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Calcium Looping technology demonstration in industrial environment: status of the CLEANKER pilot plant

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Abstract

Calcium Looping (CaL) is recognized as one of the most promising emerging technology for CO_2 capture in cement plants. The highly integrated Calcium Looping process configuration enables CO_2 capture with an efficiency target over 90% and high-energy efficiency.

The core activity of the CLEANKER project is the design, construction and operation of a CaL demonstration system including the entrained-flow carbonator (the CO_2 absorber) and the entrained-flow oxyfuel calciner (the sorbent regenerator). This demonstration system, connected to the Buzzi Unicem kiln of the Vernasca cement plant (Italy), will capture the CO_2 from a portion of the flue gases of the kiln, using as CO_2 sorbent the same raw meal that is used for clinker production.

The CLEANKER implementation plan spans four years and half, from October 2017 to March 2022 (an extension of six months has been requested due to the pandemic situation). The first two years have been devoted to the (i) detailed design of the CaL demonstration system, the (ii) characterization of raw meals as CO_2 sorbents and the (iii) erection of the demonstrator.

The pilot plant has been commissioned in October 2020 and then will be demonstrated by means of several short and long steady-state tests (during spring and summer 2021), with the aim of optimizing the operational parameters governing the CO_2 capture process and of bringing the integrated CaL technology at TRL7. The pilot plant and the conventional kiln operations will be deeply integrated: the CaL calciner will be fed by the same kind of raw meal used in the kiln for producing clinker, whereas the carbonator will treat the effluents coming from the cement plant. The CaL calciner will be fired in a recirculated oxy-fuel combustion mode, where a heavy fuel oil will be burnt with oxygen and a fraction of the CO_2-rich exhausts will be recirculated to control the oxidant composition. Before being recycled to the CaL calciner inlet, this CO_2-rich stream will be properly cooled in a regenerative riser-cyclone stage, designed to preheat the fresh raw meal-based sorbent fed to the pilot, minimizing the additional fuel supplied to run the calcium looping process. In the carbonator, the amount of sorbent (F_{Ca}/F_{CO_2}) will be tuned either by increasing

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the raw meal exchanged with the CaL calciner or by internally recycling a fraction of sorbent from the carbonator outlet to the inlet. First short campaigns will be carried out by specialized Buzzi Unicem operators (assisted by CLEANKER partners such as, Politecnico di Milano, Laboratorio Energia e Ambiente Piacenza, IKN, University of Stuttgart and VDZ) to test the process performances as a function of the type of raw meal, the amount of sorbent (solid to gas ratio in the carbonator) and the carbonation/calcination operating temperatures.
The experimental activity will prove the stability and the effectiveness of the process by running over hundreds of hours the optimal experimental configuration, capable of achieving a constant carbon capture rate higher than 90%. Besides the continuous monitoring of process temperatures, flow rates and gas compositions, the experimental campaigns will be supported by post-processing sorbent analysis, in order to evaluate the capture capacity of the raw meal and the extent of side reactions. Test results will be exploited to validate simulation models and to improve the future scale-up and the design of an industrial size CaL plant.

Keywords: CLEANKER; CCUS; CO2 capture; Calcium Looping; Cement; Clinker; Entrained Flow Reactors.

1. The CLEANKER project: background, challenges and scope

The CLEANKER project (CLEAN clinKER production by calcium looping process) project (www.cleanker.eu) aims at demonstrating the Calcium Looping (CaL) concept, in the highly integrated configuration with entrained flow reactors, as a feasible technology to reduce CO_2 emissions from the cement production process.

In the industrial sector, the cement industry is responsible for about 27% of global anthropogenic CO_2 emissions [1] and, according to IEA and ZEP studies [2, 3], it will play a central role in the achievement of the 2°C target for the global temperature increase (IEA 2DS scenario). On a global scale in fact, the cement production releases 2.2 Gt_{CO2} [4] per year with an overall share of 6-7% [5] of total worldwide CO_2 emissions.

The CLEANKER project got EC support from October 2017 to March 2022 (including the extension of six months due to the pandemic situation) under the Horizon 2020 call "Enabling decarbonisation of the fossil fuel-based power sector and energy intensive industry through CCS" (LCE 29 – 2017) to advance the integrated Calcium looping process for CO2 capture in cement plants.

The CaL technology is a regenerative process that takes advantage of the capacity of calcium oxide-based sorbents to capture CO_2 at high temperatures:

- The CO_2 from the flue gases coming from the cement kiln is captured in a reactor (the carbonator) operating at around 650°C where the carbonation of CaO to $CaCO_3$ occurs;
- The $CaCO_3$-rich sorbent is regenerated in the calciner operating above 900-920°C, where the calcination process is favoured by oxyfuel combustion. In this way, CaO is make available again in the carbonator and a gas stream of nearly pure CO_2 is released.

The exploitation of several energy and material synergies between the industrial process and the capture unit, such as the same raw material used as sorbent and for clinker production, simple retrofittability of existing kilns and the adoption of entrained flow gas-solid reactors, commonly used in cement plants, make the technology particularly appealing for its application in this sector. High energy efficiency can be achieved for the process by keeping a low overall energy consumption with a proper integration of raw meal preheating and heat recovery from the kiln flue gases.

One of the main challenges of CLEANKER is to assess the CO_2 capture performance of the raw meal, with respect to the possibility of sorbent deactivation and side products formation. Also, the fluid-dynamics of the entrained flow reactors under high solid to gas ratio needs to be better understood to validate basic reactor models currently developed.

The primary goals of the pilot plant are:

- Verify the feasibility of the integrated CaL process under a technical and economic point of view and bring it at TRL 7
- Set the basis for its industrial application in existing cement plants

- Implementing the CCUS technology in the cement industry with fast authorisation procedures and high safety conditions

To achieve these targets, experimental campaigns will be carried out on the demonstrator, that will imply short and long experimental periods. HAZOP analysis and Risk identification have also been proposed to support the initial test activity and the subsequent operations.

Nomenclature

CaL	Calcium Looping
CAV	Combustibile ad Alta Viscosità (High-Viscosity Fuel)
CCS	Carbon Capture and Storage
F_{Ca}	Molar flow of CaO fed to the carbonator of the CaL process from the calciner [kmol/s]
F_{CO2}	Molar flow of CO_2 in flue gas entering the carbonator [kmol/s]
HAZOP	HAZard and OPerability analysis
TRL	Technology Readiness Level
ZEP	Zero Emissions Platform

2. Pilot Plant description

The core idea of the integrated CaL configuration, is switching the pre-calciner of the cement plant to oxyfuel mode, so that it coincides with the calciner of the CaL system. In this way, CO_2 from fuel combustion in the calciner and from raw meal calcination is made available as concentrated CO_2 gas from this reactor. On the other hand, CO_2 released in the conventional air-blown rotary kiln from the additional fuel combustion and residual raw meal calcination is captured in the CaL carbonator. In order to test the technology at TRL7, the CLEANKER demonstrator has been designed and erected in order to do not affect the daily operation of the cement plant, treating 1% of the flue gases coming from the rotary kiln. The integration of the CLEANKER demonstrator with the cement plant is conceptually shown in **Figure 1** and **Figure 2**.

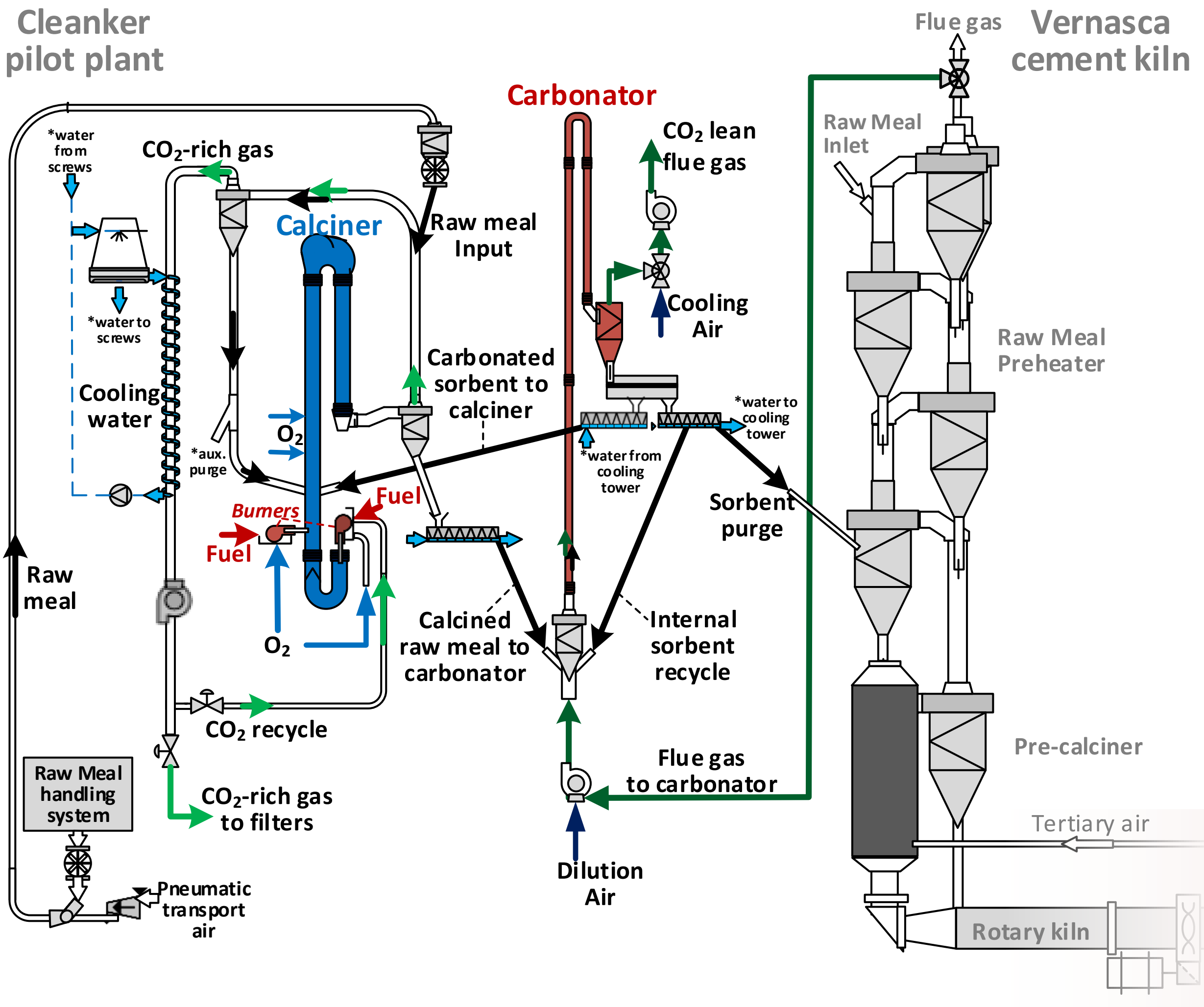

Figure 1: Simplified scheme of the CLEANKER demonstrator integrated in the Vernasca cement plant

The design of the demonstrator plant took about one year and half and ended with 693 drawings and a revision level “Q” of the flow sheet. In the third year of the implementation plan, the installation of 165 tons equipment (plus 40 tons of steel platforms and support structures), 38 major pipes, 78 expansion joints for heat compensation and 189 instrument items, has been completed according to the layout shown in **Figure 2**.

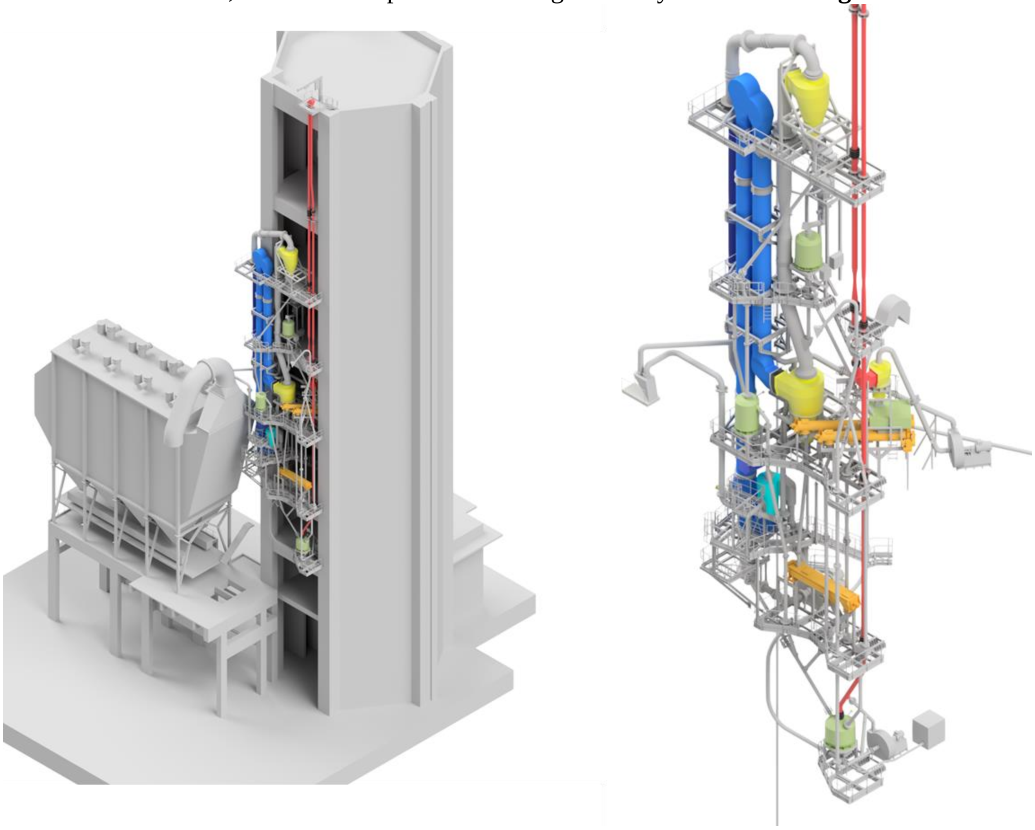

Figure 2: CLEANKER demonstrator layout - Rendering

The demonstration system is connected to the 1.3Mt/y cement plant operated by Buzzi Unicem in Vernasca (Piacenza, Italy). The core of the capture process is represented by the regenerative cycle of CO_2 adsorption/desorption processes occurring in the two entrained flow reactors, the carbonator and the calciner.

The main parts of the equipment, their function, challenges and research questions are described in the following paragraphs starting from the description of the two entrained flow reactors, the carbonator and the calciner.

2.1. Carbonator

The carbonator (**Figure 3**) consists of an entrained flow reactor, made of stainless steel, in the shape of gooseneck. It is composed of two different sections, an upcomer pipe and a downcomer pipe, for a total length of approx. 105 m. The required length is determined by the entrained flow operating principle to obtain a proper mass transfer between the sorbent and the gases. The section diameter increases from 250 mm, in the upflow section, to 350 mm in the downflow section to increase the retention time of the gas-solid flow inside the reactor. A so called “swirl head” is placed upstream the upcomer pipe to increase the residence time of the particles inside. The swirl head at the top is made removable to allow cleaning and maintenance actions that could be required in case of long-term operation.

The carbonator is fed with the gases coming from the top of the raw meal preheater of the kiln. Before entering the carbonator, these gases are diluted with low temperature air to reduce the CO_2 concentration down to 20%, reproducing the condition of rotary kiln exhausts, that in a full scale installation would be fed to the CaL carbonator. In the inlet section of the reactor (mixing chamber displayed in **Figure 4a**) the flue gases from the industrial kiln are mixed with the sorbent regenerated in the calciner and the sorbent recirculated from the carbonator outlet. At this stage of the carbonator the mixing of these three streams results in a temperature level of 600°C, which increases up to 700°C along the reactor length due to the exothermic reaction of carbonation. Despite all, along its external surface the carbonator is thermally insulated, there are still air-in leakages and heat losses which mitigate somewhat the maximum temperature inside this component.

Figure 3: View of CLEANKER carbonator

The gas flow rate expected to be processed in the carbonator is in the order of 1000 Nm3/h; the maximum gas superficial velocity is designed to be 15 m/s, leading to a residence time of the gases inside the reactor of about 10 seconds.

At the carbonator outlet, the gas-solid separation occurs in one cyclone (**Figure 4b**): the CO_2-free flue gases are sent to the stack while the recarbonated solids are collected in a hopper. The latter can be fed also with fresh raw

Figure 4: (a) Mixing chamber of the CLEANKER carbonator; (b) Cyclone downstream the carbonator; (c) View of the hopper and the two screw conveyor heat exchangers

meal for make up purposes. Downstream the hopper, the recarbonated sorbent is split in three different streams, respectively directed to the calciner (to be regenerated), the carbonator (for recirculation) and to the cement kiln (re-use the purge of the pilot). This operation is guaranteed by two screw conveyors (**Figure 4c**) powered by variable speed electric motors to better control the flow rates:

- One of them is responsible for the transport of the CO_2-rich sorbent from the carbonator towards the calciner
- The other one provides for the sorbent recirculation inside the carbonator and for the purge stream directed to the industrial process; the split between these two streams is automatically controlled by slide gates placed along the conveyors

Due to the high temperatures of the raw meal exiting the carbonator, these components are cooled down by means of a water circuit to prevent the material from overheating.

2.2. Calciner

The calcination process is carried out through the combustion of CAV, a heavy-oil fuel (88.6% C, 9.9% H, 1% S, 0.5% N, 0.4% H_2O, 1.3% ash) which is the same as the one employed in the rotary kiln. In the calciner reactor (**Figure 5**), the fuel is injected through two different burners, the first one is located on the top of the short down flow section (**Figure 6a**), while the second burner is installed in the upstream section of the calciner close to the raw meal feeding point. Since in standard operating conditions it is expected to operate the combustion in oxyfuel mode, recirculation of the CO_2-rich gas and the control on the fuel mass flow rate are crucial to keep the temperatures inside the calciner at moderate level. In particular, the design is carried out to obtain an inlet temperature of the gas of 1000°C (at the 1st burner) and a temperature at the calciner outlet of around 920°C. In this way a smooth temperature profile is achieved along the calciner, which appears to be beneficial for the activity of the solid material as CO_2 sorbent in the carbonator.

Figure 5: CLEANKER calciner integrated in the operating cement plant

The oxidant gas flow rate in the calciner is a mixture of oxygen and the CO_2-rich gas recirculated from the calciner outlet. The recycle flow rate is determined according to a gas velocity design value of 15 m/s and a volumetric flow rate at the calciner outlet between 14’000 and 15’000 m^3/h. Similarly, oxygen flow rate is controlled to keep its concentration in the outlet gas stream at 4%.

Due to the high temperatures inside the calciner, the complete inner area must be lined with refractory concrete. The turning areas at the bottom and on top of the reactor are covered by dense concrete, since the turbulent gas flow and very high temperatures may cause abrasion. Differently, in the vertical section no big abrasion is expected, thus, some good insulation refractory will be installed.

Downstream the calciner outlet a cyclone is used to separate the calcined solids from the CO_2-rich gas stream, which then it flows up towards another single stage riser-cyclone where the fresh raw meal is fed. This component accomplishes two important tasks: pre-heating the raw meal before it is introduced in the calciner, with consequent reduction of fuel consumption and needed residence time in the calciner and start the cooling of the CO_2-rich gas. Indeed, the gas recirculated to the combustion chamber is supposed to enter at around 500°C before mixing with O_2; beyond radiation and natural convection, even an active cooling with cooling water is in place.

The pre-heated solid materials are sent for most to the calciner inlet in correspondence of the second burner. The calcined raw meal collected in the first cyclone downstream the calciner is sent to the carbonator as regenerated CO_2 sorbent. Like in the carbonator, also in this case the raw material transport and cooling is performed in a screw conveyor heat exchanger (**Figure 6b**). The job of handling the hot material at an inlet temperature above 900°C, to cool it down below 700°C and to transport it, makes this component one of the most critical items of the plant. In fact, due to the extreme operating conditions, the cooling water circuit is much more complex and intense compared to what happens in the two conveyors behind the carbonator. Even in this case the presence of slide gates allows for a more flexible operation since the material can be extracted in different point of the conveyor.

Figure 6: (a) First burner of the Calciner located in the short down-flow section; (b) Screw conveyor heat exchanger behind the Calciner

3. Experimental campaigns design and plan

Nine experimental campaigns have been scheduled, five short tests of three days each one and 4 long tests of one week each one. Short tests are functional to tune the main governing parameters for the long tests.

For the short tests of the experimental campaign, that will be carried in spring/summer 2021 in Vernasca pilot plant, an experimental test matrix has been defined. The aim of the short tests is to identify the most attractive operating conditions for the longer test runs. Therefore, during these first trials, a preliminary analysis on the key governing parameters of the CaL process will be performed according to process simulations, non-validated reactor models and lab pre-tests that have led the drafting of the experimental matrix.

The main governing parameters of the CaL process include:

1. Oxydant for the calcination process: Air/Oxygen. In the standard operating conditions, the desired way to carry out the calcination for a CaL CO_2 capture process is clearly under oxyfuel mode. However, the experimental data collected during air-blown calcination tests (same condition achieved in industrial pre-calciners) will help in understanding the impact on the CaL process of operating at low calcination temperature.
2. Calciner outlet temperature. The calciner outlet temperature, as well as potential hot spots along the calciner height/length, may affect the calcination degree and the deactivation of the raw meal as CO_2 sorbent. On the other hand, the potential issue of hot spots will be addressed by the flexibility of the combustion system. Indeed, there will be the possibility to affect the temperature profile along the calciner by acting on the fuel split ratio between the two burners, as well as on the amount of post-combustion oxygen injected through two ports located downstream of the second burner.
3. Type of raw meal as CO_2 sorbent. Chemical composition, particle size distribution and Ca-Si aggregation level of the raw meal have an impact on the kinetics of calcination and carbonation reactions, hence on the global performance of the connected system.
4. Gas flow rate at carbonator inlet. This parameter allows controlling the inlet gas velocity and therefore the residence time of the gas in the carbonator.
5. Solid to gas ratio in the carbonator. This is the main driver for CO_2 capture, since it defines the amount of available sorbent per kg of CO_2. The solid to gas ratio in the carbonator can be controlled by the sorbent circulation between the carbonator and the calciner and by the carbonator internal solids recirculation.
6. Solids temperature at carbonator inlet. This parameter affects the temperature profile along the carbonator and therefore the thermodynamics and the kinetics of the carbonation reaction.

The experimental matrix proposed for the short tests foresees a total of five different campaigns. During each test, the process will be run in a different condition according to the specific values or the predefined ranges determined from the process simulation and laboratory analyses.

The first three experimental campaigns will act as preliminary trials to understand the impact of the different parameters and find the optimized conditions for the short trials #4-5 and later for the longer experimental campaigns. Indeed, the matrix will be constantly updated and modified based on the response of the pilot plant after each trial.

Looking at the non-numerical parameters, like the possibility of testing different types of sorbents or the choice between air-fired/oxyfuel calcination, it was decided to run one test involving alternative options that will differ from the standard ones. Specifically, air-fired calcination is expected for the first short test, while an alternative raw meal will be tested in a different campaign under oxyfuel mode and once the optimized conditions for the rest of the parameters have been established.

The rationale behind the matrix is also due to the close relationship between some of the key governing process parameters. For instance, the lowest level set for calciner outlet temperature will be reached during the air-fired combustion and will achieve its higher targeted value during oxyfuel tests. Again, the raw meal to kiln gas ratio and the gas flow rate at carbonator inlet have been set to vary between their maximum/minimum settled values throughout the same experimental period. For some other parameters, such as the solids percentage recirculation in the carbonator or the flow rate of recarbonated raw meal to be calcined, the idea is to vary them inside the predetermined range during each single test until an optimized configuration is obtained.

Based on the identified relevant parameters, also the measurement devices and their location along the pilot plant can be determined. According to the simplified flowsheet, showed in **Errore. L'origine riferimento non è stata trovata.**, the main input and output streams of the CaL process are gas and material flows. Therefore, gas analysers and volume flow measurements are required to monitor the CO_2 capture efficiency of the carbonator and the combustion performance in the calciner. Moreover, monitoring and sampling of the solid material circulating inside the two reactors is necessary to control the raw meal conditions and its transportation system. These operations are guaranteed by the presence of extraction ports, electronically controlled handling devices and rotary valves. Continuous pressure and temperature observations, via pressure sensors, thermocouples, and thermistors, are repeated with a logical frequency all over both reactors and all along the ducts.

In this framework, a permanent instrumentation is necessary to operate and control the demonstrator during its whole lifetime; it includes all the measurement devices described above and it is connected to the control room and a dedicated PLC software. Additional devices for further measurements, especially along the carbonator and the calciner, are expected to be non-permanently installed during the experimental test campaigns to ensure a comprehensive scientific evaluation for modelling and simulation work. They consist mainly in additional solid samples for laboratory analysis (performance evaluation of different sorbents, CO_2 capture capacity, by-products formation), and concentration measurements of gases that, along with CO_2 and O_2, also include CO, SO_2 and NO_x. The design of non-permanent is carried out in order to avoid air leakages to the system and undesired pressure fluctuations or a loss of vacuum in the reactors.

4. Conclusions

Calcium Looping CO_2 capture demonstrator at TRL7 for cement plant applications has been designed and erected at the 1.3 Mt_{cement}/y Buzzi Unicem operating cement plant located in Vernasca (Piacenza, Italy). Opening event has been celebrated in October 2020.

Different experimental campaigns have been foreseen to test the technology in operational environment, tuning the governing parameters (e.g. air/oxygen rate, operating temperatures, sorbent excess in the carbonator, sorbent internal recycle). The experiments, to be carried out in spring / summer 2021, could prove the applicability of the CaL technology to the cement manufacturing process and demonstrated that very efficient CO_2 capture can be accomplished (>90% capture) keeping the cement cost increment below 25€/t, the total fuel consumption increment below 40% and the electric consumption increment compared to state of the art plants below 20%.

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