Application of Molten Carbonate Fuel Cells in Cement Plants for CO₂ Capture and Clean Power Generation

Maurizio Spinelli^a, Matteo C. Romano^a*, Stefano Consonni^a, Stefano Campanari^a

Maurizio Marchi^b, Giovanni Cinti^b

^aPolitecnico di Milano, Department of Energy, via Lambruschini 4, 20156 Milano, Italy ^bC.T.G. - Italcementi Group, via Camozzi 124, 24121 Bergamo, Italy

1. Introduction

Control of CO₂ emissions is one of the most important challenges for the next years due to their widely acknowledged effect on climate change. Energy production from fossil fuels is responsible of a great part of the

* Corresponding author. Tel.: +39-0223993846; fax: +39-0223993913. *E-mail address:* matteo.romano@polimi.it anthropogenic CO_2 emissions. Right after power generation, cement production is the largest industrial source of carbon dioxide emissions, responsible for about 7% of the total CO_2 emission from large stationary sources. In cement plants, about 60% of the total CO_2 emissions arise from the decomposition of limestone contained in the raw meal feed, consequent to the calcination reaction ($CaCO_3 \rightarrow CaO+CO_2$); with the remaining 40% resulting from fuel combustion, necessary for the sustainment of the endothermic calcination process and the 'cooking' process producing clinker, the cement primary constituent. Due to this intrinsically high CO_2 emission process, carbon capture and storage is the only option to significantly reduce the emissions from cement plants.

A modern cement plant (Fig. 1) is composed by a 4-5-stage preheating tower, a bottom precalciner, a rotating kiln and a clinker cooler. Exhaust gases from the kiln and the precalciner go through the raw-meal preheating tower, where they preheat the solid mixture entering the process while they are cooled down from the calcination temperature (850-880°C) to 300-350°C. Afterwards, they are sent to the raw meal drier before leaving the plant with a high CO₂ concentration (>30%). We consider here the case of a reference cement plant with a production of 1.25 Mt/year of cement, whose operating conditions have been already calculated in a previous work [1].

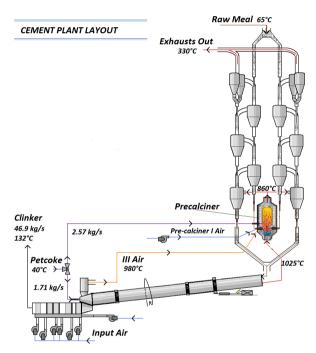


Fig. 1. Schematic layout of a cement plant with 4 stage preheating tower.

At the state of the art, the conventional technology for post-combustion capture of CO₂ is based on chemical solvents like MEA, which require a substantial energy consumption for regeneration and suffer significant drawbacks in terms of cost, degradation and environmental impact due to losses in the flue gas. An alternative promising option for short-medium term plants, already assessed by the authors, is the application of the Ca-looping process, in stand-alone cement plants or coupled with a coal-fired power plant [1,2]. A further option for longer term applications may be the use of molten carbonate fuel cells (MCFC), which can be used as CO₂ concentrators of combustion flue gases. High efficiency and high carbon capture rate using this concept have been verified through plant simulations in combined cycles [3], coal fired steam cycles [4] and gasification-based cycles [5]. The aim of the work is to assess the application of this CO₂ separation process in cement plants, in a configuration where the new MCFC system is added to the plant without significant impact on the production process apart from a change in the raw materials drying section. Different cases are investigated, using MCFCs in a single stage or multiple-stage arrangement and with different operating parameters, discussing the results in terms of energy efficiency and CO₂ emissions.

Nomenclature						
CCS	Carbon Capture and Sequestration					
CSU	CO ₂ separation and purification unit					
E_{eq}	Equivalent CO ₂ emissions (Eq. 3)					
MEA	Mono-Ethanol Ammine					
ORC	Organic Rankine Cycle					
MCFC	Molten Carbonate Fuel Cell					
SPECCA	Specific Primary Energy Consumption for CO ₂ captured (Eq. 2)					
WGS	Water gas shift					

2. Plant concept

Fig. 2 shows a simplified layout of the proposed plant. Flue gases from the cement plant are fed to the cathode of MCFC, using natural gas as fuel; the MCFC separates a large fraction of CO₂ from the flue gases and generates electricity, available for the self-consumption of the cement plant and for energy export. Gases from the fuel cell are cooled, recovering heat for a bottoming cycle; after further purification CO₂ is compressed for storage [6].

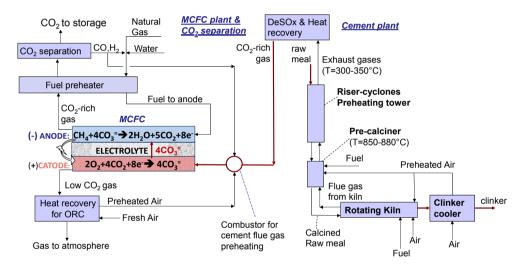


Fig. 2. Conceptual layout of cement plant integration with MCFC for CO₂ capture.

3. Methodology

Mass and energy balances have been estimated by a proprietary computer code (GS) [7] developed by the GECOS group at the Department of Energy of Politecnico di Milano to assess the performance of gas/steam cycles, CO₂ capture systems, fuel cell cycles as well as a variety of other plant options. The plant scheme is reproduced by assembling in a coherent network the different components selected in a library of basic modules, whose models have been previously implemented, including MCFCs; the model includes built-in rules for efficiency prediction of turbomachines (gas and steam turbine, compressors), as a function of their operating conditions, and calculation of gas turbine cooling flows. The CO₂ separation process is simulated with Aspen Plus® [6].

3.1 Molten Carbonate Fuel Cell

MCFCs are a well-known candidate for the generation of clean power starting from a variety of possible fuels, including natural gas, biogas and synthesis gas. MCFC works taking oxygen from the cathode side and transporting

it together with CO_2 as a carbonate ion (CO_3^-) , which permeates through the electrolyte; oxygen is then released and recombines with hydrogen at the anodic side (Fig. 2). Hydrogen can be generated by an internal reforming process which takes place in the stack, so that heat released by the fuel cell sustains the endothermic reforming reactions [3]. The flux of spent fuel exiting the fuel cell anode contains unconverted H_2 and CO mixed with steam and CO_2 . For the purpose of CCS it can be sent to a CO_2 removal section, recycling the residual H_2 and CO to the MCFC plant.

Detailed MCFC simulation requires an approach based on finite volume or finite element analysis, with a 2D or 3D geometry, based on a model calibration against a specific MCFC technology and allowing an insight on the internal behaviour of the fuel cell, evidencing for instance hot spots, uneven current density distributions, local reactant shortage issues [8]. Within this work, MCFC is simulated with GS using a simpler lumped-volume or zero-D model, calculating the fuel cell balances and avoiding an investigation of the internal behaviour of the fuel cell.

The model requires to assign reactant properties and flow rates at FC inlet and the CO_2 utilization factor (U_{CO2}) defined as the ratio between the flow rate of CO_2 permeated through the cell and the inlet flow rate of CO_2 .

It is then possible to calculate the cell current output and the exhaust stream composition, once the cell reactions and cell voltage are also known. On the anodic side the internal reforming of hydrocarbons (Eq. 1) can be assumed as a first approximation to reach a full conversion, thanks to the fast oxidation and subtraction of products:

$$C_n H_m + n H_2 O + heat \rightarrow \left(\frac{m}{2} + n\right) H_2 + nCO$$
 (1)

The other reaction occurring is water gas shift (WGS) which promotes the conversion of CO into additional hydrogen and CO₂ (anodic side), which is assumed at equilibrium at fuel cell outlet.

The voltage can be predicted by GS with a simplified approach, starting from the reversible Nernst potential (estimated using the average cell I/O compositions) and providing information on cell losses. However, in this preliminary analysis voltage is simply assumed at 0.7 V or 0.8 V in an advanced scenario to explore its effects on overall performances, leaving more detailed analysis to future works. In addition, simulations are performed fixing three parameters: i) fuel utilization factor of the fuel cell (0.75), ii) inlet and outlet temperature of gases, iii) minimum allowed molar fraction of oxygen at the outlet of the cathode. The latter ranges from 4% in the base cases to 12.2% (obtained with more air dilution of the cathode stream) in the advanced case, which aims at a higher CO₂ utilization. Imposing these values, oxygen and CO₂ utilization factors are a result of the simulation.

Table 1 presents the most relevant assumptions made for the calculation in a conservative base scenario and an advanced scenario. The assumed parameters reflect consolidated literature specifications on MCFCs [5,9].

Assumption	Base (Cases 1,2,3)	Advanced (Case 4)
Fuel utilization factor	0.75	0.75
Steam to carbon ratio	2	2
Voltage	0.7 V	0.8 V
O ₂ fraction at cathode outlet	4%	12.2%
Inlet temperature (anode and cathode)	580°C	580°C
Outlet temperature (anode and cathode)	650°C	650°C
Pressure losses on anode / cathode sides	3 kPa /2kPa	3 kPa /2kPa
Heat losses (% input thermal power)	1%	1%
DC/AC converter efficiency	94%	94%

3.2 CO₂ Separation and Purification Unit (CSU)

Downstream the MCFC, CO_2 concentration is not high enough to respect transport and storage requisites [10] and the anode exhaust still contains a significant amount of H_2 and CO that shall be separated from the CO_2 stream, for instance – as considered here – recycling it to the MCFC plant.

One promising approach for the separation and purification section (CSU) is the adoption of a refrigeration process which allows condensing and separating CO₂ from the other gases (sometimes called cryogenic process).

We consider here the option of a self-refrigerated system which uses the CO₂ separated as cooling source, based on a two-steps flash separation, following the same approach already presented in [6], to which we address the reader for further details. Liquefied stream is then pumped to 110 bar, for a long range transportation.

Organic Rankine Cycles (ORC) are gaining increasing interest and market share for the thermodynamic conversion of heat into power in applications where the low power output and/or the low temperature of the heat source would make the adoption of conventional steam cycles impractical. Cement plants are an example of industrial processes suitable for the application of exhaust gas energy recovery by ORCs, where heat is released by hot exhaust combustion gases and hot air from clinker cooling in a temperature range between 250 and 400°C, with an available thermal power between 5 and 40 MW_{th}, depending on the size and efficiency of the plant. Examples of commercial ORC installations of this type are in Morocco (Italcementi plant, 2 MW_e) and Romania (Holcim plant, 4 MW_e), as well as others in India and Germany in the 1-5 MW_e scale [11,12].

We consider here to use ORCs as heat recovery bottoming cycles downstream the MCFC, operating with exhaust gases at temperature between 350°C and 250°C. At this temperature level, the typical net electric efficiency ranges between 23 and 27% as proposed by one of the leading manufacturers [12] and widely demonstrated in literature. Instead of simulating the whole ORC unit, in order to simplify the analysis, we calculate here the electricity production of the ORC assuming an overall electric efficiency of 25%.

4. Plant layout of the MCFC and CO₂ separation system

The plant layout considered in this analysis for the MCFC and CO₂ separation system is shown in Fig. 3.

Gas fed to the MCFC is extracted from the outlet of the preheating tower of the cement plant at 315°C. This choice is non-invasive for the cement plant and suitable for application on existing plants (stream #1). Before entering MCFC, flue gases are cooled and sent to a cleaning section, which is critical for the reliable operation of the fuel cell. In this analysis we have considered to include (i) a filtering section to separate dust, and (ii) a sulfur removal section (stream #2), although also other contaminants (Cl, Hg, other heavy metals) could be taken into account depending on further investigation on fuel cell tolerance. The content of SO₂ from the cement plant is rather low (~50 ppm) thanks to the continuous contact between the gases and CaO-rich solid streams in the cement plant, where CaO acts as a sorbent like in flue-gas desulfurizers (FGD). As a term of comparison, inside the FGD of a state-of-the-art of pulverized coal power plant, SO₂ content is reduced to 30ppm approximately, but it could be further be reduced with the addition of extra washing steps and achieve concentrations lower than 5-10 ppm. However, some literature work mention tolerance limits <1 ppm [13] requiring further cleanup. Within this analysis, we do not consider any specific technology and we neglect the related possible energy penalties, while we take into account the necessity of cooling the flue gases and sustaining pressure drops in the loop.

After cleanup, the exhaust gases are mixed with additional ambient air (#13), providing oxygen for fuel oxidation (#3), then reheated to 580°C. Heating is first carried out by a regenerative gas-gas heat exchanger (up to 400°C) and then by burning residual CO and H₂ stream coming from the CO₂ purification section (#4).

Gas exiting the cathode side of the cell is sent to a heat recovery section, preheating primary air at 400°C and releasing heat for the ORC plant, then released to ambient (#7). The stream leaving the anode side is cooled in a second heat recovery section for natural gas and water preheating (#10). Finally this rich CO₂ stream is directed to the CSU section, where high-purity CO₂ is separated from a H₂/CO-rich stream, partly burned for air heating and partly recycled as MCFC fuel.

On the other side we assume to feed the MCFC using natural gas as fuel, desulphurized through zinc oxide beds, although other approaches (e.g. active carbon filters [14]) could be addressed. Natural gas is mixed with a stream of hydrogen rich syngas, heated up to 300°C (mainly in a regenerative heat exchanger) and sent to an hydrogenation reactor where sulfur compounds are converted to H₂S, which is then adsorbed in a ZnO bed (# 8).

Fuel is then mixed with steam and preheated up to 580°C before entering the MCFC (stream 9). Inside the MCFC natural gas is reformed and hydrogen is oxidized, while the carbon dioxide content at the cathode decreases, reducing the specific emission of the cement plant. Exhaust gases of the MCFC anode, with a high CO₂ content, are then cooled down in regenerative heat exchangers and sent to the CSU (stream 11).

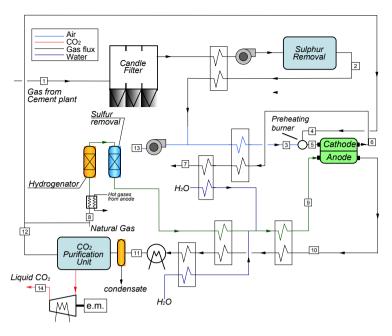


Fig. 3: Detailed plant scheme of MCFC integration downstream the cement process (Case 1 and Case 4).

Composition of natural gas is assumed according to [10] (mol. fractions CH_4 89%, C_2H_6 7%, C_3H_8 1%, C_4H_{10} 0.1%, C_5H_{12} 0.01%, CO_2 2%, N_2 0.89%) with LHV 46.482 MJ/kg and CO_2 specific emission 56.99 g_{CO2}/MJ_{LHV} . Other main assumptions for cycle calculation are presented in Tab. 2.

Tab. 2: Assumptions for cycle simulation.

:				
Heat exchangers				
Minimum ΔT in gas-gas heat exchangers, °C	25			
Minimum ΔT in condensing-liquid heat exchangers, °C	3			
Minimum ΔT in other heat exchangers, °C	10			
Heat losses, % of heat transferred	0.7			
Pressure drop liquid / gas phase, bar	0.4 / 2			
CO ₂ compression				
IC compressor isentropic / electric-mechanical efficiency, %	84 / 94			
Pump hydraulic / electric-mechanical efficiency, %	80 / 94			
Last stage IC compressor CO ₂ discharge pressure, bar				

5. RESULTS

5.1 Case 1 – Single MCFC module

In the basic scenario, the fuel cell is operated at reactant inlet / outlet temperature of 580 /650°C with a voltage of 0.7 V; oxygen molar fraction at cathode outlet is imposed to 4% by varying the air mass flow rate added to cement plant flue gases. Assuming this constraint and being the single passage fuel utilization factor imposed to 75%, the overall CO₂ utilization factor is a result of the simulation. The power of the fuel cell is determined by the mass flow rate of cement plant flue gases, which imposes the mass flow rate of natural gas fed to the MCFC. With these assumptions, the plant can guarantee a limited CO₂ capture ratio, although with a good net electric efficiency (46%). ORC electric output is large enough to cover the auxiliaries electric consumption, mainly related to the compression and purification unit, leaving a net electric power output of 35.2MW_e, well above the electricity

consumption of the reference cement plant (~9MW_e), resulting in the possibility of a net export of electricity. Conditions of the most significant streams are shown in Tab. 3.

Tab.3: Thermodynamic data of main streams of MCFC plant in Case 1.

Point	T [°C]	p [bar]	m [kg/s]	M [kmol/s]	Molar concentration [%]									
				_	Ar	CO	CO_2	H_2	H ₂ O	N ₂	O_2	CH ₄	C_2H_6	C ₃ H ₈
1	315	1.01	92.8	2.80	0.7	0.0	33.8	0.0	4.5	59.1	1.8	0.0	0.0	0.0
2	41.1	1.05	94.4	2.89	0.7	0.0	32.8	0.0	7.5	57.3	1.7	0.0	0.0	0.0
3	450	1.07	135.7	3.98	0.8	0.0	23.8	0.0	5.9	55.6	13.8	0.0	0.0	0.0
4	40.6	1.12	2.3	0.12	0.0	28.9	24.9	46.1	0.0	0.1	0.0	0.0	0.0	0.0
5	579.9	1.07	138.0	4.40	0.7	0.0	23.0	0.0	6.5	62.9	6.9	0.0	0.0	0.0
6	649.9	1.05	120.7	3.96	0.8	0.0	18.2	0.0	7.2	69.7	4.0	0.0	0.0	0.0
7	209.6	1.01	120.7	3.96	0.8	0.0	18.2	0.0	7.2	69.7	4.0	0.0	0.0	0.0
8	21.1	1.12	1.8	0.10	0.0	1.8	3.4	2.8	0.0	0.8	0.0	83.5	6.6	1.0
9	579.7	1.12	5.5	0.30	0.0	0.6	1.1	0.9	67.7	0.3	0.0	26.9	2.1	0.3
10	650	1.09	22.8	0.79	0.0	4.9	44.9	7.3	42.8	0.1	0.0	0.0	0.0	0.0
11	30	1.01	22.8	0.79	0.0	4.9	44.9	7.3	42.8	0.1	0.0	0.0	0.0	0.0
12	30	1.01	2.4	0.12	0.0	28.9	24.9	46.1	0.0	0.1	0.0	0.0	0.0	0.0
13	20	1.01	41.3	1.43	0.9	0.0	0.0	0.0	1.0	77.3	20.7	0.0	0.0	0.0
14	30	150	14.3	0.33	0.0	1.1	98.3	0.4	0.0	0.2	0.0	0.0	0.0	0.0

5.2 Case 2, 3: Double and triple 'sequential' MCFC module options

We explore here the option of a plant where multiple MCFC modules are arranged sequentially, in series on the cathode stream, providing adequate intermediate cooling and oxygen addition. The motivation behind this idea is that a single FC suffers working at high reactant utilization, lowering the minimum reactant concentration and negatively affecting the cell voltage; by splitting the process on more FCs it is possible to avoid penalizing the whole process due to the increasingly lower reactant concentrations, while intermediate air addition allows restoring a higher O₂ concentration. Of course complexity and costs grow up substantially, calling for a next economic analysis. Moreover specific technological issues related to the proposed 'sequential' configuration (e.g. pressure loss balances and thermal losses) would arise, which will be investigated in future works.

Two different cases have been investigated, with a double and a triple fuel cell configuration. The concept is shown in Fig. 6 for the double fuel cell configuration, where the corresponding thermodynamic properties of main streams are reported in Tab. 4.

Cathode gases exiting the MCFC module are mixed with fresh air providing additional O₂ for fuel oxidation and cooling the gas before entering the following cell module. MCFCs are calculated keeping similar operating conditions for each module, i.e. assuming for simplicity a "standard" inlet temperature of 580°C, an outlet gas temperature of 650°C and a fuel utilization factor of 75% (U_F). The plant layout includes splitting of fuel among the MCFCs as well as additional fresh air streams with related fans and preheating sections, in order to provide the same oxygen molar ratio at each cathode inlet. In this way the average CO₂ concentration is higher with respect to a hypothetical case in which all fresh air is added to the gas stream before the first cell inlet. However the progressive reduction of CO₂ concentration could bring about differences in each FC performance, not considered in this study.

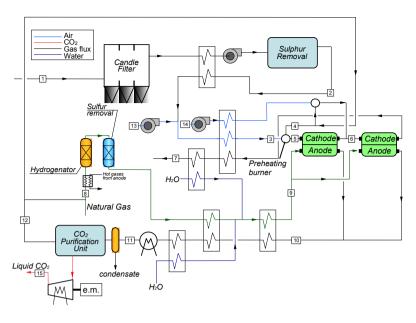


Fig. 6 Detailed plant scheme with double MCFC configuration applied to cement plant (Case 2).

Tab.4 Thermodynamic data of main streams - (Case 2).

Point	T [°C]	p[bar]	m [kg/s]	M [kmol/s]] Molar concentration [%]									
				•	Ar	CO	CO_2	H_2	H_2O	N_2	O_2	CH ₄	C_2H_6	C_3H_8
1	315	1.01	92.7	2.80	0.92	0.0	0.0	0.0	1.0	77.3	20.7	0.0	0.0	0.0
2	41.7	1.07	94.4	2.89	0.68	0.0	32.7	0.0	7.6	57.2	1.7	0.0	0.0	0.0
3	400	1.07	137.1	4.37	0.78	0.0	21.7	0.0	5.4	64.0	8.2	0.0	0.0	0.0
4	40.6	1.12	3.3	0.16	0.00	28.9	25.4	45.6	0.0	0.1	0.0	0.0	0.0	0.0
5	580	1.07	140.4	4.47	0.74	0.0	23.1	0.0	6.9	62.6	6.6	0.0	0.0	0.0
6	579.9	1.05	145.2	4.80	0.83	0.0	16.0	0.0	6.6	70.0	6.5	0.0	0.0	0.0
7	199.7	1.01	128.8	4.39	0.91	0.0	11.3	0.0	7.3	76.5	4.0	0.0	0.0	0.0
8	25.4	1.12	4.3	0.23	0.00	8.5	8.9	13.4	0.0	0.6	0.0	62.8	4.9	0.8
9	579.7	1.12	11.8	0.65	0.00	3.0	3.1	4.7	64.9	0.2	0.0	22.1	1.7	0.3
10	650	1.09	44.3	1.53	0.00	4.7	44.3	7.0	43.9	0.1	0.0	0.0	0.0	0.0
11	30	1.01	44.3	1.53	0.00	4.7	44.3	7.0	44.0	0.0	0.0	0.0	0.0	0.0
12	30	1.01	4.6	0.23	0.00	28.9	25.4	45.6	0.0	0.1	0.0	0.0	0.0	0.0
13	20	1.01	42.7	1.48	0.92	0.0	0.0	0.0	1.0	77.3	20.7	0.0	0.0	0.0
14	20	1.01	20.8	0.72	0.92	0.0	0.0	0.0	1.0	77.3	20.7	0.0	0.0	0.0
15	30	150	27.5	0.63	0.00	1.0	98.3	0.4	0.0	0.2	0.0	0.0	0.0	0.0

5.3 Case 4 and comparison of results

CO₂ capture efficiency and other main results of the simulation are reported in Tab. 5. An efficient measure of the process quality is the index "Specific Primary Energy Consumption for CO₂ captured" or SPECCA, defined as:

$$SPECCA \left[\frac{MJ}{kg_{CO2}} \right] = \frac{(1/\eta - 1/\eta_{ref})}{E_{ref} - E} \times 3600$$
 (2)

where η is the net electric efficiency of system and E is the CO_2 specific emission (kg_{CO2}/MWh_{el}) of the system with CO_2 capture, while 'ref' refers to a reference power with no capture plant using the same fuel, here a combined cycle. SPECCA measures in a comprehensive way the amount of fuel thermal energy required to avoid the emission of one kg of CO_2 . It results to be much lower for the proposed MCFC plants than for a conventional 'post-combustion' capture system based on amines (MEA system).

The quantity E_{eq} is the equivalent CO_2 emission, defined to compare specific emission with other power plants

fed by natural gas. Equivalent CO₂ emissions are calculated by considering the credits from the CO₂ captured from cement flue gases, obtaining negative equivalent emission of up to -1000 g/kWh.

$$E_{eq} \left[\frac{g_{CO2}}{kWh_e} \right] = \frac{3600 \times \left(\dot{m}_{CO2, emitted} - \dot{m}_{CO2, cement} \right)}{P_e}$$
 (3)

Looking at the results of Cases 1,2 and 3 it is possible to evidence how the electric efficiency does not change much (46.7% and 47.3% for the cases with two and three MCFC modules, including the energy penalty related to CO_2 compression and purification), while the CO_2 capture efficiencies becomes 56% for the two-MCFC configuration and to 76% for the three-MCFC option and SPECCA shows increasingly low values. Since most of CO_2 derives from cement plant flue gases, the value of CO_2 avoided index is very close to CO_2 capture efficiency (48% and 70%, respectively). The electricity output is associated to a "negative" CO_2 equivalent specific emission, calculated in comparison with other power plants fed by natural gas, since the FC works with the additive CO_2 sources coming from the cement production process: the partial sequestration of this CO_2 (negative term in Eq. 3) brings the equivalent CO_2 emission down to very low values (< -1200 g/kWh_e).

In Case 4, following the same plant scheme of Fig. 3, the advanced single-module configuration shows better values for both electric efficiency (53%) and carbon capture efficiency (67%). Thanks to the increased cell voltage, the thermal energy released for capturing each CO₂ moles decreases significantly, allowing for a higher CO₂ utilization factor (70%). As a consequence the resulting SPECCA is by far the best value (0.44).

Tab.5: Results of cer	ent plant integrated with	MCFC with the different	configuration options.

	Case 1	Case 2	Case 3	Case 4
Energy and CO ₂ balances	1 MCFC	2 MCFC	3 MCFC	1 MCFC - Advanced
Q LHV, in [MW _{LHV}]	76.62	134.84	177.57	178.4
Fuel cell power [MW _e]	36.72	68.63	95.32	106.1
ORC Power [MW _e]	6.29	9.09	9.61	8.31
Auxiliaries [MW _e]	-7.78	-14.79	-20.86	-19.86
Overall net power [MW _e]	35.23	62.94	84.07	94.58
Net electric LHV efficiency	46.0%	46.7%	47.3%	53.0%
CO ₂ from cement plant flue gas [kg/s]	41.63	41.63	41.63	41.68
CO ₂ from natural gas to anode side [kg/s]	3.01	6.17	9.04	9.05
CO ₂ from natural gas to cathode side [kg/s]	1.26	1.18	0.69	0.77
CO ₂ captured [kg/s]	14.22	27.29	38.86	37.80
CO ₂ released in ambient [kg/s]	31.73	21.78	12.54	13.82
CO ₂ emissions [g/kg _{clinker}]	666.2	457.41	263.36	290.15
Equivalent CO ₂ emissions [g/kWh]	-1016.6	-1135.3	-1245.7	-1061.1
Fuel cell CO ₂ utilization factor	0.286	0.257/0.357	.236/.317/.474	0.7
CO ₂ capture efficiency	30.9%	55.5%	75.6%	73.2%
CO ₂ Avoided, cement plant	23.9%	47.7%	69.9%	66.9%
SPECCA	1.21	1.03	0.89	0.44

6. Conclusions

A preliminary analysis about the potential of MCFC integration in a cement plant has been performed. The MCFC operates downstream the cement plant process, after a gas cleanup phase, using at the cathode the cement plant effluent with addition of air providing oxygen for the cell reactions. The FC operates with natural gas as fuel, reformed internally after steam addition. The reactant preheating process is arranged to recover heat from the FC unit as well as to exploit the possibility of burning part of the unused fuel exiting the fuel cell. Single and multiple 'sequential' FC module configurations are considered, increasing the fraction of CO₂ separated. Final purification of the CO₂ is carried out with a cryogenic process.

Results show a good and very promising behavior of the proposed plant, which guarantees a strong reduction of CO₂ while producing electricity from the fuel cell and the ORC unit. The proposed configuration allows to avoid from 30% to 75% CO₂ emission adopting one to three sequential fuel cell configurations with a baseline performance scenario or a single fuel cell configuration operating with advanced parameters; the resulting power

plant generates from 35 to 95 MW_e and negative CO₂ equivalent emissions. Future work will be dedicated to better evaluate the technology taking into account a more detailed analysis of fuel cell performances and exhaust gas cleanup, based on the support of experimental data, as well as investigating the system economics by the point of view of final costs of CO₂ separated, of electricity and clinker production.

References

- [1] Romano MC, Spinelli M, Campanari S, Consonni S, Cinti G, Marchi M, Borgarello E. "The Calcium looping process for low CO₂ emission cement plants" 6th Int. Conference on Applied Energy ICAE2014-294, 2014.
- [2] Romano MC, Spinelli M, Campanari S, Consonni S, Cinti G, Marchi M, Borgarello E, "The Calcium looping process for low CO₂ emission cement and power", Energy Procedia; 37:7091–7099, 2013.
- [3] Campanari S, Chiesa P, Manzolini G, "CO₂ capture from combined cycles integrated with Molten Carbonate Fuel Cells" Int. J. of Greenhouse Gas Control, 4: 441-451, 2010.
- [4] Campanari S, "Carbon dioxide separation from high temperature fuel cell power plants" J. of Power Sources; 112: 273-289, 2002.
- [5] Spallina V, Romano MC, Campanari S, Lozza G, "Application of MCFC in Coal Gasification Plants for High Efficiency CO2 Capture" J. of Engineering for Gas Turbines and Power; 134: 011701, 2007.
- [6] P. Chiesa, S. Campanari, G. Manzolini, "CO₂ cryogenic separation from combined cycles integrated with molten carbonate fuel cells," Int. J. Hydrogen Energy, vol. 36, no. 16, pp. 10355–10365, Aug. 2011.
- [7] "GECOS research group" [Online]. Available: www.gecos.polimi.it/software/gs.php.
- [8] P.Iora, S. Campanari, "Development of a Three-Dimensional Molten Carbonate Fuel Cell Model and Application to Hybrid Cycle Simulations" J. of Fuel Science and Technology, vol.4 (501-510), DOI: 10.1115/1.2756850, nov. 2007.
- [9] Campanari S., Iora P., Macchi E., Silva P. "Thermodynamic analysis of integrated MCFC / Gas Turbine cycles for sub MW and multi-MW scale power generation", ASME J. of Fuel Cell Science and Technology, Vol. 4, pp. 308-316, DOI: 10.1115/1.2744051, Aug. 2007.
- [10] Franco F., et al "Common framework and test cases for transparent and comparable techno-economic evaluations of CO₂ capture technologies the work of the European Benchmarking Task Force" Proc. of GHGT-10, Amsterdam (NL), Sept. 2010.
- [11] "Ormat." [Online]. Available: www.Ormat.com.
- [12] "Turboden" [Online]. Available: www.turboden.com.
- [13] NETL "Fuel Cell Handbook", 7th edition. US Department of energy, Nov. 2004.
- [14] S. Campanari, P. Chiesa, G. Manzolini, S. Bedogni "Economic analysis of CO2 capture from combined cycles using MCFCs", Applied Energy, DOI 10.1016/j.apenergy.2014.04.011, vol. 130, 562–573, 2014.