.49
Coal lower calorific value	MJ/kg		25.17	
Input coal thermal energy	MW_{th}	-	154.65	234.15
Steam turbine output	MW_e	-	58.15	54.35
Gross electric power output	MW_e	-	58.15	54.35
Ancillary power consumption of cement plant	MW_e	16.25	42.52	34.18
Net electric power output	MW_e	-	15.63	20.17
Net electrical efficiency	%	-	10.10	8.61
CO_2 capture rate	%	0.00	90.00	90.00
Specific CO_2 emissions (on-site)	kg/t cement	728.53	120.69	135.75
Specific CO_2 emissions (power export)	kg/t cement	42.05	-62.32	-79.88
Specific CO_2 emissions (overall cement plant)	kg/t cement	770.39	58.37	55.87
Specific capture CO_2 stream	kg/t cement	0.00	962.31	1,214.09

For cement production plants, the process decarbonization implies a significant reduction of specific CO_2 emissions from 770 to 56 - 58 kg/t cement. Between the two post-combustion CO_2 capture technologies, the calcium looping cycle shows promising advantages such as higher overall energy efficiency by about 2 net percentage points which translates into a lower CO_2 capture energy. In addition, as for power plants, the spent sorbent can be reutilized within the cement production technology (clinker production) with advantages in term of environmental impact as well as positive economic elements.

3.3 Integrated steel mills

A conventional integrated iron and steel plant size of 4 Mt/year Hot Rolled Coil (HRC) was considered in three operational scenarios: Case 3.a without carbon capture, Case 3.b with post-combustion CO_2 capture using a calcium looping cycle and Case 3.c with post-combustion CO_2 capture using a MEA-based gas-liquid absorption cycle.

For the benchmark cases 3.a and 3.c, own modelling and simulation analysis (Chisalita et al., 2019) as well as relevant literature sources were used (IEAGHG, 2013). Table 4 shows the key performance indicators for integrated iron and steel production plants in both scenarios with and without carbon capture. The evaluated decarbonized steel plants were designed without any electricity import (all ancillary power being generated by a captive power plant within steel mill boundaries). If needed, external natural gas was used in the captive power plant of the steel mill to compensate the energy deficit. As steel mill flue gases treated for decarbonization, the following units were considered: steam plant, hot stoves, lime kilns and coke ovens. The overall power efficiency of CaL case is superior to the MEA gas-liquid absorption case due to better thermal integration (as presented above) as well as lower energy duty for CO_2 capture (solvent regeneration duty consumes low pressure steam).

Table 4: Key performance indicators for integrated iron and steel plants

Plant indicator	Units	Case 3.a	Case 3.b	Case 3.c
Input natural gas thermal energy	MW_{th}	669.78	1,156.78	544.10
Gas turbine output	MW_e	-	91.12	202.35
Steam turbine output	MW_e	224.69	366.09	105.25
Gross electric power output	MW_e	224.69	457.21	307.60
Ancillary power consumption of steel mill	MW_e	9.65	132.58	159.75
Net power output	MW_e	215.04	324.63	147.85
Net power efficiency	%	32.12	28.06	27.17
Carbon capture rate (for captive power plant)	%	0.00	90.00	0.00
Power plant specific CO_2 emissions per MWh	kg/MWh	2,455.40	242.33	370.10
Power plant specific CO_2 emissions per t HRC	kg/t HRC	980.50	166.12	229.48
CO_2 capture rate (for CO_2 capture unit)	%	0.00	90.00	90.00
Specific CO_2 emissions (overall steel plant)	kg/t HRC	2,092.53	640.05	833.61
Specific captured CO_2 stream	kg/t HRC	0.00	1,495.18	1,615.76

For integrated iron and steel production plants, the process decarbonization for key units (steam plant, hot stoves, lime kilns and coke ovens) implies a significant reduction of specific CO_2 emissions from about 2100 to 640 - 833 kg/t HRC. As for other two investigated processes (power generation and cement production) also for integrated steel mills, the post-combustion CO_2 capture using the calcium looping cycle shows promising advantages in term of reduced CO_2 specific emissions for the same carbon capture rate (90 %). Also, the spent sorbent can be reutilized within the iron and steel production technology (e.g., lime kilns and sinter production units) with relevant advantages in term of environmental impact as well as economic elements.

4. Conclusions

Three fossil energy-intensive industrial processes were evaluated in view of decarbonization using the innovative calcium looping cycle in a post-combustion CO_2 capture configuration. These industrial sectors are responsible for a high share of global anthropogenic CO_2 emissions: 25 % for heat and power sector, 5 % for cement production and 6 % for ferrous metallurgy. The assessments, based on modelling, simulation, process integration tools, show that the CaL cycle has significant advantages over MEA-based gas-liquid absorption in term of higher overall energy efficiencies (about 2 – 3 net efficiency percentage points) which implies lower CO_2 capture energy penalty and lower specific CO_2 emissions. One can mention additional key advantages: better economics compared to MEA concept, ability to use spent sorbent within the process for desulfurization (power generation) or production (cement and steel) purposes. However, the calcium looping technology still requires further developments from the current stage (1 – 10 MW size) to full industrial size (hundreds of MW).

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