



# Calcium looping CO<sub>2</sub> capture technology with extreme oxy- coal conditions in the calciner

(CAO<sub>2</sub>)

*FINAL REPORT*

**Calcium looping CO<sub>2</sub> capture technology with extreme oxy-coal conditions in the calciner  
(CAO<sub>2</sub>)**

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European Commission

# Research Fund for Coal and Steel

## **Calcium looping CO<sub>2</sub> capture technology with extreme oxy-coal conditions in the calciner (CAO<sub>2</sub>)**

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### **Final report**

Directorate-General for Research and Innovation

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## **1. ABSTRACT**

The CaO<sub>2</sub> project has demonstrated in a large pilot (2-3 MWth) a process variant of the CO<sub>2</sub> capture postcombustion calcium looping system for coal based power plants. This optimised process scheme is intended to minimize or even avoid the need of a CO<sub>2</sub> recycle to the oxyfired circulating fluidized bed calciner, by exploiting the endothermic nature of the calcination reaction and the large solid flow circulating from the carbonator. This variant can reduce significantly capital cost (reduced calciner and air separation units) and operating cost (reduced O<sub>2</sub> and fuel requirements in the calciner) thereby improving the competitiveness of the system.

An extensive work on sorbent performance has been done, identified main criteria which could indicate a good performance of the sorbent in this kind of systems, especially from the mechanical point of view.

During the project it has been demonstrated the possibility to operate the pilot in La Pereda with a maximum of 75% of oxygen in the oxidant flow to the calciner, which confirms the main target of the project. Additional modelling works and experimental at lab scale show that this value could be even higher without major operating risks, which could improve the performance figures estimated for the technology. So, no major showstoppers have been identified to design and operate future CaL systems using pure O<sub>2</sub> as the oxidant feed to the calciner.

## 2. FINAL SUMMARY

The main objective of the project was to demonstrate the possibility to increase the oxygen in the oxidant flow to the calciner over the state of the art at the beginning of the project, reaching ultrahigh oxycalcination conditions. The analysis of the effects on these new operating conditions using tests at different scales and a deep research on sorbent properties and selection has been the core activities of the project.

During the execution of the project and as part of WP1, a first set of general guidelines for appropriate limestone selection has been defined. A first simple decision table has been proposed to quickly select natural limestone in function of its microstructure and the cycling conditions of the CaL process. This guideline is nevertheless a first indication, and a testing phase is recommended in any case, due to the different performances identified with limestones tested.

Regarding the fabrication of pellets, results in the project indicates great limitations of their use in real plants due to poor mechanical strength, although the results in terms of absorption rate is quite interesting.

Beyond the operational problems and limitations identified in the facilities used in the project, it can be confirmed that the main target of the project has been successfully fulfilled. The initial tests carried out in Cranfield laboratory rig and particularly the experimental results from la Pereda pilot, confirm that it is possible to operate the calciner of a Calcium Looping system under oxygen-rich conditions, thanks to the endothermic nature of the calcination reaction and the large flow of solids circulating from the carbonator to the calciner. In that sense, the key to operate the calciner with very high inlet oxygen concentration is that the heat sink due to the calcination compensates the heat source due to the combustion reactions. In a conventional oxygen-blown combustor, this would not be possible due to limitations of the heat extraction by heat transfer only.

The axial temperature profiles measured along the calciner during the rich-O<sub>2</sub> tests in La Pereda (up to 75%v O<sub>2</sub>) showed the absence of hot spots as long as a sufficient circulation and bed inventory of solids is attained in the calciner. WP4 modelling works for higher calciner size also indicates a similar performance also over that value.

The performance of the carbonator when the calciner is operating at high O<sub>2</sub> concentrations can be analysed using a methodology and reactor model parameters consistent with those obtained in previous works under milder operating conditions. Therefore, the experimental results obtained in the project will contribute to reinforce data-base of experimental information applicable to future scale-ups of the CaL process.

Other relevant progress in the state of the art from the new experimental campaigns under the CaO<sub>2</sub> project in la Pereda relates the analysis of the average CO<sub>2</sub> carrying capacity of the sorbent in CaL systems. We have confirmed a certain reduction of this parameter respect to the expected value when operating the system under the oxy-fuel combustion tests in la Pereda pilot plant. This reduction has been attributed to the particles undergoing additional carbonation and calcination cycles in the calciner. In order to minimize these undesired effects, it is important to ensure that the calciner operates under conditions far from equilibrium and/or with as short as possible residence time of solids in the calciner.

Based on the results of the tests in La Pereda and the modelling works developed in WP4, no showstoppers have been identified to design and operate future CaL systems using pure O<sub>2</sub> as the oxidant feed to the calciner, perhaps using calciner designs operated at higher velocities and O<sub>2</sub> staging (options not allowed in the la Pereda pilot) to minimize solid residence times of the

particles and negative impacts on sorbent performance from the high temperature CO<sub>2</sub>-rich atmospheres in the calciners.

Simulation done in WP4 indicates that there is still room for optimization and improving the initial design considered. One option to achieve better capture efficiency is to cool down the solid material from calciner before feeding it to carbonator thus avoiding local calcining conditions. Otherwise, the cooling and heat losses in the calciner should be minimized to minimize the necessary fuel input. In the calciner, the number of feeding points for the solids from carbonator could be increased to avoid local cold spot, which causes re-carbonation. Other alternative could be feeding the fresh limestone to carbonator which results indicate that could be a valid choice. The cold make-up material helps to control the temperature and as the fresh make-up is preheated in the carbonator, it does not cause an unnecessary cold spot in the calciner.

Regarding the benefits from the technical and economical point of view of increasing the percentage of oxygen in the oxidant flow to the calciner, are significant, mainly in a reduction of total CAPEX and in a general efficiency gain, which has other impacts (reduction of space required, water consumption....). In terms of Cost of electricity the impact is limited (a reduction in the cost of electricity around 2% for the case analysed in this project), due to the scale effects and the extra energy generated in the low oxygen concentration case.

Sensitivity analysis have been done for the most critical parameters. Due to the high investment costs needed for the implementation of this technology, the most sensible parameters are those related to the financial costs and the annual operational hours of the plant which at the end, impact directly in the final price of the electricity needed to amortize the investment costs. In this two parameters, the effects of the proposed improvements tested in the CaO<sub>2</sub> project are more significant. Fuel costs modifications are less critical but also are important for the improvements reached in the project.

### **3. SCIENTIFIC AND TECHNICAL DESCRIPTION OF THE RESULTS**

#### **3.1. Objectives of the project**

The main objective of the project was to demonstrate the possibility to increase the oxygen in the oxidant flow to the calciner over the state of the art at the beginning of the project, reaching ultrahigh oxycalcination conditions.

As a general comment all the objectives inside of the project has been fulfil although in some cases some operating limitations has reduced the number of valid results as in case of WP2 for the pellets tests and WP3 during La Pereda tests.

In more detail, the main partial objectives divided by Workpackages for the project were:

#### **WP1**

- Task 1.1: To research about calcination and sulfation rates under the new operating conditions of very high oxygen concentration.
- Task 1.2: To investigate the relationship between the performance of the sorbent and their chemical composition and geological characteristics.
- Task 1.3: To research on new low cost pelletization techniques to produce better quality sorbents.

#### **WP2**

- Task 2.1: To carry out experiments under real conditions of the selected limestone samples to generate knowledge regarding mechanical performance.
- Task 2.2: Upgrade and oxycalcination tests in the lab plant in Cranfield in order to supply experimental data at lab scale under high rates of O<sub>2</sub> and in order to provide information for model validation

#### **WP3**

- Task 3.1: Modify La Pereda pilot plant in order to be able to carry out experimental campaigns under the new operating conditions.
- Task 3.2: To test and validate in La Pereda the feasibility to operate with high oxygen conditions in the oxidant to the calciner.

## **WP4**

- Task 4.1: Develop 3D model for the oxyfired calciner at high O<sub>2</sub> concentrations based on La Pereda case.
- Task 4.2: Develop property models for realistic large scale fluidised bed conditions.
- Task 4.3: Simulate interconnected calciner-carbonator reactor system and evaluate effect of new calciner design on system performance.

## **WP5:**

- Task 5.1: To simulate the calcium looping with the new operating conditions at full scale size and compare it with the state of the art.
- Task 5.2: To carry out an economical and technical reassessment of the technology and the improvements reached by the new operating conditions.

## **WP6:**

- To coordinate the project and the communications with the European Commission.
- To create a project webpage for project dissemination.
- To fulfil RFCS reporting requirements.
- To prepare and publish at least 5 papers and participate in 5 public workshops or conferences..

### **3.2. Comparison of initially planned activities and work accomplished**

The works initially planned in the WP1 were mainly completed, although in the area of pellets, the poor results obtained in terms of mechanical integrity, force to refocus the activity in new solutions that could improve the initial performance.

In WP2 the main modification in the work planning has been produced in the Cranfield lab facility. Due to the delays accumulated in the refurbishment works in the facility and the need to feed the testing of WP3 with results, a change in the fuel used in the pilot was done. Tests in Cranfield was made with natural gas instead of solid fuel, which would have complicated the execution of the tests in due time. The change also allowed to reach higher percentages in the facility, and in that sense test at 100% pure oxygen were executed.

In WP3, the major difficulty to fulfil the initially planned activities were related to the operating limitations of the plant, which has complicated the execution of the initial planning and at the end has limit the possibility to test higher concentrations of oxygen over 75%. Nevertheless the clearly results obtained and the support works done in WP4 indicates clearly that higher concentrations are feasible. In the other hand also the number of operational problems, mainly mechanical problems in the installation has limited the extension of the initial planned test matrix and the number of useful operating hours in the facility (see 4.3). Nevertheless results obtained are enough solid to confirm the feasibility of the new operating conditions.

In WP4, the planned activities were mostly accomplished. The 3D-modelling results of the calciner showed that the locally high thermal input due to combustion at high oxygen concentration could be balanced by the endothermic calcination reaction and the process temperatures could be controlled at desired range. The simulations of interconnected calciner-carbonator looping systems showed how the operating conditions in the two reactors can be controlled with the available means, e.g. solids circulation between reactors and the fuel input to calciner. The la Pereda pilot test results with very high inlet oxygen concentration were accomplished later in the project, thus, this test data will be utilized later for further model validation and the work will be reported as a journal article. Similarly, the simulation of a large scale (200 MWth) CaL system with high inlet O<sub>2</sub> (> 80%,vol) calciner, which was reported in Deliverable D4.4 will be published as a journal article during 2018. The work related to heat integration of the total process, which was initially included in WP4 was transferred to WP5.

Activities in WP5 have accomplished the scope of work and the planning envisaged with no major deviations from the plan.

### **3.3. Description of activities and discussion**

The work of the CaO<sub>2</sub> project is divided into six work packages (WP). The results of the work developed during the Project is presented combining contribution and achievements of each partner for each WP and Task.

#### **WP1 Sorbent performance under the new reaction conditions**

This workpackage was devoted to experimental activities in a range of laboratory scale facilities at CSIC, Cranfield University and Carmeuse attempted to characterise sorbent performance (CO<sub>2</sub> carrying capacity after calcination and sulfation reactions, rates of reactions and rates of attrition) for a range of limestone characteristics and synthetic materials (pelletized materials) that could be candidates for future large scale testing under O<sub>2</sub> rich. The work was organised in different task, which results are summarized below:

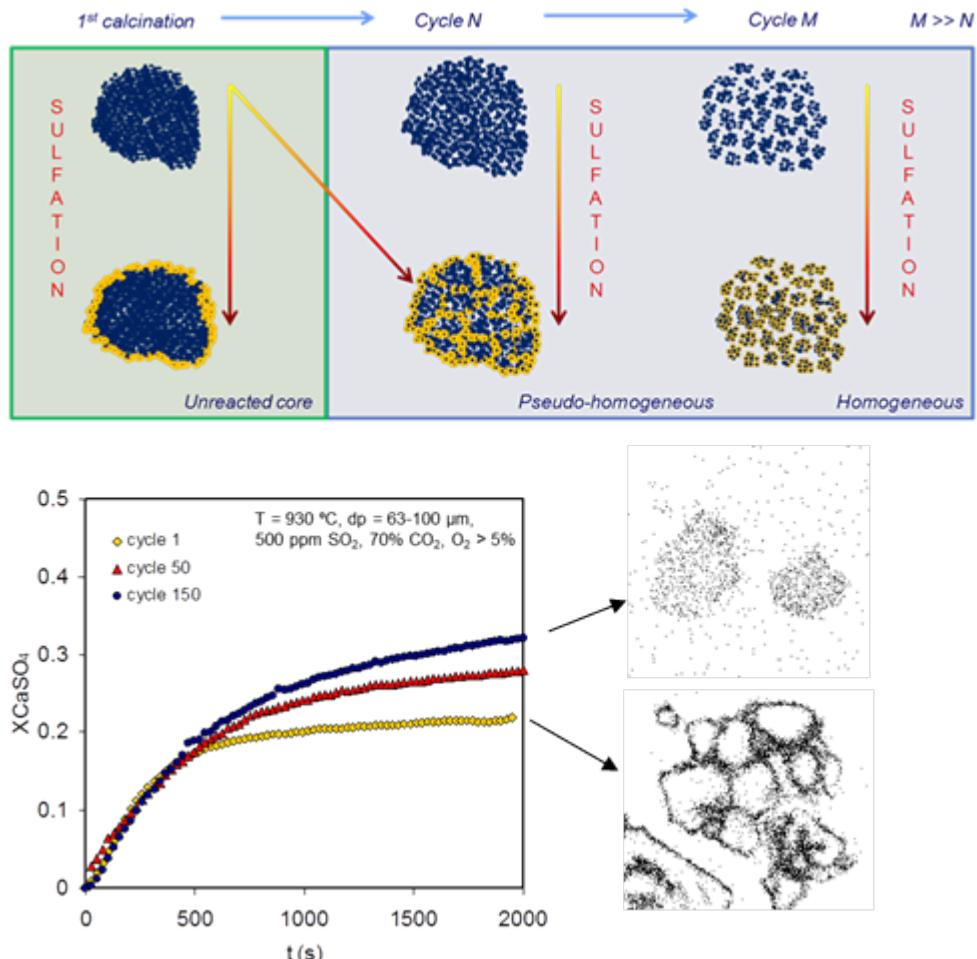
#### **Task 1.1 Calcination and sulfation rates under the O<sub>2</sub> rich combustion-calcination conditions**

The main purpose of this task was to enlarge the experimental database of kinetic data relevant for the key reactions taking place in the oxyfired calciner operated under O<sub>2</sub> rich conditions: the calcination of the sorbent and the sulfation rates of the resulting CaO. Both reactions are known to have a large impact on CO<sub>2</sub> carrying capacities of the sorbent in the carbonator: the carrying capacity, X<sub>N</sub> or X<sub>ave</sub>, decreases sharply with the number of calcination cycles depending on the temperatures and atmospheres of calcination. They are also known to decrease with increasing conversions of CaO to CaSO<sub>4</sub>. Therefore, any progress in the scaling up of reactor conditions in the CaO<sub>2</sub> project or any interpretation of experimental results from the large pilots (see WP3) requires a careful tuning of the kinetic information at particle level concerning these reactions. Deliverable D1.1 presented the main results obtained from thermogravimetric studies at CSIC with the materials of reference for the CaO<sub>2</sub> project (the limestone “Brecal” used in la Pereda pilot and 4 limestones of different geological origin characterised and supplied by Carmeuse). Other results related to attrition performance of the materials (see WP2) have also included some information on reaction sorbent performance. A scientific paper, including these experimental and modelling results on the sulfation kinetics in these conditions has also been published in *Fuel* Journal, (Cordero, J.M., Alonso, M., Modeling of the kinetics of sulphation of CaO particles under CaL reactor conditions, Vol 150, 15 June 2015, Pages 501-515, Fuel 2015). This manuscript is also placed in the Open Access Repository of CSIC.

Concerning the main results linked to the investigation of calcination reaction under O<sub>2</sub> rich conditions, we confirmed a key difference between previous knowledge on calcination of CaCO<sub>3</sub> particles and the calcination conditions expected in CaL systems: the calcining particles have typically low carbonate content in CaL systems. In addition, the CaCO<sub>3</sub> is homogeneously distributed over a certain specific surface of CaO. This tends to lead to faster calcination rates than expected. An equation based on the classic grain model that fits well the experimental results of calcination under homogeneous-type of reactions conditions (see Deliverable 1.1 for details) has been chosen and adapted to the CaO<sub>2</sub> calciner conditions. This has been shown to fit of experimental data in a wide range of calcination curves, including those with the highest CO<sub>2</sub> content and calcination temperatures that are the most relevant for the CaO<sub>2</sub> project.

Concerning sulfation rates studies, experimental results described in D1.1 indicate that the Increasing number of calcination carbonation cycles (that promote a well known sintering mechanism) were also promoting higher CaO conversions to CaSO<sub>4</sub> in some sorbents. The experimental work (in a TG analyser at CSIC) covered operating temperatures of the CaL system from 650 °C in the CFB carbonator to 930 °C in the oxy CFB calciner. In the experimental procedure employed, the sample

was subjected to the desired number of calcination carbonation cycles before the sulfation tests were undertaken. The experimental data were interpreted by using the Random Pore Model (RPM) that once adjusted with suitable kinetic parameters, facilitated the interpretation of results from the experiments in la Pereda pilot (see WP3). Figure 1.1 summarizes some results concerning sulfation studies.



**Figure 1.1** Top) Schematic of the sulfation pattern model adopted to fit experimental results in D1.1 and Cordero et al (2015) Bottom) Example of experimental results from the TG investigating sulfation rates (effect of the number of carbonation-calcination cycles on the sulfation conversion curves), including SEM/EDX images of sulphated sorbent particles (dark dots are CaSO<sub>4</sub>) at different number of calcination-carbonation cycles. See D1.1 for details and Cordero et al (2015).

### Task 1.2 Correlation of stone fundamental properties with sorbent performance in CaL Attrition performance.

The calcium looping system is using a high amount of natural limestone (about 0.1 to 0.15 Mio t by TWhe) which is used as sorbent to trap the CO<sub>2</sub> coming from the power plant. The sorbent is further regenerated in a circulating looped system which induce a significant amount of thermal and mechanical constraint on the sorbent.

The main purpose of this task T1.2 was to establish relevant correlations between the chemical or physical properties of the raw limestone and its performance in the CaL system, mainly the capture and the attrition of the sorbent.

A specific focus was set on the attrition as there is relatively few relevant publications in the literature about this phenomenon while this could have potentially a high impact on the CaL system operations (material losses, higher purged material flow).

In order to characterise the limestone raw material, the following tasks were accomplished:

- Geological description (petrography) and positioning in the Dunham classification
- Chemical analysis
- Particle size distribution

On top of these preliminary analysis, an extensive evaluation of CaL performance (capture and attrition) was conducted by the CSIC both at lab and pilot scale (30 KW).

A reference limestone (Brecal) was also analysed and tested to compare with the one supplied by Carmeuse.

The following table shows the various tests and analysis undertaken.

**Table 1.1:** Limestone Tests

Sample	Carmeuse scope			CSIC scope		
	Basic analysis		PSD	Carrying capacity	Attrition	
	Geology	Chemistry			TGA lab	30 Kw pilot
<b>A</b>	x	x	x	x	x	x
<b>B</b>	x	x	x	x	x	x
<b>C</b>	x	x	x	x	x	x
<b>D</b>	x	x	x	x	x	x
<b>Brecal</b>	x	x	x	x	x	x
<b>M64</b>	x	x	x	x		x
<b>M65</b>	x	x	x	x		x
<b>M66</b>	x	x	x	x		x
<b>M67</b>	x	x	x	x		x
<b>M68</b>	x	x	x	x		x
<b>M78</b>	x	x	x	x		x
<b>M69</b>	x	x	x	x		x
				PSD		
				100-300 µm		
				200-400 µm		
				0-600 µm		
				0-1 mm		

All the detailed results are presented in the deliverable D.1.2.

As it is explained in the report, this is not easy at this stage to propose a universal limestone quality that would globally present good behaviour in every CaL system and operational conditions.

Nevertheless, we tried in this study to propose a simple semi-quantitative methodology that would be a first tool for raw material selection.

First of all, from a technical point of view, (so out of economic considerations), the ideal limestone selection will be based on the operating conditions of the CaL system (number of cycles, possibility to operate at low, medium or high purging rate).

**Table 1.2:** Operating conditions matrix

Cycling conditions	Typical N value	Capture perf. Indicator		Attrition Perf. Indicator	
		Decay k	Residual act. Xr	Total TPGI	Delta MDPG
Low cycling rate	N <20	High	Low	Medium	Low
Medium cycling rate	N 20 to 50	Medium	Medium	Medium	Low
High cycling rate	N > 50	Low	Medium	High	Medium

In order to establish some guidelines, the following table attempts to fix some criteria (low or high performance limits) for both attrition and capture efficiency :

**Table 1.3:** Operational criteria

Performance		Criteria		Low perf.	High perf.
Capture (TGA test)		decay factor k		0,6	0,5
		residual activity Xr		0,07	0,1
Attrition hot test 30 KW		TPGI (total) - 5h30		70	50
		Delta MDPG LS-calc		70	30

Based on that criteria, we can here classify the limestone upon their overall attrition and capture performance:

**Table 1.4:** Limestone Sample performance

	Parameter	Unit	Sample ID											
			Brecal	A	B	C	D	M64	M65	M66	M67	M68	M78	M69
Geological description	Main facies			G	MW-GP	Ma	W-P (porous)	W	G	W-P (porous)	G-P	W-P-G	G-P	G-P
Capture (TGA test)	decay factor k		0,547	0,63	0,6	0,71	0,55	0,46	0,58	0,52	0,48	0,45	0,69	0,53
	residual activity Xr		0,073	0,109	0,068	0,069	0,075	0,086	0,125	0,069	0,06	0,102	0,074	0,12
Attrition hot test 30 KW	TPGI (total) - 5h30	%	59	61	54	58	77	ND	ND	ND	ND	ND	ND	ND
	Delta MDPG LS-calc	µm	138	21	64	106	44	ND	ND	ND	ND	ND	ND	ND
Overall rating	Attrition & capture		Medium	Good	Medium	Bad	Medium	ND	ND	ND	ND	ND	ND	ND

Where Ma = Marble, M = Mudstone, W = Wackestone, P = Packstone, G = Grainstone (ref to Dunham limestone classification).

It is to be noticed that the attrition behavior for limestone M64 to M69 could only be tested at lab scale only. As this test was not sufficiently correlated with the behavior at pilot scale, we could not really consider their attrition performance in the final evaluation.

At a glance and roughly speaking, we can consider that most of the sedimentary limestone rocks (M-W-P-G) are suitable for CaL applications with the exception of particular texture such as recrystallized marble (limestone C type). High porosity limestone such as limestone D should be also preferably rejected when high cycling rate (with N>50) are needed.

According this final evaluation:

- Limestone A would be the first choice
- Limestone B and D would be second choice (similar to Brecal reference)
- Limestone C would be the last choice

Besides these considerations, what it is important to highlight is that if the limestone could not be a choice for any reason but an imposed entry data, the CaL plant could or should be ideally operated in

function of the limestone behavior and the potential use of the purge material (easiness to re-use it in other industrial processes). Obviously, this could impact significantly in the final design/size of the plant.

As conclusion for this T1.2 task, we can say that:

- There could be important variations either in the attrition or in the capture performance of natural limestone, mainly depending of its microstructure. A particular attention should be paid when selecting the limestone as it may influence a lot the CaL system operations. In general, sedimentary limestone rocks has better performance with the exception of particular cases such as recrystallized marble which must be avoided. Grainstone limestone probably is the best option based on the results obtained.
- Although the microstructure and grain size could be important for a preliminary screening of possible acceptable limestone, it is recommended a more detailed qualification in the selection and acceptance of a limestone to be used in a CaL system. The raw limestone must be qualified by CaL dedicated lab/pilot test before being used in an industrial application, as performance of the limestone must fit in the design criteria of the installation.
- For the specific evaluation of the real attrition test, the evaluation should be ideally done in a small pilot which appears to be more relevant to estimate the attrition in CaL process real conditions comparing with other more simple and limited approaches as a crushing strength test.
- In the range of  $\text{CaCO}_3/\text{MgO}$  content tested in this study, the chemical composition of the limestone has no impact compared to its microstructure.

These general guidelines are of course only preliminary conclusions due to the following limitations :

- Relatively few samples were tested, mainly on the 30 kw test, to establish strong conclusions compared to the variety of natural limestone available on the earth.
- The limestone materials are by definition natural components. We tried to classify them by category in function of their microstructure but there is always a part of subjective interpretation that could involve skewed conclusions.

### **Task 1.3. Low cost sorbent pelletization techniques.**

As indicated in the workprogramme, the CaO2 project included some activities in T1.3 to investigate the viability of low cost technical solutions to implement in future  $\text{CO}_2$  capture plants a pelletisation process step that would allow for the recycle of fine CaO-rich material to the calcium capture loop, thereby reducing limestone consumption and solid residue generation from the capture plant. Only extremely low cost process options and additives were considered in the CaO2 work programme under Task 1.3 (results reported in D1.3). One of the researched technology initially in the project by ENDESA was a semi-dry granulation system, with a potential to reuse fines produced in the system due to their low costs. This granulation technology use a rotative mechanical process to reduce the water and mineral additive consumption of other methods and is used to facilitate pneumatic transport of solids. The control of water and percentage of mineral additive creates bounds among limestone particles which allows a control of the size of the granulate. Different percentages of water and additive was tested in order to increase the mechanical properties of the granulates. The most promising samples were tested using crushing strength measurements by CSIC. Unfortunately none of the materials tested in T1.3 passed preliminary screening criteria at lab scale (i.e. crushing strength measurements and jet cup test). All values of crushing strength (CS) of the pellets were lower than 2N, that would make them unsuitable for high velocity fluidisation because of the intense attrition.

Consequently, the granulation method proposed by Endesa was discarded, as not promising alternatives to improve the performance of this process was envisaged. Therefore, the work under this task focused on additional pellets and associated test from Cranfield University, that presented more promising mechanical properties and which characteristic are presented in D2.3.

Different materials were produced and tested at Cranfield: with 10% cement and lime (Sample 1), with 10% templating agent and lime (Sample 2), with 10% templating agent, 10% cement and lime (Sample 3), and doped with sea water, with 10% templating agent, 10% cement and lime (Sample 4). The samples have been tested for reactivity in a thermogravimetric analyser (TGA), in a bubbling fluidised bed reactor (BFB) and also for compression strength. The TGA results can be found in Figure 1.2 and the BFB results can be found in Figure 1.3.

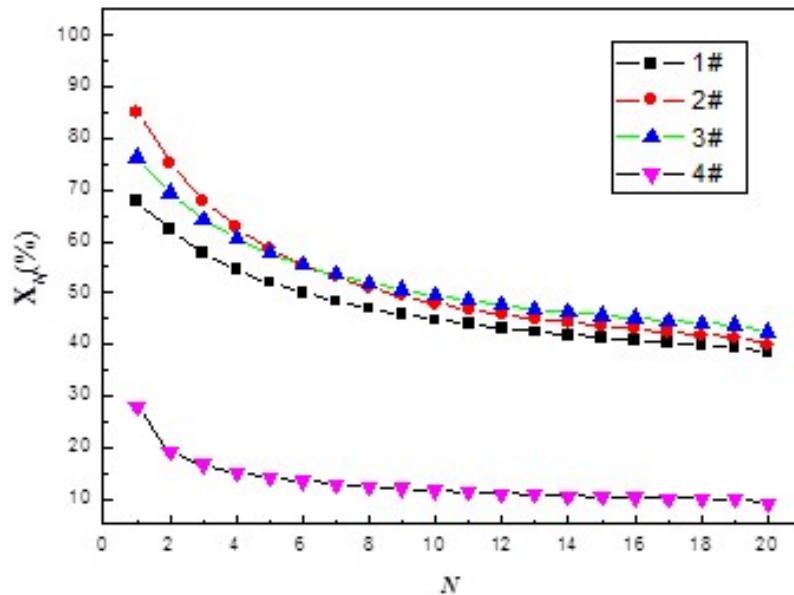


Fig. 1.2: Carbonation conversion of sorbents during 20 cycles (10 min calcination at 850 °C in 100% vol N2 and carbonation during 20 min at 650 °C in 15% vol CO2)

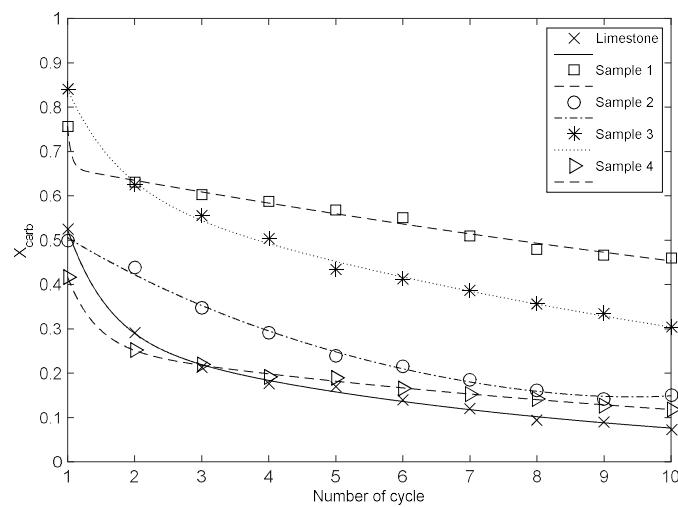


Fig. 1.3: Xcarb (%) by pellets and original limestone; carbonation 850°C for 15 min (90% CO2); calcination 850°C for 15 min (20% CO2)

The use of templating materials for the production of CaL sorbents is shown to be beneficial in the TGA analysis, when the calcination was done under mild conditions (850°C in pure N2); however when the pellets were tested in the BFB the reactivity decreased substantially when compared to biomass-free pellets. These findings appear to be linked to the crushing strength tests where only the

biomass-free pellets showed substantial strength after calcination. There is a need for further improvement in this method of preparation and a necessity for more attrition tests to determine which mechanisms are more critical in terms of attrition of biomass-containing pellets and in future we will explore methods of improving the pelletisation process.

All the synthetic sorbents showed higher performance than the initial limestone when tested in a fluidised bed. However, the calcium aluminate pellets (Sample 1) showed superior capture capacity over the templated pellets when cycles were performed in a BFB. The CO<sub>2</sub> uptake by Sample 1 in the BFB was 0.22 gCO<sub>2</sub>/gsorbent, which was the highest amongst the materials.

## **WP2 Screening experiments with several coals and sorbents using lab scale Calcium looping pilots**

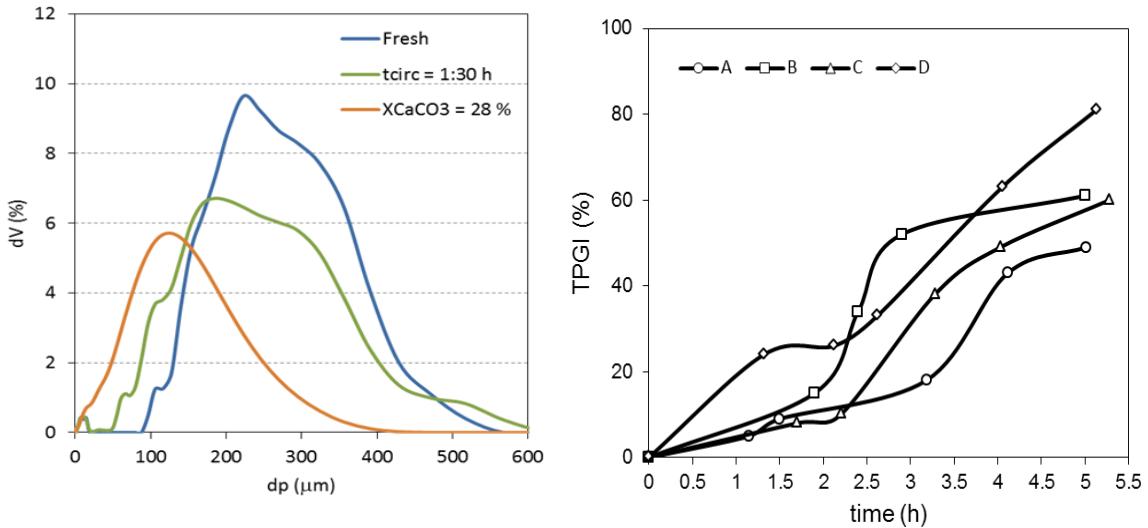
### **Task 2.1 Screening of sorbents**

This Task in WP2 targeted the search for better methodologies to characterise limestone materials regarding attrition performance in CaL systems. According to previous knowledge, attrition of limestones and limes during the operation of CaL systems can be more significant in systems with intense and fast calcination processes, like the O<sub>2</sub>-rich combustor-calciner planned in the CaO<sub>2</sub> project. Certain attrition of the material is inevitable and it translates into an increase in the make-up flow of solids in order to compensate the losses CaO in the system. Also, from previous experience in la Pereda pilot plant, there was great uncertainty about the possibility to face additional difficulties for the safe operation of the plant under O<sub>2</sub> rich calcination conditions, due to unacceptable material losses of fine sorbent material detected in the cyclones under some conditions. However, this problem was identified early in the project to be more linked to fluid dynamic effects connected to the gas leakage from the loop seals to cyclones in the pilot, thereby reducing their solid capture efficiencies. Furthermore, experiments in a 1/5 transparent cold model of the la Pereda pilot, built at INCAR-CSIC, led to the installation of conic fennels in the dipleg of the cyclones to reduce the crossection of the solid standpipes and largely solved these cyclone inefficiency problems. However, intense particle attrition in CaL pilots has been reported by several researchers and is obvious when attending to the changes in particle size distributions in la Pereda and other pilots. More detailed attrition studies are still needed to rank limestones and use such ranking as one of the key criteria for sorbent selection in future commercial CaL projects.

Carmeuse was the industrial partner more engaged in the studies in this T2.1 and CSIC was the main partner conducting the experiments and data analysis reported below.

The detailed results of this Task were reported in Deliverable D 2.1 (Report on the performance of sorbents during screening test) and D2.3 (Report on lab pilots experiments with pelletized fines) and the latest interpretation of these results have been submitted for publication to the peer reviewed journal (Alonso et al , *Powder Technology*, 336, Pages 273-281 2018). Therefore, the main findings and some example of results to illustrate experimental tools and methodologies are summarized in the next paragraphs.

Since attrition performance of limestone is highly sensitive to the source/characteristics of the limestone material, the need for a better methodology to assess attrition performance of limestones in CaL systems was identified as one of the gaps of knowledge to be investigated within the CaO<sub>2</sub> project. Carmeuse selected four reference limestones (A,B,C,D) with different geological origin and crystallinity properties and supplied CSIC with 100-200 kg batches of these materials for detail attrition studies by crushing strength, jet cup rig and attrition test during dedicated experiments in the 30kW CaL pilot of CSIC. In order to quantify attrition performance of limestones, different attrition indexes are available in the literature and the main ones were compared against data sets of Particle Size Distributions obtained from experiments in the CaL pilot of INCAR-CSIC and other lab scale equipment (Crushing strength apparatus, jet cup rig and TG analyzer as detailed in D2.1). It was confirmed that three prevalent attrition mechanisms act upon the limestones: fragmentation (by mechanical forces leading to particle breakage of comparable particle sizes), decrepitation (linked to mechanical stresses during the fast calcination process while particles release CO<sub>2</sub>) and abrasion (leading to fine particles generation while the parent particle rounds up). These mechanism operate in different extent depending on the limestone origin and the lifetime of particles in the CaL solid circulation loop. Great differences in the performance of the selected limestones were observed, which confirmed the value of experimental testing in the 30kW rig (high velocity, high temperature) for sorbent screening purposes. Of the several attrition indexes reported in the literature tested in the CaO<sub>2</sub> project, the Total Particle Generated Index (TPGI) and the Maximum Diameter of Particles Generated (MDPG) indexes (as proposed by Amblard et al 2015) were found to be the most useful to quantify attrition phenomena and rank limestones.



**Fig. 2.1.** Left): Example of results on the evolution with time of the Particle Size Distributions of limestone A from Carmeuse during experiments in the 30 kW pilot plant at CSIC. Blue line is the fresh material (99%CaCO<sub>3</sub>, t=0), green line after 1:30 h of circulation time with no calcination and orange line after extensive calcination (CaCO<sub>3</sub>content reduced to 28%). Right): Evolution with time of TPGI (Left) for all limestones tested in the 30 kW pilot plant (see D2.1, D2.3 and Alonso et al , 2018 for details)

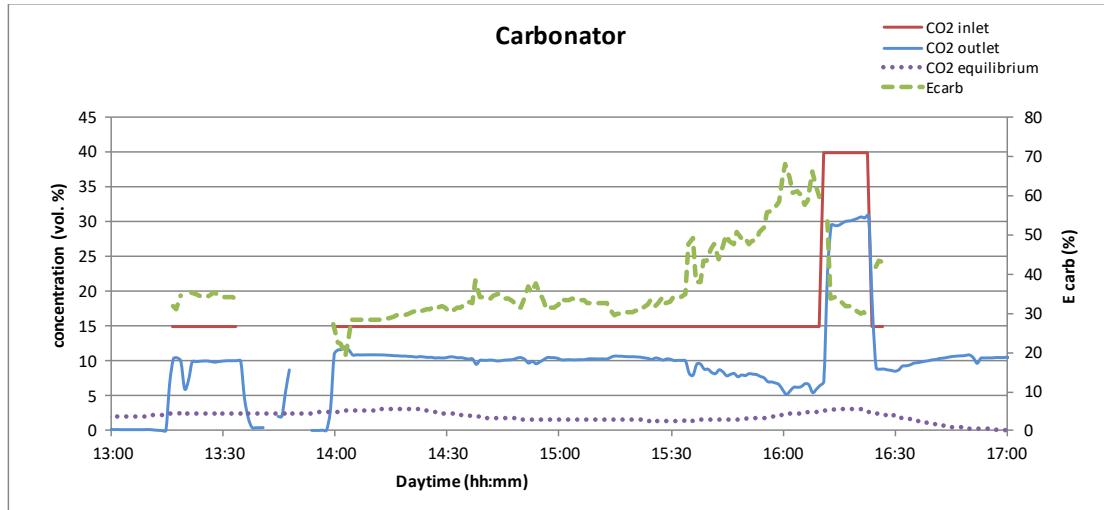
As can be seen in the example of results of Figure 2.1, fragmentation of limestone particles before calcination was an important phenomenon observed in some limestones (three out of the four) during the start-up of the tests (i. e., under gas velocities up to 3 m/s and temperatures approaching 800°C, but still un favourable for fast calcination). Changes in the PSD curves (see for example blue line vs green line in Figure 2.1 left) were caused by the breakage of the larger particles into similar coarse fragments without significant generation of fines. The behavior of other limestones is discussed in D2.1 and D2.3. As can be seen comparing the green line with the orange line, the calcination of the sorbent A in the example of Figure 2.1 leads to decrepitation induced by the fast calcination rates.

Experimental data like the one in presented in Figure 2.1 (left) has been used to calculate some attrition indexes reported in the literature (like the TPGI mentioned earlier represented on the right). Extensive experimental testing at smaller laboratory scale (crushing strength of a large number of particles and lab scale test in jet cup rig at CSIC with limestones and calcined materials) have also been carried out to characterize the limestones and try to establish certain correlations with the results from the 30kW rig. With this methodology, the predominant attrition mechanisms have been identified and the solids can be compared and ranked according to the extent of particle attrition, which makes it valuable for the screening of sorbents in calcium looping systems. However, it has been impossible to achieve a credible correlation of the attrition indexes measured in the 30 kW screening test campaigns with the more fundamental attrition parameters derived from crushing strength measurements or from jet cup experiments. Therefore, the main take away from this task T2.1 is the future need to characterize attrition of materials for CaL under realistic calcination conditions and times using small CaL pilots, since the main mechanism for attrition of limestones in these systems remains linked to the fast calcination process of the particles and the high velocities in the CFB reactors, that are difficult to replicate in smaller test facilities

## Task 2.2 Oxycalcination experimental tests at lab-scale

Deliverable D2.2 describes the reconstruction, commissioning and successful tests using Cranfield's 25 kWth pilot plant. This pilot plant consists of a bubbling fluidised bed calciner and an entrained fluidised bed carbonator. A successful demonstration of the use of pure O<sub>2</sub> at the inlet into the calciner was achieved when combusting natural gas (NG) in the bubbling fluidised bed calciner, which was

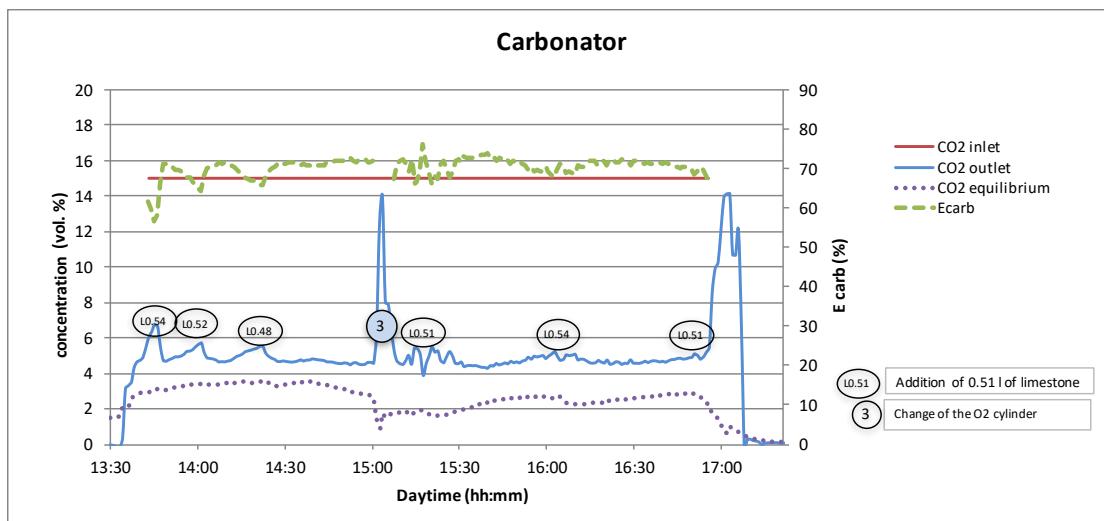
achieved by using the heat for the calcination reaction and for the heating of circulating material. The tests were performed with a UK-local limestone (Longcliffe). In this deliverable, results from the use of smaller fraction (100–200 µm) and higher fraction (300–400 µm) are described. The higher fraction performed much better and a continuous process could be maintained while combusting NG in pure O<sub>2</sub> in the calciner. The results from these tests can be seen in Figures 2.2 and Fig 2.3.



**Fig. 2.2:** CO<sub>2</sub> concentration at the inlet and outlet of carbonation and capture efficiency with smaller limestone particle size (100–200 µm)

**Table 2.1:** The balance of solid material and its sieve analysis for test with smaller particle size (100–200 µm)

fraction	limestone	carbonator	calciner	cyclone calciner	cyclone carbonator
total mass (g)	21859	4373	3852	6303	148.0
>212-212 µm	0%	63%	6%	1%	0%
212-150 µm	18%	22%	75%	32%	0%
150-125 µm	40%	8%	11%	17%	10%
125-63 µm	41%	7%	7%	47%	15%
63<63 µm	2%	0%	0%	3%	75%



**Fig. 2.3:** CO<sub>2</sub> concentration at the inlet and outlet of carbonation and capture efficiency with larger limestone particle size (300–400 µm)

**Table 2.2:** Weight balance of solids and sieve analysis of the inputs (limestone) and outputs (other) for experiment with larger particle size (300–400 µm)

fraction	limestone	carbonator	calciner	cyclone calciner	cyclone carbonator
degree of calcination		58%	76%	59%	37%
BET (m <sup>2</sup> /g)	<1	1.4	1.9	3.7	2.0
total mass (g)	14476	1939	4161	1998	115
>355-355	21%	16%	4%	0%	0%
355-300	43%	45%	38%	1%	1%
300-250	33%	26%	48%	3%	0%
250-212	2%	4%	9%	7%	1%
212-150	0%	3%	1%	35%	14%
150-63	0%	5%	0%	41%	46%
63-<63	0%	0%	0%	12%	38%

As it can be seen above the use of smaller particle size was not beneficial as expected on the capture efficiency for this particular experimental rig, which might be expected from higher contact area between particles and the gas. Practically all the added limestone with the size <150 µm was very quickly carried over from the calciner to the downstream cyclone. Therefore, it was challenging to maintain the necessary inventory of lime in the rig needed to achieve higher carbonation efficiency. When the particle size was shifted towards a larger fraction (300–400 µm), the inventory was easily maintained inside the reactors. This led to a stable capture efficiency of around 70%.

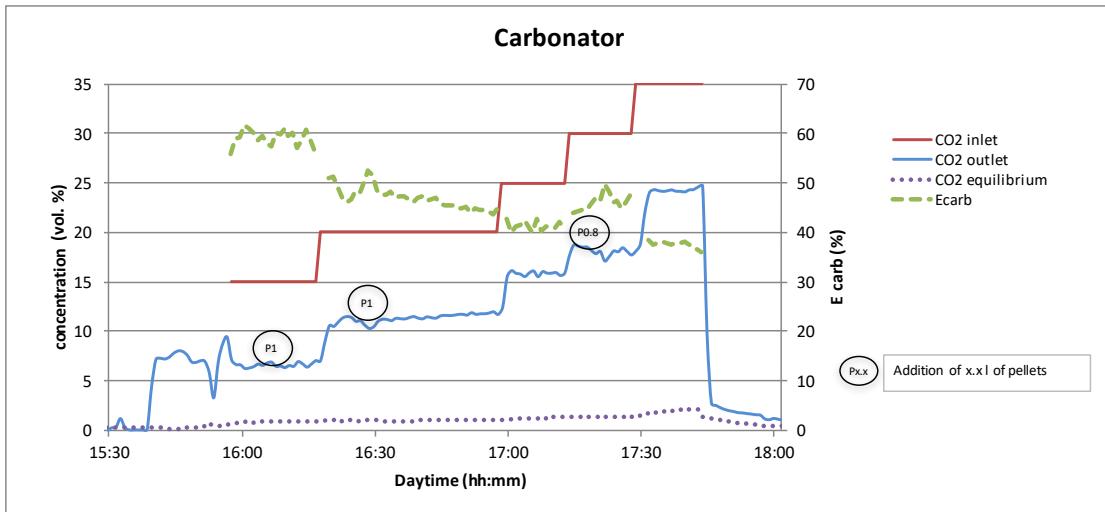
The main outcome of Task 2.2 is that use of pure oxy-calcination conditions in the calciner was proved at pilot scale during the course of this testing campaign with positive results and further discussion on these experimental tests and results can be found in previous reports.

### **Task 2.3 Validation at lab scale of pelletized material**

As part of the CaO2 project workplan, and considering the uncertainties noted on the possible material losses in the pilot as (see section 2.1 above), it was decided to experimentally explore low cost technical solutions to implement pelletisation processes that would allow for the recycle of fine CaO-rich material to the calcium capture loop, thereby reducing limestone consumption and solid residue generation from the capture plant. However, since the limestone cost are known to be low, the opportunity window for pelletisation and fine recycle techniques are obviously limited. Only extremely low cost process options and additives were considered in the CaO2 work programme under Task 1.3 (results reported in D1.3). In addition, some granulation suppliers of Endesa had also committed samples for testing.

The original scope of this deliverable D2.3 was to report lab scale studies and pilot results from the 30kW test facility at INCAR-CSIC using these pelletized materials. Unfortunately, none of the materials tested in T1.3 passed preliminary screening criteria at lab scale (i.e. crushing strength measurements and jet cup test as described in D2.3 or in D1.3). Only pellets delivered by Cranfield early in 2017 presented promising mechanical properties. However, it was not possible to generate sufficient quantities and qualities of materials to conduct experiments in the 30 kW pilot at INCAR-CSIC as anticipated in the project work programme. Therefore, the scope of D2.3 was different to what was expected, as the experimental effort by CSIC reported in D2.3 was devoted mainly to test attrition properties and CO<sub>2</sub> carrying capacity properties of additional limestones supplied from Carmeuse from different origins, 1 particular limestone already tested in la Pereda pilot yielding extremely high attrition rates and new candidate pelletized material sintetized at CSIC (based on calcium silicates) aditives. The results in D2.3 were qualitatively in line with the discussion given in the previous section T2.1 and in a recent paper submitted for peer-review publication (Alonso et al , *Powder Technology* 2018) and are no further discussed in this final report.

At Cranfield a test was carried out to demonstrate the possibility of the use of pellets prepared within WP1 in a pilot plant with 100% O<sub>2</sub> at the inlet into the calciner and the secondary aim was to use different concentration of CO<sub>2</sub> at the inlet into the carbonator (15%–35%). The results are shown in Figure 2.4.



**Fig. 2.3:** CO<sub>2</sub> concentration at the inlet and outlet of carbonation and capture efficiency with calcium aluminate pellets

The results for the capture efficiency are summarised in Figure 2.4. The main limitation is the amount of available adsorbent for the CO<sub>2</sub> in the carbonator. The total amount of CO<sub>2</sub> captured increases, because of higher partial pressure of CO<sub>2</sub>, but the total efficiency decreases. Possible solutions would be the use of taller carbonator which would allow longer retention and contact time of the calcined sorbent particles and the gas or the use of more limestone circulating inside the rig between calciner and carbonator.

The carbonation efficiency of the experimental run with pellets was lower compared to the previous experiments with limestone, however, the pellets showed can be used in combination with limestone for the CaL process. The fragmentation results showed that some of the pellets broke down or attrited but the bulk of the pellets were retained within the CaL rig.

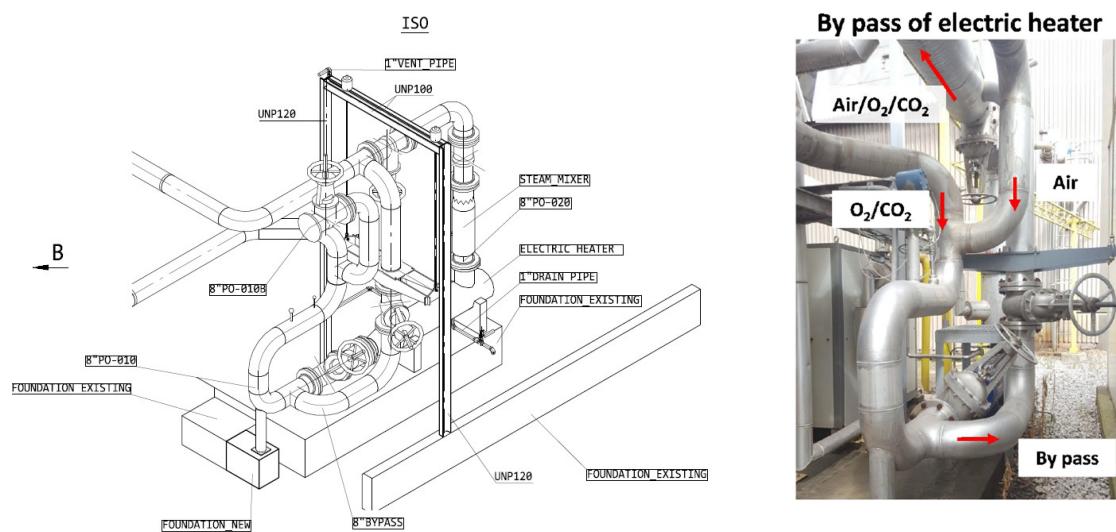
This experimental run demonstrated that the pelletised spent material can be potentially reused in the operation of the calcium looping rig in combination with fresh limestone. In the current experiment in total 58% wt. of the solid inventory of the rig were pellets. There are however some other complications related to their use, like the excessive release of steam during their quick heating above 900°C and their tendency to produce agglomerates during their introduction to the reactor and heating process.

## **WP3 Testing campaigns in la Pereda pilot at 2-3 MWth scale when operating with ultrarich O<sub>2</sub> feeds to the calciner**

In this section we report the main changes commissioned on the la Pereda Calcium Looping pilot (T3.1) and the experimental results (T3.2) obtained during the CaO<sub>2</sub> project, when targeting maximum O<sub>2</sub> concentration in the calciner of the pilot. This also includes an interpretation of experimental results using basic reactor methodologies to close up mass and energy balances in the pilot system.

### **Task 3.1: Design and commissioning of the modifications required to validate the ultrarich O<sub>2</sub> calcination**

Testing experimentally the concept of Oxygen-rich conditions in the calciner of the existing pilot, with guarantees of safe operation, was a challenging task because the existing pilot that was not design for this purpose and never worked on O<sub>2</sub> concentrations higher than 35%v. Mainly because targeting increasing input concentration of O<sub>2</sub> in the existing calciner necessarily implies (for the same nominal combustion conditions in terms of temperature and oxygen excess) lower velocities and/or higher fuel flows. In addition, due to the reduction of the gas flow fed to the calciner operating under ultra-rich O<sub>2</sub> conditions, the whole oxidant flow has to be fed through the bottom of the calciner (with the exception of a minor amount needed to cool the burner). This has been taken into account to the required modifications of the pipeline that feeds the gases to the different parts of the calciner. Several approaches were identified to operate the calciner of the pilot plant under ultrarich O<sub>2</sub> conditions at sufficient gas velocity exploiting as much as possible the elements that are already available in the facility. In order to find operation windows with low gas velocities several cases were solved (in terms of mass and energy balance in the facility) tuned with experimental observations from the 1/5 cold model of the la Pereda pilot at CSIC and from previous experience in the pilot on solid circulation flows, material losses in the cyclones and operation of the double loop seals (allowing for internal recycle of solids in both the carbonator and calciner). These were described in detail in D3.1. All partners involved in this task agreed on the detailed design characteristics of the necessary retrofits and Andritz proceeded to the detailed design of the new oxidant lines (see Figure 3.1).



**Figure 3.1.** Left) Example of detailed design of the new bypass of the electrical heater with the new pipes allowing for pure O<sub>2</sub> feed to the calciner. Right) overview of the final system as commissioned in the la Pereda pilot

Operational procedures were revised by the partners in order to guarantee safety conditions in all the cases, analysing the control system status and the required additional safety controls. A specific safety meeting was held in Graz with the members of the workpackage in order to train the operator leaders about the new safety issues and review in detail all the systems involved and analyse the impact of the new operating conditions in the updated design of the plant. Additional measurements (P,T) and

technical specifications were prepared by ENDESA and procurement process was organised by ENDESA and HUNOSA. However, a very significant delay (5 months) was accumulated due to the very long supply schedule provided by the manufacturers of the gas valves for pure oxygen application (four providers were contacted to reduce the time, but in all the cases the term of supply were very long).

In order to compensate partially the delays in task 3.1, and to reinforce the experience in operating the pilot under higher solid circulation rates and inventories needed for safe operation of the calciner, several test campaigns were carried out under standard contents of O<sub>2</sub> in the calciner. These are however better described in the next section.

### **Task 3.2: Test campaign**

The test campaigns agreed by all partners in this WP adopted a step-by-step strategy to keep safety in the operation of the pilot as the main objective. Many experiments have been devoted to improve our understanding of the system and design those experiments under O<sub>2</sub> rich conditions. The summary of experimental periods during the CaO2 project, including a brief summary of main targets and achievements is presented in Table 3.1

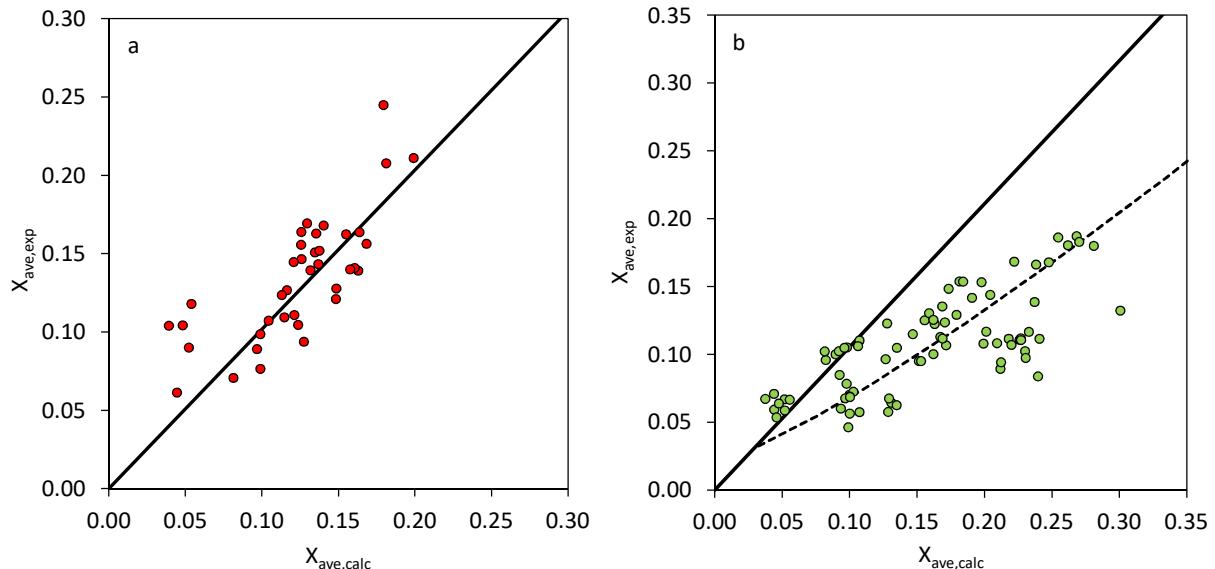
**Table 3.1.** Summary of experimental campaigns in la Pereda pilot during CaO2 project

Objectives	Description/Achievements	Publication of results	Week/Year*
Identify operating windows for safe operation at low gas velocities in the calciner	-Experiments aimed to study low velocities in calciner while achieving solid circulation rates around at 5kg/m <sup>2</sup> s -Measuring solid circulation operating the calciner with low gas velocities and different double loop seal set ups (internal circulation) -Narrow operation window identified (velocities cannot be lower than 4 m/s)	-Results reported in Midterm and Deliverable 3.2	47/2015 29/2016
Effect of calciner operating conditions on the sorbent activity	-Improving the methodology to close solid mass balance in long term experiments -Measurement of sulfate content and CO <sub>2</sub> carrying capacity (X <sub>ave</sub> ) of solid samples under oxycombustion and air-fired conditions in the calciner - Main findings: additional reduction of X <sub>ave</sub> when operating the system under the oxy-fuel combustion and close to equilibrium	-Results reported in Midterm, Deliverable 3.2 and scientific paper (Diego et al. <i>Int. J. of Greenhouse Gas Control</i> , 2017)	20/2015 22/2015 23/2015 25/2015 51/2016
Safe operation of the calciner under O <sub>2</sub> -rich conditions	-Experiments to gain experience in the operation of the calciner under O <sub>2</sub> -rich conditions - Carbonator fluidized with air to maintain solid circulation and maximize heat extraction from the system. -Successful calcination experiments with an oxygen concentration in the oxidant up to 75% <sub>v</sub> . -Smooth operation of the calciner. No hot spots found operating while under O <sub>2</sub> -rich conditions (as long as high inventories and solid circulation are attained in the calciner)	Results reported in D 3.2 and scientific paper (Arias et al. "Calcium looping performance under extreme oxy-fuel combustion conditions in the calciner", <i>Fuel</i> , Submitted 2018)	43/2016* 47/2016
CO <sub>2</sub> capture tests with O <sub>2</sub> -rich conditions in the calciner	- CO <sub>2</sub> capture by CaL demonstrated with the calciner operated with a maximum oxygen concentration in the oxidant up to 75% <sub>v</sub> . - CO <sub>2</sub> capture efficiencies achieved to be close to the limit by the equilibrium. Reactors performance consistent with previous findings. - Main drawbacks: Several failure trials due to the problems in the solid circulation between reactors and oxidant gas mixer. Limited experimental time due to the availability issues of the power plant supplying flue gases.	Results reported in D 3.2 and scientific paper (Arias et al., <i>Fuel</i> , Submitted 2018)	45/2016* 48/2016* 50/2016 21/2017* 24/2017 25/2017 26/2017

\*Aborted campaigns after start up completed due to mechanical failures (no valuable experimental results).

During the design and procurement period of the new oxidant gas lines for pure O<sub>2</sub> feeding to the pilot, experimental campaigns (up to the end of 2016) were devoted to gain experience and knowledge on the operation of the pilot under the low gas velocities expected under the O<sub>2</sub> rich test. Low gas velocities in the calciner will impact solid circulation rates and many other phenomena (including attrition of the sorbent) affecting the sorbent performance. Also one of the most important variables affecting the performance of CaL systems is the average CO<sub>2</sub> carrying capacity of the sorbent, X<sub>ave</sub>. There is sufficient evidence in the literature on the potential negative impact on such sorbent performance of the CO<sub>2</sub> rich conditions expected in the calciner when operating under oxy-fuel conditions. However, there was no experimental information available on the evolution of sorbent activity in continuous pilot systems. The experimental work carried out during preliminary test of the

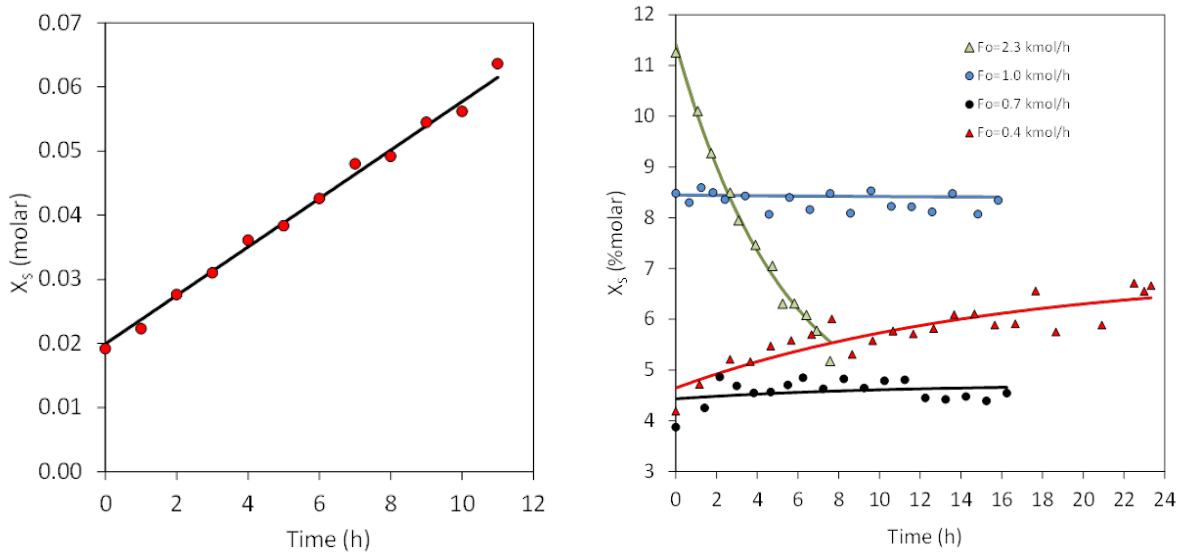
CaO<sub>2</sub> project allowed to complete an analysis of the evolution of this key variable in la Pereda pilot plant with the calciner operating under oxy-fuel conditions. A methodology based on a closure of mass and particle population balances has been used to estimate  $X_{ave}$ . It was observed that when the calciner reactor was operated in conditions far from the equilibrium of CO<sub>2</sub> on CaO, a good agreement was found between the experimental  $X_{ave}$  values (see D3.3 for details and Diego et al, Int. J. of Greenhouse Gas Control, 2017). However, we confirmed a CO<sub>2</sub> carrying capacity lower than expected in some tests in oxy-combustion mode, in particular when the calciner was operating close to equilibrium temperature of CaCO<sub>3</sub> decomposition under the average atmosphere in the calciner. These results are summarized in Figure 3.2.



**Figure 3.2.** Comparison between the calculated and the experimental values of the average CO<sub>2</sub> carrying capacity of the particles under (a) air and (b) oxy-fired conditions in the calciner. Dashed line is the calculated  $X_{ave}$  value assuming a single additional carbonation-calcination cycle per passage of a particle through the calciner (see D3.3 for details or Diego et al Int. J. of Greenhouse Gas Control, 2017)

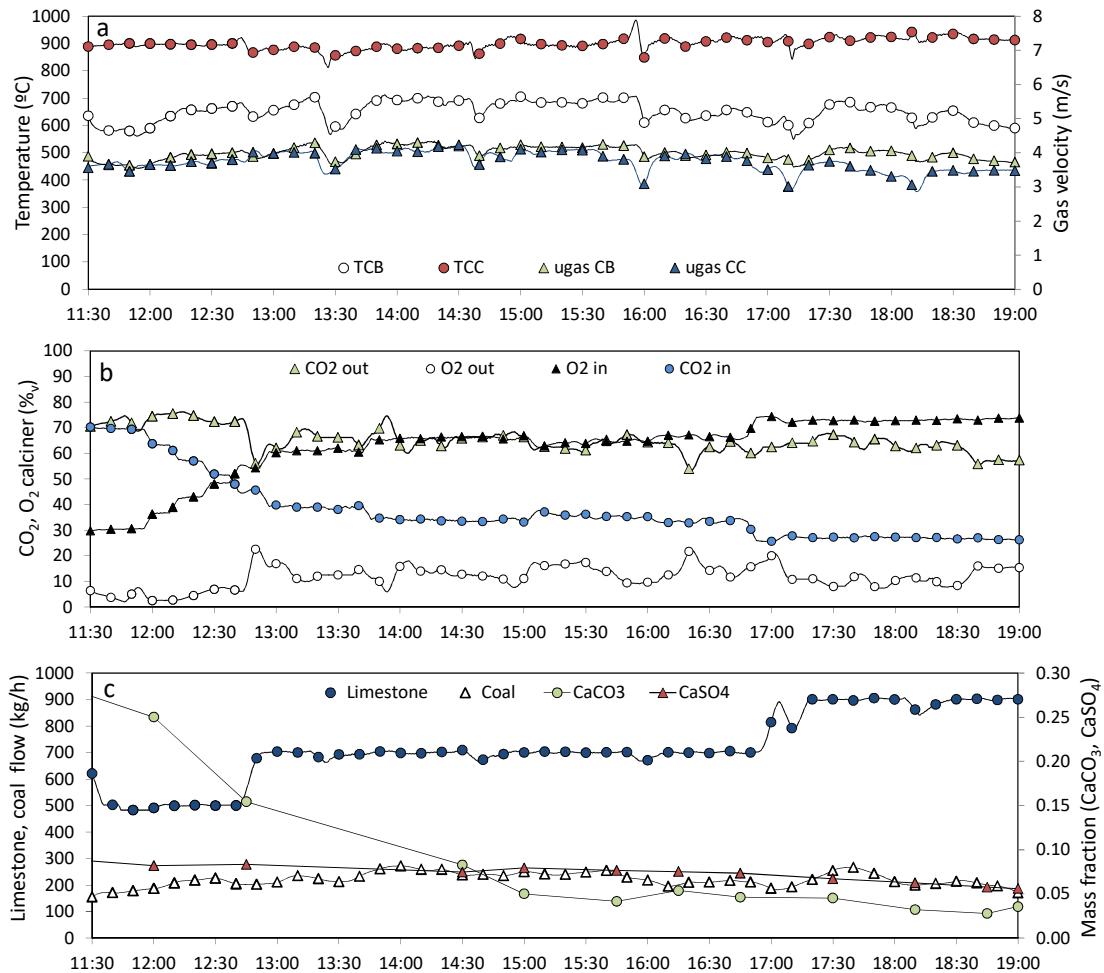
Departure from ideal sorbent behavior and more intense deactivation was found to increase with longer residence times in the calciner ( $\sim 3$  min). Therefore, we speculate that this deactivating effect may be due to the effective increase in the number of carbonation-calcination cycles of the particles, caused by switching between carbonating and calcining conditions inside the calciner (see also modelling results by LUT in WP4). Future designs of calciners operating under O<sub>2</sub> and CO<sub>2</sub>-rich conditions need to target shorter residence times of the particles in the calciner (i.e. lower solid inventories). However, such mode of operation is not possible in the existing la Pereda pilot because safe operation under O<sub>2</sub>-rich conditions required under all circumstances sufficient solid bed inventories (preferably  $>300$  kg/m<sup>2</sup>) and intense solid circulation rates (preferably  $> 7$  kg/m<sup>2</sup>).

Another important factor known to strongly influence the average activity of the sorbent in all CaL systems is the conversion of active CaO to CaSO<sub>4</sub>. As noted in Table 3.1 (second line), the long duration experiments conducted in preparation of O<sub>2</sub> rich test, under minimum solid losses from the reactors after retrofitting cone fennels in the cyclones and tuning gas and solid flows in the double loop seals, allowed for an effective closure of solid mass balances in the pilot using the CaSO<sub>4</sub> content,  $X_s$ , as a tracer. This is possible because the extremely high efficiency of the carbonator and calciner reactors to desulfurise their flue gas streams down to less than 15 ppmv of SO<sub>2</sub> under most normal operating conditions. Therefore, assuming that all sulfur coming in the flue gases entering the carbonator or the calciner with the fuel reacts to form CaSO<sub>4</sub>, it is possible to fit the evolution of the content of CaSO<sub>4</sub> and close the overall solid mass balances in the pilot. Results from these studies are summarized in Figure 3.3 and were presented in detail in D3.3 and the methodology to solve the mass balances regarding  $X_{ave}$  and  $X_{sulf}$  as a function of solid circulation and reactor efficiencies under different conditions were discussed also in a scientific publication resulting from these activities (Diego et al Int. J. of Greenhouse Gas Control, 2017).



**Figure 3.3.** Closure of the sulphur balances. Right) in the absence of a make-up flow of limestone in a steady state period with 6.7 kmol of CaO, with no relevant solid losses in the cyclones as confirmed by the linear increase of  $X_s$  with time. Left) evolution of the sulphur content for different values of limestone make up flows (coloured lines are mass balance model prediction).

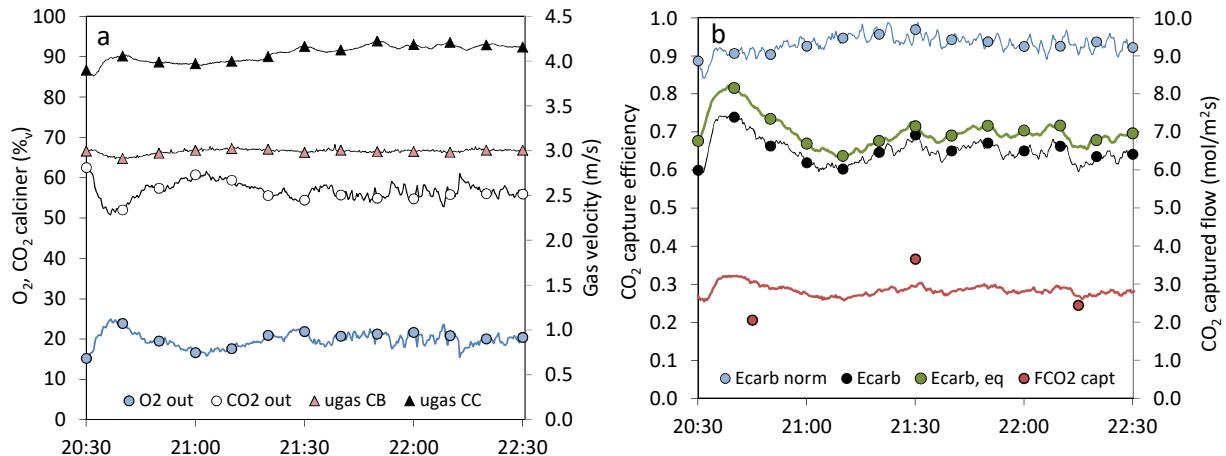
As noted in Table 3.1, once that these studies were concluded, and a sufficient experience on the control of solid circulation flows between reactors was achieved to guaranty safe operation of the calciner, O<sub>2</sub> rich test started. A first set of experimental campaigns (weeks 43 and 47 of 2016) were carried out in O<sub>2</sub>-rich calcination mode (reaching 75%v O<sub>2</sub> content) while keeping the carbonator fluidised with ambient air, in order to maximize the cooling of the solids arriving to the calciner. The results of these tests have been reported in D3.3 and an example is plotted in Figure 3.4. This shows the main variables during an oxy-calcination test in which a maximum oxygen concentration in the oxidant of 74%v was reached in the oxidant feed to the calciner. The carbonator was fluidized with air to cool down the circulating solids and maximize the fuel input to the calciner. During this experiment, a gas velocity of 4.0 m/s and a temperature of 650°C were maintained in the carbonator reactor. The calciner, however, was operated with an average temperature of 900 °C and a gas velocity also around 4.0 m/s. The test started with an inventory of partially carbonated solids derived form a mix of solids from previous experiments composed of 25.0%w CaCO<sub>3</sub> and 8.2%w CaSO<sub>4</sub>. A continuous limestone flow of 500 kg/h was fed into the calciner at the beginning of the test. Between 11:50 and 13:00, the oxygen concentration at the inlet was gradually increased from 28 up to 60%v. However this had no influence on the average temperature in the calciner temperature, as can be seen from Figure 3.4a. During this period, the inventory of solids in the system was gradually calcined as can be observed from the reduction in the CaCO<sub>3</sub> content of the solids in Figure 3.4c. Consequently, the limestone flow was increased to 700 kg/h at around 13:00 in an attempt to maintain the calciner temperature. Between 13:00 and 16:00, an average coal flow of 240 kg/h was fed into the calciner which resulted in a thermal input of 2.0 MW<sub>th</sub>. At 16:00, the CaCO<sub>3</sub> content of the solids stabilized at a value of around 5%w. From this point the thermal input into the calciner was slightly reduced to 1.75 MW<sub>th</sub> in order to maintain the average reactor temperature at a value of 900 °C. Finally at 17:00, the oxygen composition in the oxidant was increased to 74 %v and the limestone flow was kept at 900 kg/h until the end of the experimental period.



**Figure 3.4.** Example of Experimental results to test O<sub>2</sub> rich calcination conditions in the calciner ( $G_{sCC}=5.5 \text{ kg/m}^2\text{s}$ ,  $W_{CC}=495 \text{ kg/m}^2$ ,  $W_{CB}=165 \text{ kg/m}^2$ ).

Figure 3.5 correspond to a CO<sub>2</sub> capture test where the oxidant fed into the calciner contained 74%v of oxygen. The gas velocity in the calciner during this period was 4.0 m/s and an average calcination temperature of 885 °C was maintained. The carbonator was operated at a gas velocity of 3.5 m/s. The average carbonation temperature remained at around 700 °C due to a solid circulation rate between reactors ( $G_{sCB}$ ) of 10.7 kg/m<sup>2</sup>s.

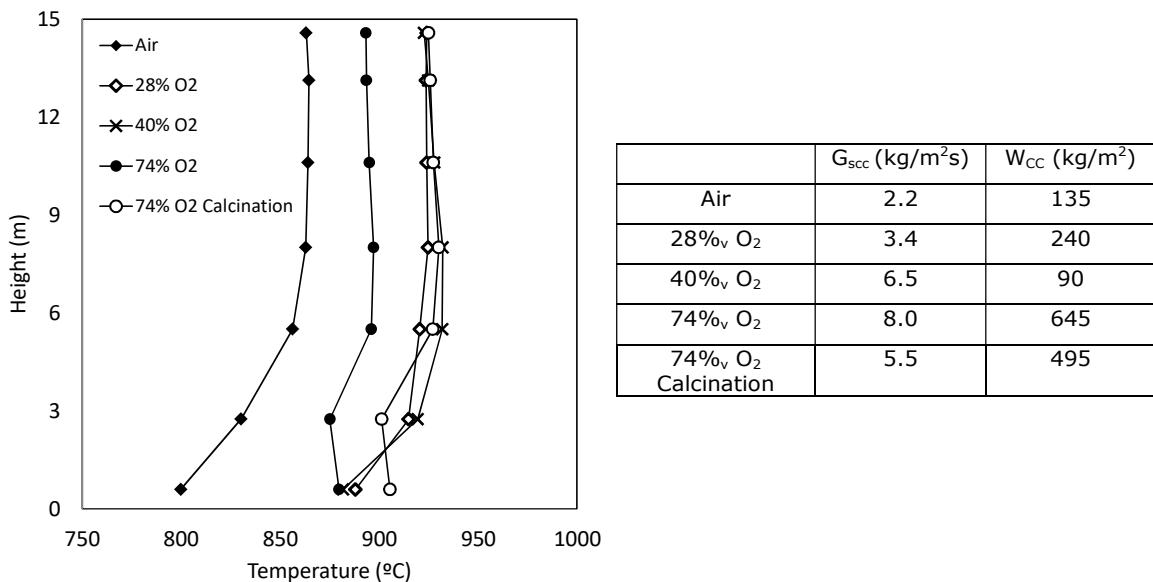
Figure 3.5b shows the experimental capture efficiency in the carbonator. During this period, an average CO<sub>2</sub> capture efficiency of around 0.65 was achieved due to the relatively high operation temperature in the carbonator (700 °C). Under these conditions, the minimum equilibrium CO<sub>2</sub> partial pressure allowed by the equilibrium is around 0.035, which lead to a maximum CO<sub>2</sub> capture efficiency of 0.70. Looking at the results presented in Figure 3.5b, a more useful parameter for analyzing the performance of the carbonator is the normalized CO<sub>2</sub> capture efficiency ( $E_{carb,norm}$ ) which is obtained from the ratio between  $E_{carb}$  and  $E_{carb,eq}$ . As can be seen in Figure 3.5b (blue line), an average  $E_{carb,norm}$  of 0.96 and 0.93 were achieved during these experimental periods, showing that the carbonator is operating with an efficiency close to that permitted by the equilibrium.



**Figure 3.5.** Example of Experimental results with O<sub>2</sub> rich calcination conditions in the calciner and CO<sub>2</sub> capture in the carbonator (see Annex of D3.3 for details and discussion in Arias et al, Fuel 2018 ( $T_{CC}=885$  °C,  $T_{CB}=700$  °C,  $G_{SCB}=10.7$  kg/m<sup>2</sup>s, coal flow=205 kg/h, limestone flow=120 kg/h,  $W_{CC}=640$  kg/m<sup>2</sup>,  $W_{CB}=460$  kg/m<sup>2</sup>)).

For a steady state, the closure of the energy balance in the calciner in these conditions was solved including heat losses in the pilot calibrated from previous experiments. The operating temperature in the calciner could rise to as much as 2110 °C according to the heat balance, which reinforces the need to ensure a sufficient circulation of solids for safe operation of the pilot.

The performance of the carbonator has been analyzed during the oxy-fired experimental campaigns using the methodology described in D 3.3. The experimental normalized CO<sub>2</sub> capture efficiency ( $E_{carb,norm}$ ) obtained during the oxy-fired experimental campaigns was in agreement with the expected value and with the results reported in previous works where the calciner was operated under standard oxy-fuel conditions.



**Figure 3.6 .** Average, axial temperature profiles along the riser of the calciner for different oxidant compositions and solids circulation rates and inventory of solids in the calciner.

Regarding the operation of the calciner, Figure 3.6 shows the temperatures profiles along the riser obtained from several experimental tests carried out at different oxygen concentrations. The values shown in this figure represent the average time values obtained from experimental measurements

taken during a period of at least two hours at each height. This figure also includes in tabulated form two critical parameters linked to the fluid-dynamic behavior of solids in the calciner: the total solid circulation rate through the riser ( $G_{SCC}$ ) and the bed inventory ( $W_{CC}$ ). The curve on the left-hand side corresponds to an experiment using air as oxidant in the calciner while the other curves on the right correspond to the oxy-fired experimental campaigns with different oxygen concentrations. As can be seen, the dominant factors in the temperature profile in the calciner are connected with fluid-dynamic parameters (i.e. circulation of solids, inventory of solids) rather than the enhanced combustion intensity related to the increase in  $O_2$  concentrations. The figure confirms that, with a sufficiently high value of circulation of solids from the carbonator and of a solids inventory in the calciner, it is possible to maintain a quite uniform axial temperature profiles in the calciner. This is consistent with previous modeling studies presented in Deliverable 4.3. The key take away from these results is the confirmation of the possibility to operate the calciner of future large scale CaL system under ultra-rich oxygen conditions, thereby reducing further the footprint and cost of the capture system.

Overall, the results have demonstrated the feasibility of operating the calciner of a calcium looping system under ultra-rich oxygen conditions at a relevant scale, although much work would be needed to validate the results at higher velocities in the calciner and higher thermal inputs, for which it would not be safe to operate the pilot of la Pereda. The axial temperature profiles measured along the calciner during the rich- $O_2$  tests (up to 75%v  $O_2$ ) showed the absence of hot spots as long as a sufficient circulation and bed inventory of solids is attained in the calciner. The performance of the carbonator when the calciner is operating at high  $O_2$  concentrations can be analyzed using a methodology and reactor model parameters consistent with those obtained in previous works under milder operating conditions. Therefore, the experimental results presented in this work will contribute to reinforce data-base of experimental information applicable to future scale-ups of the CaL process.

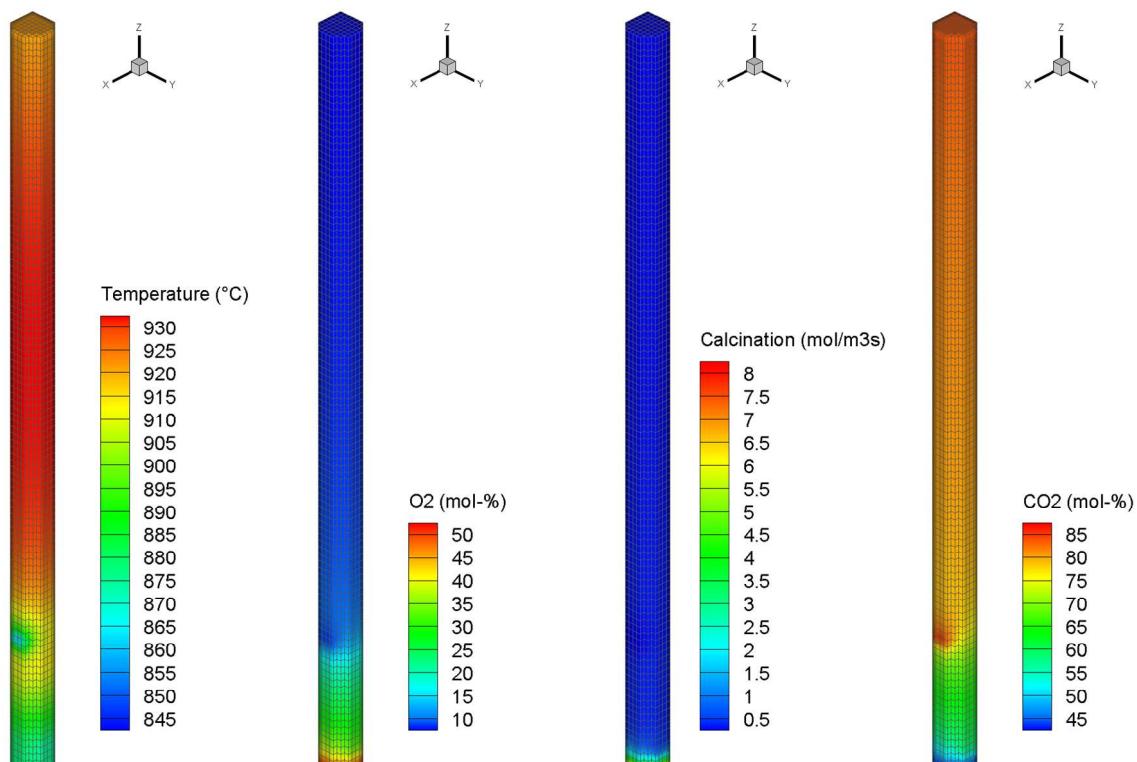
Other relevant progress in the state of the art from the new experimental campaigns under the  $CaO_2$  project in la Pereda relates the analysis of the average  $CO_2$  carrying capacity of the sorbent in CaL systems. We have confirmed a certain reduction of this parameter respect to the expected value when operating the system under the oxy-fuel combustion tests in la Pereda pilot plant. This reduction has been attributed to the particles undergoing additional carbonation and calcination cycles in the calciner. In order to minimize these undesired effects, it is important to ensure that the calciner operates under conditions far from equilibrium and/or with as short as possible residence time of solids in the calciner.

No showstoppers have been identified to design and operate future CaL systems using pure  $O_2$  as the oxidant feed to the calciner, perhaps using calciner designs operated at higher velocities and  $O_2$  staging (options not allowed in the la Pereda pilot) to minimize solid residence times of the particles and negative impacts on sorbent performance from the high temperature  $CO_2$ -rich atmospheres in the calciners.

## **WP4: Calciner reactor modelling with rich O<sub>2</sub> feed and scale up tools**

### **Task 4.1 Detailed 3D modelling of the combustor-calciner operating in ultrahigh O<sub>2</sub> concentration**

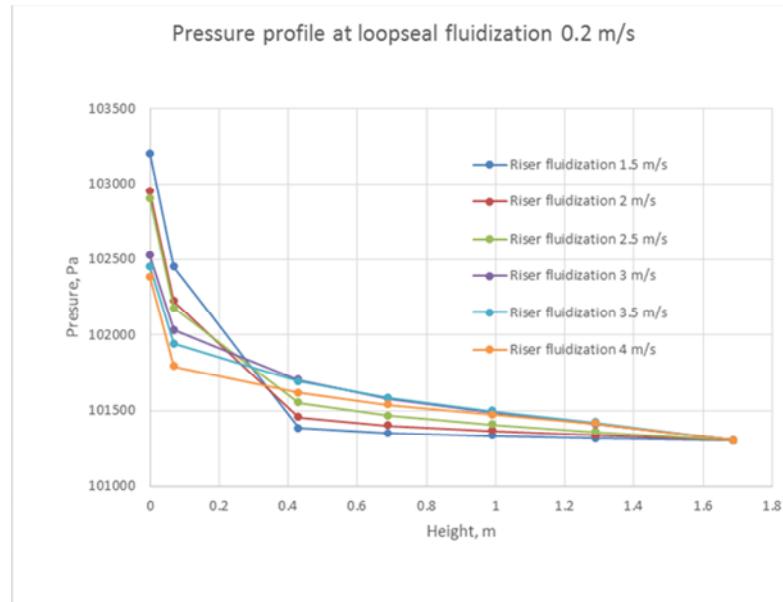
Deliverable D4.1 presented 3D-modelling of a pilot-scale calciner with O<sub>2</sub> concentration in the grid gas varying 70–100%-vol. The secondary gas inlets were using CO<sub>2</sub> to increase the gas velocity and solid mass flow rate, thus, the global O<sub>2</sub> content in the inlet gases was reduced to 30–46 %-vol. The simulation results showed that the endothermic calcination reaction and the cold material flow from the carbonator could absorb the heat of the combustion reactions at high oxygen concentration and the reactor temperature could be controlled without local hot spots (Figure 4.1).



**Figure 4.1.** Example 3D-modelling results of oxygen fired calciner.

### **Task 4.2 Development of property models for realistic fluidised bed conditions**

Deliverable D4.2 reported the property models and other submodels, which were applied in 1D and 3D models. The validation of the models were based on bench scale and pilot scale studies in CaL conditions and on earlier carried work in oxygen fired CFB development. In addition, cold model tests with limestone used at la Pereda were carried out to study the fluid dynamical behaviour of the circulating material (Figure 4.2).



**Figure 4.2.** Effect of fluidization velocity on pressure profile in cold model.

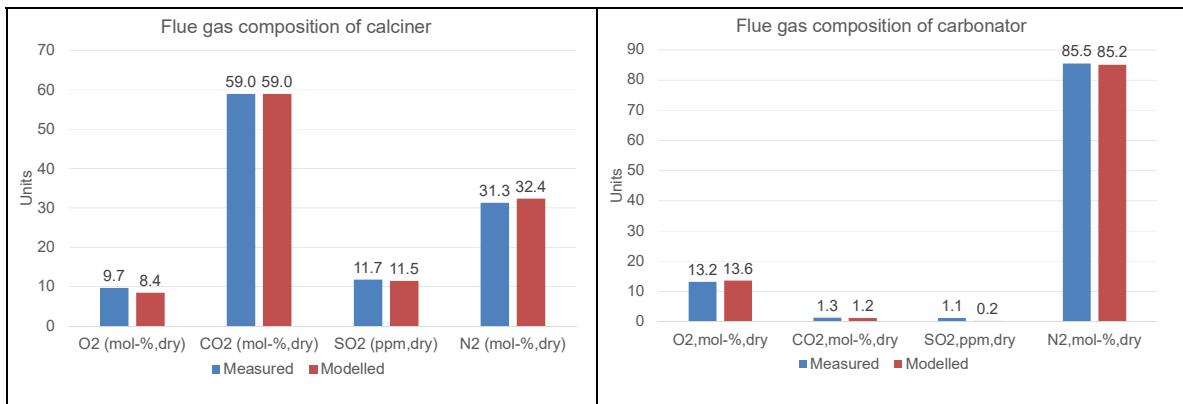
### **Task 4.3 Simulation of interconnected carbonation-calcinator reactor system and evaluation of effect of new calciner design on system performance**

As indicated in the workplan, this task has included activities related to process simulation work of the interconnected carbonator and calciner reactor system, including the modelling work to support the closure of carbon and sulphur balances in la Pereda pilot as a function of solid circulation rates and average conversions of solids during the experiments. The activities involving models to interpret experimental result from la Pereda in WP3 have been conducted by CSIC and have been described in previous Task 3.2 in D3.3 and in this task in D4.3.

Furthermore, CSIC has incorporated some of these findings in a recent peer reviewed publication (“CO<sub>2</sub> capture in existing power plants using second generation Ca-Looping systems firing biomass in the calciner”, by I. Martínez, B. Arias., G.S. Grasa, J.C. Abanades , International Journal of Cleaner Production, 2018) that considers and quantifies the benefits on CaL system energy efficiencies of the option of pure-O<sub>2</sub> firing of the calciner, with overall energy efficiency of 32.9-33.6% (LHV-based) consistent with the more detailed analysis reported in WP5 below.

In the 1D-model by LUT, each component in the CaL process is described by user generated functions in the Matlab® Simulink environment. The user generated functions solve time dependent mass and energy balances for each control volume, which gives possibility to use the model either in steady-state or in dynamic mode. The calciner and carbonator reactors are divided into 1D control volume elements which are assumed to be perfectly mixed. The 1D model and a calculation example were presented in Deliverable D4.3.

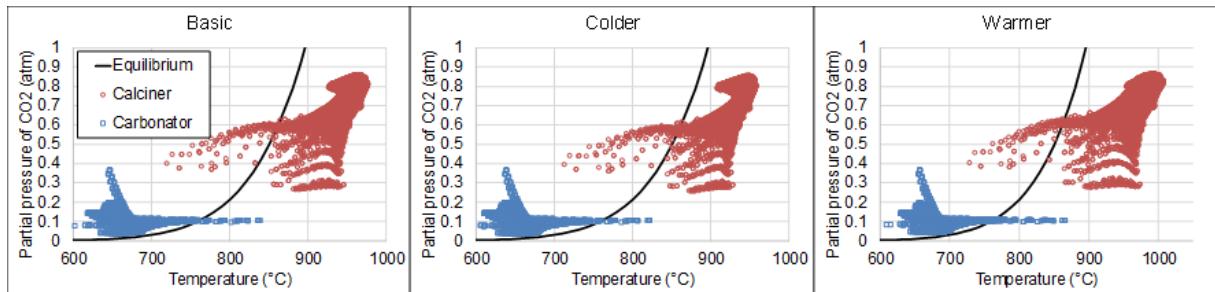
Deliverable D4.3 reported 3D-simulation of interconnected reactors of the la Pereda tests with 30.5%-vol inlet O<sub>2</sub> for calciner. The measured gas compositions could be simulated accurately (Figure 4.3).



**Figure 4.3.** Measured and modelled flue gas compositions of calciner and carbonator of la Pereda plant (D4.3).

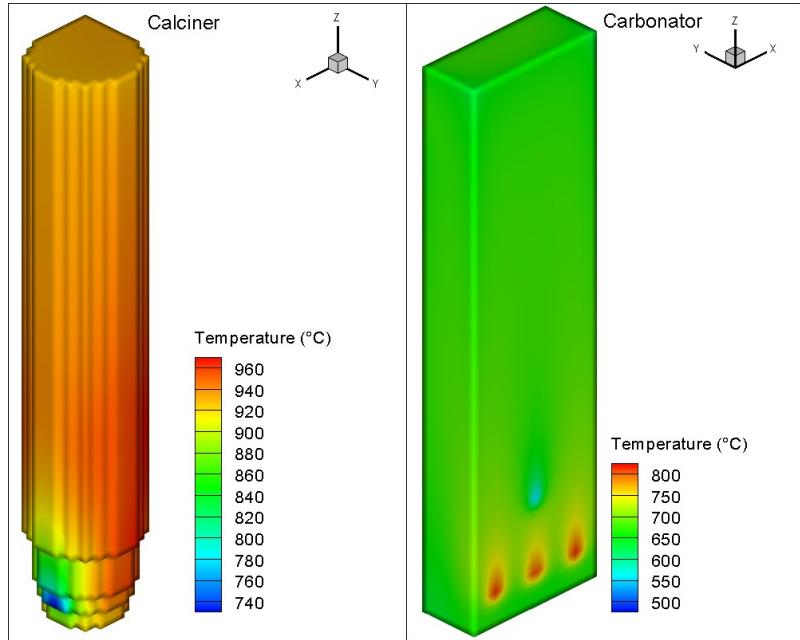
Deliverable D4.4 reported a 3D-modelling of a large scale (>200 MWth) CaL system with high inlet O<sub>2</sub> to calciner. The calculation study included three cases with varying system temperature controlled by fuel input to calciner. The inlet oxygen concentration of the calciner was 83%-vol, which leaves room for process control based on inlet O<sub>2</sub>.

For optimal operation, the temperature level should be above the calcination temperature in the calciner and below it in the carbonator. In a large scale system, this is practically impossible as shown in Figure 4.4, which reports the local temperature and CO<sub>2</sub> partial pressure in all calculation cells compared with the equilibrium curve for each case.



**Figure 4.4.** All calculation cells temperature and local CO<sub>2</sub> partial pressure with calcination equilibrium curve for all three cases, in order basic, colder and warmer (D4.4).

In the calciner, the local cold spots are found near the feed points of cold material from the carbonator. Similarly, on the carbonator, the local hot spots are found near the feed points of hot material from the calciner. Following figure presents the modelled temperature profiles of the basic case (not in scale: height of the calciner is 30 m and the height of the carbonator is 40 m).



**Figure 4.4.** Modelled temperature profiles for basic case of the 200 MWth CaL system (D 4.4).

Table 4.1 presents CO<sub>2</sub> capture efficiency in the carbonator, calcination efficiency and the sulphur capture efficiency in the calciner as well as the heat extracted from the carbonator for the three cases. The best capture efficiency is achieved in the case where thermal power in the calciner is lowest. In that case, the calcination efficiency is lowest. In the basic case, the calcination efficiency is better and the CO<sub>2</sub> capture efficiency is almost as good as in the colder case. In the warmer case, the CO<sub>2</sub> capture efficiency is clearly smaller, which is due to hot spots near the feed points.

**Table 4.1. Sorbent reaction efficiencies for a 200 MWth CaL system (D4.4).**

	Basic	Colder	Warmer
Calciner thermal power (MW)	210.7	206.3	217.1
Heat extracted from carbonator (MW)	49.9	48.3	52.1
CO <sub>2</sub> capture efficiency (%)	73.7	74.3	71.6
Calcination efficiency (%)	96.5	92.5	98.9
Sulphur capture efficiency (%)	99.8	100.0	98.2

Based on Deliverable D4.4, the operation is possible even at oxygen concentration above 80%-vol as the heat sink due to the calcination compensates the heat source due to the combustion reactions. In a conventional oxygen-blown combustor, this would not be possible due to limitations of the heat extraction by heat transfer only.

The following development ideas and conclusions were found:

- Local hot spots and calcining conditions in carbonator could be avoided by cooling down of solid materials from calciner before feeding to carbonator.
- Otherwise, minimization of heat losses in calciner to minimize the fuel input is important.
- Larger number of feed points in calciner could be used to prevent local cold spots and subsequent re-carbonation.
- The heat extracted from carbonator can be used to generate steam.

- Feeding the cold make-up limestone to carbonator helps to control the carbonator temperature. In addition, preheating the make-up in carbonator reduces the risk of cold spots in the calciner.
- Adjusting the circulation rate between the reactors is essential for controlling the temperature levels, i.e. large enough temperature difference between the reactors.
- The amount of sulphur entering the system in fuel and in flue gas from the power plant should be minimized (application of low-sulphur fuel, desulphurization of the flue gas). Any excess sulphur may result in enrichment of calcium sulphate and poor performance.

## **WP5: Power simulation and integration of the power generation system and economic benchmarking**

### **Task 5.1: Process simulation of the process operating at ultra high concentration O<sub>2</sub> in the oxidant**

The objective of this task was to assess the new process operating conditions and compare the performance against the state of the art of the calcium looping technology. To accomplish this task, the knowledge acquired during the experimental tests will be considered as a base for closing the boundary conditions of the CaO<sub>2</sub> case.

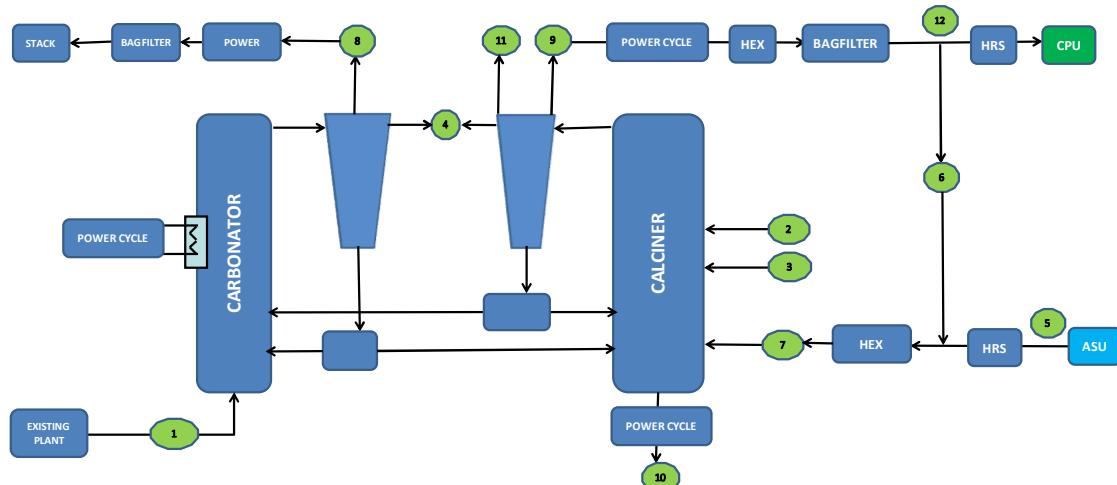
The simulation includes the results for two cases, the standard concentration of O<sub>2</sub> based on previous state of the art and the ultra high O<sub>2</sub> conditions. The simulation model resolve mass and energy balances of the complete system and integrates the operating conditions identified in the tests in La Pereda, involving different performance of the sorbent in the system for each case. The power generation from the extra heat available in the cycle is also resized and balanced with the new conditions and heat available in the system.

For the base case the maximum concentration of O<sub>2</sub> tested at pilot in previous projects (40% O<sub>2</sub>. ref-Caoling project) was considered as the reference. In the case of the CaO<sub>2</sub> case, the most important differences comparing with the base case were:

**Table 5.1. Main design differences between Base and CaO<sub>2</sub> cases**

	Base Case	CAO <sub>2</sub> case
O <sub>2</sub> % concentration:	40%	80%
Temperature calciner	900 °C	920 °C
Attrition	6,75%	8%

The rest of the main technical parameters has been kept similar for the two cases in order to facilitate the comparison of results. The following figure shows the general intergration scheme followed for the two cases



**Figure 5.1. plant process diagram.**

The results shows a more compact design of the full concept, including lower size of the ASU and CPU, which brings to a reduction of the auxiliary electricity consumption and in an overall improvement of the concept. Fuel consumption is higher in the Base Case which also brings to an extra heat available for extra production of additional electricity. This additional electricity compensates partially the inefficiency of the concept, limiting the global performance differences.

The following table shows a resume of the main technical parameters considered in the integration:

**Table 5.2. Main technical parameter comparison**

	Base Case	CAO2 case	
Coal consumption	253,30	224,21	Ton/h
Limestone consumption	144,288	145,476	Ton/h
O2 consumption	542,16	494,64	Ton/h
Fly ash	23,04	21,924	Ton/h
Purge	99,9	97,2	Ton/h
CaL power gross output	593,4	517,6	MW
CaL power net output	268,17	231,69	MW
ASU+ CPU consumption	250,40	232,16	MW
Other auxiliary power consumption	74,83	53,75	MW
CO2 Ratio of capture in the CPU	95	95	%
CO2 captured	1113	1046	Ton/h
CO2 emitted	145	141	Ton/h

Detailed information on the simulation cases is included in the deliverable “D 5.1- Simulation model of the full process operating at ultra high concentration of O2 in the oxidant”.

### **Task 5.2: Economic evaluation of the technology applied at commercial scale**

Inside of this task an economical comparison between the base case (state of the art) and the CaO2 case presented in task 5.1, was made by ENDESA. The main objective of this task is to evaluate the benefits of reducing the recirculation flow in the calciner in order to move to under ultra high oxidant calcination conditions.

In order to ensure the consistency of the results, it was selected the methodology published by the Technology Task Force of the ETP-ZEP (European Zero Emission Platform) already used in other similar projects. This methodology allows establishing a better comparison of the advances obtained in this project against the standard configuration of the calcium looping and against other alternatives and studies carried out in the last years. The two parameters that are considered to compare the results are the Levelised Cost of Electricity and the CO<sub>2</sub> capture and avoidance costs.

The two cases considered in the analysis are:

- Base Case: Standard configuration of the calcium looping with a 40% O<sub>2</sub> in the oxidant.
- CaO<sub>2</sub> Case: Configuration with 80% O<sub>2</sub> in the oxidant..

The following table shows the project results comparing the COE for the two cases under analysis:

**Table 5.3:** COE for the two cases considered.

Reference case + Calcium looping	BASE CASE	CaO <sub>2</sub> CASE
Net Power (MWe)	1022,47	985,99
Annual equivalent operation time (hours)	7500	7500
Efficiency %	35,31	36,63
Coal consume CaL (Ton/year)	1899720	1681560
Limestone consume CaL (Ton/year)	1082160	1091070
Purge production CaL (Ton/year)	749250	729000
Coal cost (€/Ton)	50,54	50,54
Limestone cost (€/Ton)	29	29
Purge cost (€/ton)	-20	-20
Annual Production (MWh)	7668527	7394942
Plant lifetime (years)	40	40
Interest rate (%)	8	8
<b>Investment Total Cost (M€)</b>	<b>3153,84</b>	<b>2996,26</b>
<b>Annual Total Cost (M€)</b>	<b>515,26</b>	<b>488,20</b>
Fixed Operating Costs (M€)	67,52	64,63
Total Variable Operating Costs (M€)	183,26	172,31
Annual Amortization Costs (M€)	264,48	251,27
<b>C.O.E. (€/MWh)</b>	<b>67,19</b>	<b>66,02</b>
Emission Factor (gCO <sub>2</sub> /KWh)	141,81	143,49
CO <sub>2</sub> produced (ton/year)	1.087.466	1.061.073
Assigned CO <sub>2</sub> (ton/year)		
Deficit CO <sub>2</sub> (ton/year)	1.087.466	1.061.073
CO <sub>2</sub> credit cost in future market (€/Ton)	30	30
CO <sub>2</sub> costs (M€/year)	32,62	31,83
<b>C.O.E. with CO<sub>2</sub> credit (€/MWh)</b>	<b>71,45</b>	<b>70,32</b>

Cost of electricity (COE) shows better figures for the CaO<sub>2</sub> Case than for the Base Case. The reduction reached for the total COE is a reduction of 1,7%. In terms of CAPEX a reduction of about 9% will be reached for the CCS related equipment, mainly due to the reduction of costs on the calciner and air separation units, civil works, as well as other auxiliary systems.

The emission factor is also higher in the Base Case. The following table shows the figures in €/ton CO<sub>2</sub> for the two cases:

**Table 5.4:** CO<sub>2</sub> captured costs

	€/Ton	BASE CASE	CaO2 CASE
CO <sub>2</sub> captured cost		26,93	26,52

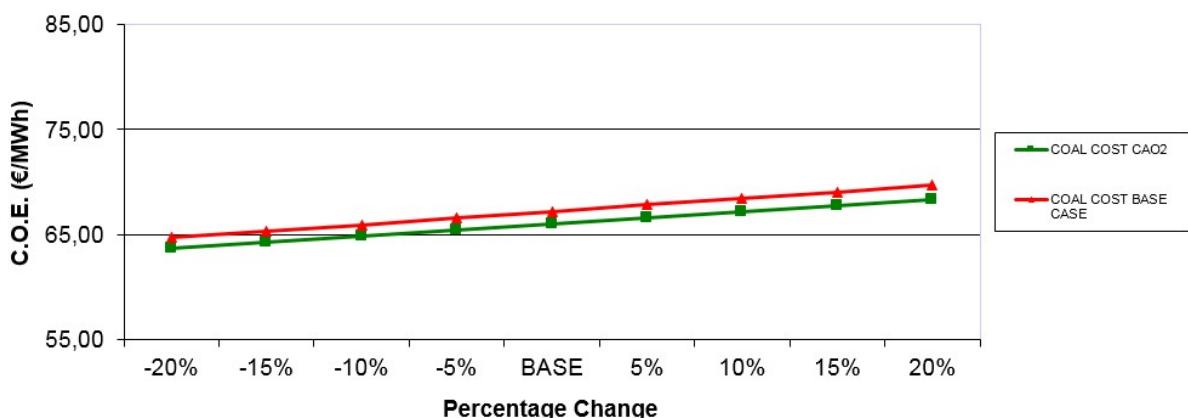
In order to understand better the economics of the concept, and the influence of certain parameters for each of the different configurations analysed in this document, different sensitivity analysis have been carried out in order to identify the most critical parameters for the two option including coal cost, limestone cost, interest rate, purge cost, efficiency of the CaL, Investment cost and annual operation hours.

The following studies have been completed:

**Table 5.5:** Sensitivity analysis

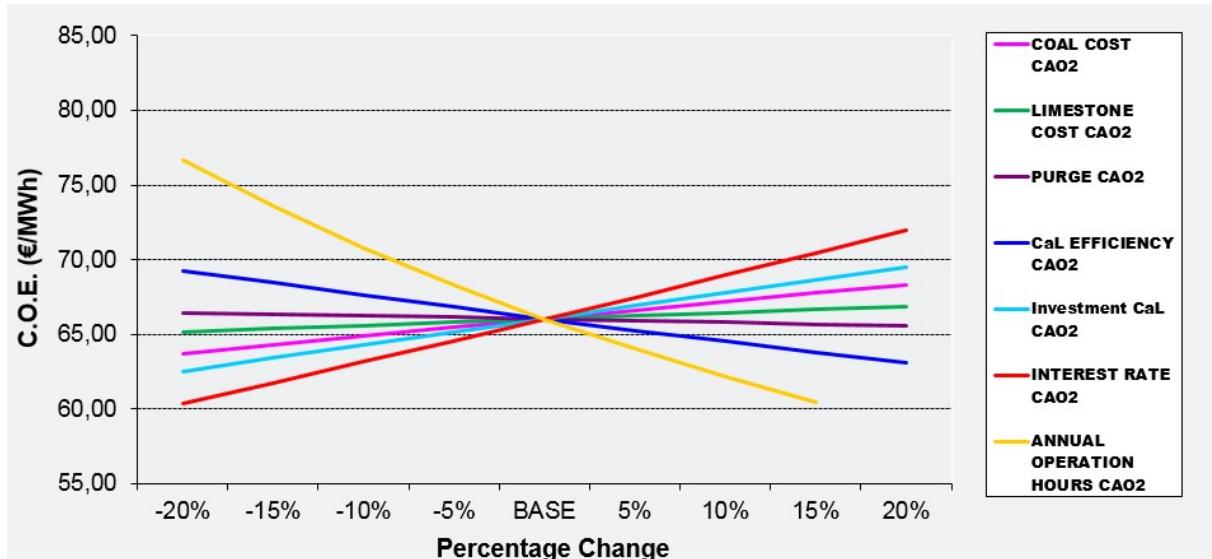
	Min	max
<b>FUEL COST</b>	-20%	20%
<b>LIMESTONE COST</b>	-20%	20%
<b>PURGE INCOME</b>	-20%	20%
<b>EFFICIENCY of the CaL power cycle</b>	-20%	20%
<b>CaL UNIT INVESTMENT COST</b>	-20%	20%
<b>INTEREST RATE</b>	-20%	20%
<b>ANNUAL OPERATION HOURS</b>	-25%	15%

As an example the following figure shows the influence of the fuel costs in the COE. The comparison among base case and CaO2 case show very small changes in the Delta COE, as is the case for most of the parameters analysed. This small modification is also due to the impact of the existing plant in the COE value calculated (close to 60%).



**Figure 5.2:** Sensitivity analysis for coal cost.

The following figure gives an indication on the COE's impact on each of the key selected parameters for the Case 2 which is the most efficient of the three cases analysed:



**Figure 5.3:** Sensitivity analysis for CaO2 Case.

Due to the high investment costs needed for the implementation of this technology, the most sensible parameters are those related to the financial costs and the annual operational hours which at the end, impact directly in the final price of the electricity needed to amortize the investment costs. Operational costs and fuel costs modifications are less critical.

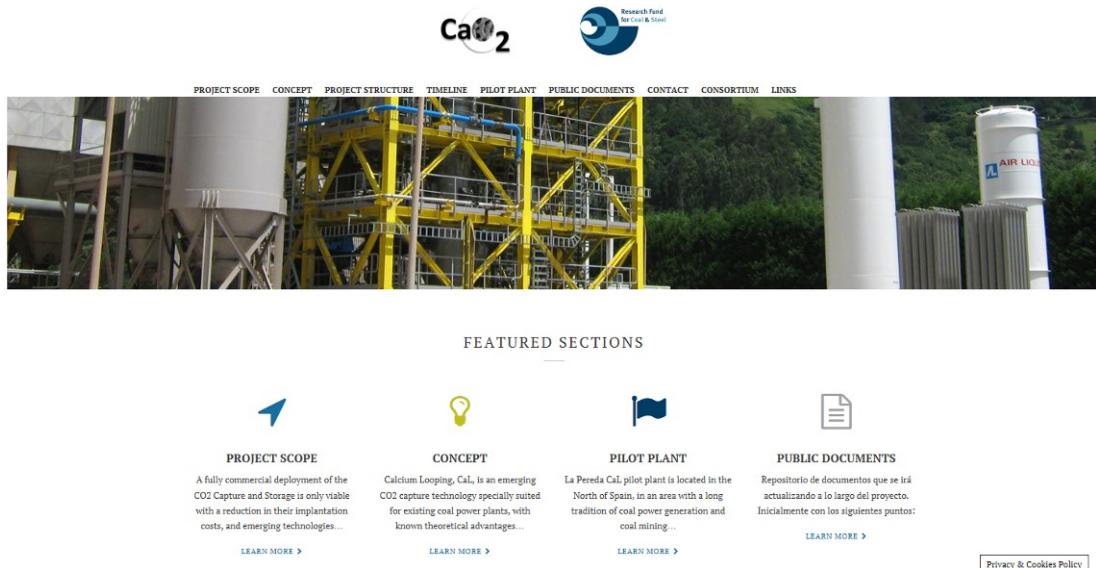
The full description of the results, the complete sensitivity analysis and the basis considered for the estimation are presented in the deliverable D5-2 – Technoeconomics study at full commercial scale.

## **WP6 Coordination, management and dissemination.**

The aim of this workpackage has been to coordination the main technical activities of the consortium and disseminate the main results obtained in the project. The main effort has been done using technical publications and networking of the partners of the Consortium.

Two changes in the Grant Agreement was requested to the European Commision including an extension of the project duration, due to delays during the retrofitting of La Pereda pilot.

A webpage has been prepared as main coordination and dissemination tool of the project. Regarding information in the webpage public information generated in the project has been updated and upload in the webpage in order to facilitate the dissemination of the main results. The address of the website is <http://cao2.eu>.



**Figure 6.1 . CaO2 website**

General information of the project has been also included in the webpage of the coordinator.

10 scientific publications has been produced during the execution of the project. In chapter 4.5.2 of this document there is a complete description of the scientific papers published during the project.

The results of the project has been disseminated inside of several forums especially inside of the High temperature Solid Looping Technology international IEA network, where main active parties working with this technology are presented. Also the project has been presented in the GHGT event which can be considered the most important event dealing with CO<sub>2</sub> capture technologies in the world.

### **3.4. Conclusions**

Although some initial limitations of the pilot plant has reduced the number of experimental results, the new operational conditions with high concentration of Oxygen in the calciner has been tested and validated successfully in continuous operation mode in la Pereda pilot plant. These experiments have demonstrated the feasibility to increase the oxygen over 75% and the possibility to eliminate the need of CO<sub>2</sub> recirculation in the calciner. As has been demonstrated in the WP5, this improvement would enhance the competitive advantages of the technology when incorporated into large-scale coal power plants, increasing the efficiency of the process.

As a resume of the project the following conclusions can be made:

- In the range of CaCO<sub>3</sub>/MgO content tested in this study, the chemical composition of the limestone has no impact compared to its microstructure regarding mechanical performance of the sorbent.
- All the limestones tested at lab scale display a similar behavior in terms of chemical reactivity along cycling and in line with previous research works with other natural limestones, confirming the low variability of this parameter in most of the sorbents.
- A first simple decision table is proposed to quickly select natural limestone in function of its microstructure and the cycling conditions of the CaL process. Most of the sedimentary limestone rocks (M-W-P-G) are suitable for CaL applications with the exception of particular texture such as recrystallized marble (limestone C type), which must be avoided. High porosity limestone such as limestone D should be also preferably rejected when high cycling rate (with N>50) are needed. As a general criteria, Grainstone limestone seems to be one of the best options in most of the cases, allowing higher number of cycles in the system while keeping a relatively good residual activity.
- It would be anyway too risky to make the final selection of the limestone only on its microstructure, grain size or chemistry, and this parameters must be considered only as a prescreening criteria. The raw limestone must be qualified by CaL dedicated small lab test before being selected in an industrial application, as is the best procedure to obtain more accurate attrition values.
- A significant percentage of the natural limestones are feasible as feedstock in a CaL system, and limestone availability therefore, must not be a strong limitation for the technology. Nevertheless, once the design of an industrial plant has been defined, the range of valid limestone is more limited and their feasibility for that design must be carefully checked before introducing a change in the feedstock of the plant.
- All the synthetic sorbents tested in the lab fluidised bed showed higher performance than the initial limestone. However, the biomass-free pellets showed superior capture capacity over the biomass-containing pellets. The initial CO<sub>2</sub> uptake by best pellet was 0.22 gCO<sub>2</sub>/gsorbent.
- The mechanical performance of the synthetic sorbent shows very poor performance. A significant improvement is needed for the use of these kind of material in CaL plants.

- The initial tests carried out in Cranfield laboratory rig and particularly the experimental results from la Pereda pilot, confirm that it is possible to operate the calciner of a Calcium Looping system under very high oxygen percentage conditions.
- The axial temperature profiles measured along the calciner during the rich-O<sub>2</sub> tests in La Pereda (up to 75%v O<sub>2</sub>) showed the absence of hot spots as long as a sufficient circulation and bed inventory of solids is attained in the calciner.
- Average CO<sub>2</sub> carrying capacity of the sorbent in CaL systems under oxy-fuel combustion conditions is slightly lower than the expected value probably due to the particles undergoing additional carbonation and calcination cycles in the calciner (non-productive internal cycling inside the reactor). Influence of higher operative temperature in the calciner could also promote this faster degradation, although main influence seems to be the internal cycling in the reactor. In order to reduce this undesirable effect, a good ad-hoc design of the calciner though an optimised distribution of solids inlets, could avoid cold spots in the calciner and consequently carbonation areas where internal cycling could be produced. This will reduce significantly the higher sorbent degradation observed under oxyfuel combustion conditions.
- No major showstoppers have been identified to design and operate future CaL systems using pure O<sub>2</sub> or close to pure as the oxidant feed to the calciner, perhaps using calciner designs operated at higher velocities and O<sub>2</sub> staging.
- Simulation done in WP4 indicates that there is still room for optimization and improving in the initial design considered. (cool down the solid material from calciner before feeding it to carbonator, feeding the fresh limestone to carbonator...)
- Cost of electricity (COE) shows better figures for the new operating conditions proposed in the CaO<sub>2</sub> project, based on the large scale selected to carry out the technoeconomical evaluation (80% O<sub>2</sub>). The reduction reached for the total COE in this case, is a reduction of around 1,7%. Obviously, higher improvement will be reached with pure O<sub>2</sub> concentration.
- A 9% reduction could be reached in the CAPEX associated to the CCS system, thanks to the reduction of the size mainly of CaL and Air Separation Unit equipment.
- For a similar capture rate and CO<sub>2</sub> purity, the overall efficiency of the reference plant integrated with a CaL plant, for the conditions considered in the analysis, will increase 1,3 percentage points when oxygen percentage at the inlet of the calciner is increased from 40% to 80%, reaching a global efficiency value of 36,63%. On the other hand, although it is a more efficient concept, the power output of the combined system is reduced in a 3,5% due to the lower overall coal used in the integrated concept and consequently the lower extra heat available in the CaL system. Nevertheless due to the reduction of the CAPEX and OPEX, the ultrahigh concentration concept reach lower production costs.
- CO<sub>2</sub> avoided cost is reduced by a 3,7% in the CaO<sub>2</sub> Case compared against the Base Case.
- The sensitivity analysis shows that influence of the new operating conditions are higher on those sceneries impacting in the number of hours of operation of the system amortization parameters and fuel costs. A reduction of the hours of operation up to 5500 hours (instead of 7500 hours considered in the base case) leads to an increase of the COE from 66,02 €/MWh to 76,7 €/MWh for the CaO<sub>2</sub> Case.

### **3.5.           Exploitation and impact of the research results**

The results of the project has demonstrated that there is still space to improve a very promising technology, the calcium looping technology as an emerging CCS technology for the future. The improvements reached jointly with other improvements identified in the area of the sorbent activation in the last years, as the case demonstrated in ReCaL project, are reducing the costs of the electricity production significantly. Nevertheless the current cost level introducing these improvements is still too high to promote an industrial development, at the current scenarios. In that situation if we want to reach further significant reduction of costs it will require a new breakthrough configuration or sorbent modification.

The new operating conditions tested in the CaO2 project can be considered as a new state of the art for the CaL technology and seems that could be easily implemented in the possible calcium looping plant that could be considered in the future. Nevertheless the exploitation of this improvement is completely associated to the successful of the exploitation of the CCS technologies.

To complete the validation of the ultra rich oxygen calcination conditions obviously will be required further tests in a facility able to work at pure O<sub>2</sub> levels. Nevertheless as indicated in the conclusions it is not expected any technical trouble in that approach.

The results obtained with the new pelletization techniques shows good results in terms of sorbent activity but poor results in terms of mechanical properties, which obviously limit their possible exploitation. Further development are required in this field in order to get exploitable results.

For the future exploitation of the results in a short term is important to highlight the networking activities that partners of the Consortium are doing in the High temperature Solid Looping Technology international IEA network, where main active parties working with calcium looping are participating. Additionally contacts with members of other European Projects will be important in order to establish a solid relationship that can improve the options to exploit this technology, especially in other industrial sectors.

#### **3.5.1.           Patents**

No patents have been presented for the developments of the project.

#### **3.5.2.           Publications and Workshops**

During the whole project 10 publications has been prepared and published in international engineering journals:

- Cordero, J.M., Alonso, M., Modeling of the kinetics of sulphation of CaO particles under CaL reactor conditions, Vol 150, 15 June 2015, Pages 501-515, Fuel 2015.

- *Borja Arias, M. Elena Diego, A. Méndez, J. Carlos Abanades, Luis Díaz, M. Lorenzo, A. Sanchez-Biezma, "Operating experience in la Pereda 1.7 MW<sub>th</sub> Calcium Looping pilot", 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, Energy Procedia 114: 149-157 (2017)*
- *Jarno Parkkinen, Kari Myöhänen, Juan Carlos Abanades, Borja Arias, Timo Hyppänen, "Modelling a calciner with high inlet oxygen concentration for a calcium looping process", 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, Energy Procedia 114: 242-249 (2017)*
- *M. Erans, T. Beisheim, V. Manovic, M. Jeremiáš, K. Patchigolla, H. Dieter, L. Duan and E. J. Anthony, "Effect of SO<sub>2</sub> and steam on CO<sub>2</sub> capture performance of biomass-templated calcium aluminate pellets", Faraday Discuss., 2016, 192, 97-111.*
- *M.E. Diego, B. Arias, J.C. Abanades, "Evolution of the CO<sub>2</sub> carrying capacity of CaO particles in a large calcium looping pilot", International Journal of Greenhouse Gas Control, 62, 69-75, 2017*
- *I. Martínez, B. Arias, G.S. Grasa, J.C. Abanades. "CO<sub>2</sub> capture in existing power plants using second generation Ca-looping systems firing biomass in the calciner". Journal Cleaner Production, doi:10.1016/j.jclepro.2018.03.189, 2018.*
- *B. Arias, M.E. Diego, A. Méndez, M. Alonso, J.C. Abanades. "Calcium performance under extreme oxy-fuel combustion conditions in the calciner". Fuel, 222, 711-717, 2018.*
- *M. Alonso, B. Arias, J.R. Fernández, O. Bughin, J.C. Abanades. "Measuring attrition properties of Calcium Looping Materials in a 30 kW<sub>th</sub> pilot plant". Powder Technology, 336, Pages 273-281 2018.*
- *B. Arias, A. Méndez, M.E. Diego, M. Alonso, L. Díaz, M. Lorenzo, A. Sanchez-Biezma, J.C. Abanades. "Experiments in the Calcium Looping pilot of "la Pereda" while operating the calciner at high O<sub>2</sub> concentrations". International Conference Greenhouse Gas Control, GHGT-14 2018.*

The project was presented in the CCS most important worldwide conference, the GHGT-13 during 14th-18th November 2016 in Lausanne, Switzerland. Initial experimental results and modelling were presented in this conference. In order to present final results an abstract has been submitted to the same conference, GHGT-14, to be held in Melbourne during 2018.

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## **6. LIST OF ACRONYMS AND ABBREVIATIONS**

CaL – Calcium looping

TGA – Thermogravimetric analysis

CFB – Circulated Fluidised Bed

FB – Fluidised Bed

BFB – Bubbling Fluidised Bed

RPM – Random Pore Model

FGD – Flue Gas Desulphurisation

CFBC – Circulated Fluidised Bed Combustion

LHV – Low Heat Value

CCS – Carbon Capture and Storage

IEA – International Energy Agency

ETP-ZEP - European Zero Emission Platform

COE – Cost of Electricity

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The CaO<sub>2</sub> project has demonstrated in a large pilot (2-3 MWth) a process variant of the CO<sub>2</sub> capture postcombustion calcium looping system for coal based power plants. This optimised process scheme is intended to minimize or even avoid the need of a CO<sub>2</sub> recycle to the oxyfired circulating fluidized bed calciner, by exploiting the endothermic nature of the calcination reaction and the large solid flow circulating from the carbonator. This variant can reduce significantly capital cost (reduced calciner and air separation units) and operating cost (reduced O<sub>2</sub> and fuel requirements in the calciner) thereby improving the competitiveness of the system.

An extensive work on sorbent performance has been done, identified main criteria which could indicate a good performance of the sorbent in this kind of systems, especially from the mechanical point of view.

During the project it has been demonstrated the possibility to operate the pilot in La Pereda with a maximum of 75% of oxygen in the oxidant flow to the calciner, which confirms the main target of the project. Additional modelling works and experimental at lab scale show that this value could be even higher without major operating risks, which could improve the performance figures estimated for the technology. So, no major showstoppers have been identified to design and operate future CaL systems using pure O<sub>2</sub> as the oxidant feed to the calciner.

*Studies and reports*

