Grant Agreement Number:
641185

Action acronym:
CEMCAP

Action full title:
CO_2 capture from cement production

Type of action:

H2020-LCE-2014-2015/H2020-LCE-2014-1

Starting date of the action: 2015-05-01
Duration: 42 months

D12.1
Results from 30 kW_{th} CaL CFB experiments (M18)

Due delivery date: 2016-11-01
Actual delivery date: 2016-10-21

Organization name of lead participant for this deliverable:
Spanish Research Council (CSIC)

Project co-funded by the European Commission within Horizon2020		
Dissemination Level		
PU	Public	X
CO	Confidential , only for members of the consortium (including the Commission Services)	

Deliverable number:	D12.1
Deliverable title:	Results from 30 kW_{th} CaL CFB experiments
Work package:	WP12. Calcium looping capture
Lead participant:	CSIC

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Abstract

The integration of the CaL process into the cement plant requires operating the carbonator reactor under new conditions (i.e., higher carbonator CO_2 load, more active sorbent, smaller particle sizes etc). This report analyzes the impact of some of these new CaL operating conditions on the performance on the carbonator reactor. For this purpose, a 30 kW_{th} testing facility has been retrofitted and operated under conditions closer to those expected in a cement plant application. A wide range of sorbent activities has been tested, up to those corresponding to large make up flows of $CaCO_3$ that will be characteristic in CaL applications in cement plants. The high activity of the sorbent has allowed to achieve capture efficiencies close to those theoretically allowed by the equilibrium, despite the low inventory and gas solid contact times in the carbonator. The results obtained have been interpreted using a basic reactor carbonator model that has required little modifications respect to previous versions, developed for power plants. Therefore, the results presented in this work provide further confidence about the scalability of CaL for capturing CO_2 in cement plant.

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1 SCOPE AND INTRODUCTION

Calcium looping, CaL, was early recognized as a technology with a high potential to reduce CO_2 emissions in cement plants, with an early "C3 Capture" FP6 project (2005-2008) involving CEMEX looking at the integration CaL solid purges from power plants into cement plants (Trevino and Martínez 2009). In order to exploit the synergy between CaL and cement plants, several process schemes have been proposed with different degrees of integration between the cement plant and the CaL system. In principle, CaL could be used to capture CO_2 as standalone postcombustion system retrofitted to the cement plant without any integration other than the connecting pipe of flue gases and some means to use in the clinker oven the purge solid material coming from the CaL system (Trevino and Martínez 2009, Vatopoulos and Tzimas 2012, Ozcan, Ahn et al. 2013, Atsonios, Grammelis et al. 2015, Spinelli, Martínez et al. 2016). For this purpose, a CaL configuration based on circulating fluidized bed reactors, similar to that used for capturing CO_2 from power plants, may be suitable. The main differences respect to a standard CaL configuration in power plants are related with the high CO_2 load to the carbonator (due to the higher concentration of the flue gas from the cement plant) and the higher activity sorbents as a consequence of an operation using larger limestone make-up flows in the calciner. Also, the operation with fine particles would facilitate the use of the rich-CaO purge in the cement plant(Spinelli, Martínez et al. 2016).

More integrated schemes are also being proposed in order to reduce the energy consumption in the calciner of the CaL system. Some of these processes are aimed to fully substitute the existing precalciner in cement plants by the Calcium looping system, so that the raw materials fed to the plant are abandoning the calcium loop fully calcined before entering the clinker oven (Rodríguez, Murillo et al. 2012, Romano, Spinelli et al. 2013, Spinelli, Martínez et al. 2016). In these systems, the raw material is calcined in an oxy-fired calciner after being preheated, and only a fraction of the rich-CaO material is sent to the carbonator in order to capture the CO_2 from the rotary kiln flue gas (the rest of the calcined material is directed to the kiln). Some of these specific configurations have overlooked in the past the challenges to operate the kiln when feeding CaO rich materials with typical particle size distributions of CFB reactors (i.e. with a substantial fraction of CaO particles around and above 100 micron). This kind of configurations would most likely require a further milling/mixing step before the material enters the kiln. Therefore, it may be highly beneficial to use entrained flow reactor in order to handle the small particle size ranges used for the raw mills, leading to advanced process schemes of the full cement plant that can be better integrated with the Calcium looping system to minimize energy requirements (Romano, Spinelli et al. 2013) (See also Deliverable 4.3 of the CEMCAP project).

Despite the increasing number of publications highlighting the theoretical advantages of CaL technology in cement plant environments, there is little experimental information related to the performance of the main reactors operating under conditions closer to those expected in CaL systems capturing CO_2 from cement plant (i.e., higher carbonator CO_2 load, more active sorbent in the solid circulation loop because of increased make up flows of $CaCO_3$, smaller particle sizes to facilitate clinker reactions in the rotary kiln etc.).

In this context, the scope of this Deliverable 12.1 has been to experimentally investigate some of these new CaL operating conditions on the performance on the carbonator reactor dealing with the CO_2 capture step in the capture system. For this purpose, experimental campaigns have been carried out in a 30 kW_{th} pilot plant made up of two interconnected circulating fluidized bed reactors. This pilot plant has been retrofitted to operate under the new experimental conditions (i.e., high CO_2 load, high make up flows and small particle size). A basic reactor carbonator model is applied to interpret the results obtained from the pilot and provide a better basis for future scale up of the technology.

The description of 30 kW_{th} facility used to carry out the experimental campaigns and the modifications made in the pilot to operate under the new conditions is presented in Section 2. The analysis of the results by carrying out the closure of carbon mass balances is included in Section 3. A more detailed summary of the experimental information and data sets generated during the testing campaigns can be found in the Annex II.

2 EXPERIMENTAL FACILITY AND MATERIALS

2.1 Description of the 30 kW_{th} test facility

The results presented in this report were carried out in the 30 kW_{th} pilot plant at INCAR-CSIC. This pilot is composed by two interconnected fluidized bed reactors acting as carbonator and calciner with an internal diameter of 0.1 m and a total height of 6.0 and 6.5 m respectively. Each riser is equipped with a primary cyclone to separate the gas flow from the solid particles and a bubbling fluidized-bed loop seal to close the pressure balance. Each riser is equipped with six ovens each. These are installed in the first 2.5 m of the reactors. Five of the ovens, with an individual capacity of 3.0 kW, have a cylindrical shape and can be open. This feature can be used to cool down the carbonator when necessary (when it is not enough to switch off the ovens to maintain carbonator temperatures). In the bottom of the risers, where gas and particles are injected, there is an oven with a capacity of 3.8 kW. Four additional heating elements (1.5 kW) have been installed in the upper part of the riser of the carbonator. In addition, the loop-seals are also heated with two individual ovens (3 kW) to avoid the cooling-down of the solids during circulation and facilitate high temperature conditions during initial calcination of the material added to the system. All the ovens are controlled independently. The upper part of the risers and the solid recirculation system is isolated using ceramic refractory fiber, which has been reinforced and enlarged for these tests in order minimize heat losses. These modifications allowed increasing the effective thermal power available for calcination, as necessary to operate with high limestone make-up flows.

During capture experiments, a simulated flue gas is fed to the carbonator by mixing air, CO_2 and steam. Air supply to the risers and loop seals can be done by using two blowers with a maximum capacity of 40 and 90 m^3/h respectively. Gas flow rates are adjusted using mass flow controllers. To generate a synthetic combustion flue gas, pure CO_2 from a 200 litres liquid Deward can be fed and mixed with the air into the carbonator. A small steam generator has also been installed to supply a continuous flow of water vapor to the carbonator up to 2.0 kg H_2O/h. The calciner can be fed with coal and limestone using two independent solid feeding systems. They consist in a hopper with a screw feeder in the bottom which velocity can be varied. Fuel and limestone are injected at the bottom of the risers though an inclined stand pipe with the fluidization gas. Hoppers are sealed to avoid gas leakage from the risers and can be slightly pressurized to facilitate the feeding of solid. Fuel and limestone flow to the risers can be controlled adjusting the velocity of the screw feeder, as the feeding system is calibrated for each fuel batch before testing starts.Two gas analysers are used to measure the composition of flue gas leaving each reactor. The risers are also fitted with zirconia oxygen probes so that local O_2 content can be measured. There are several ports for measuring pressure and temperature in order to facilitate the control of the pilot and the analysis of the experimental results. All the electric signals from the thermocouples, pressure transducers, gas analyzers, and mass flow controllers are collected in a computer.

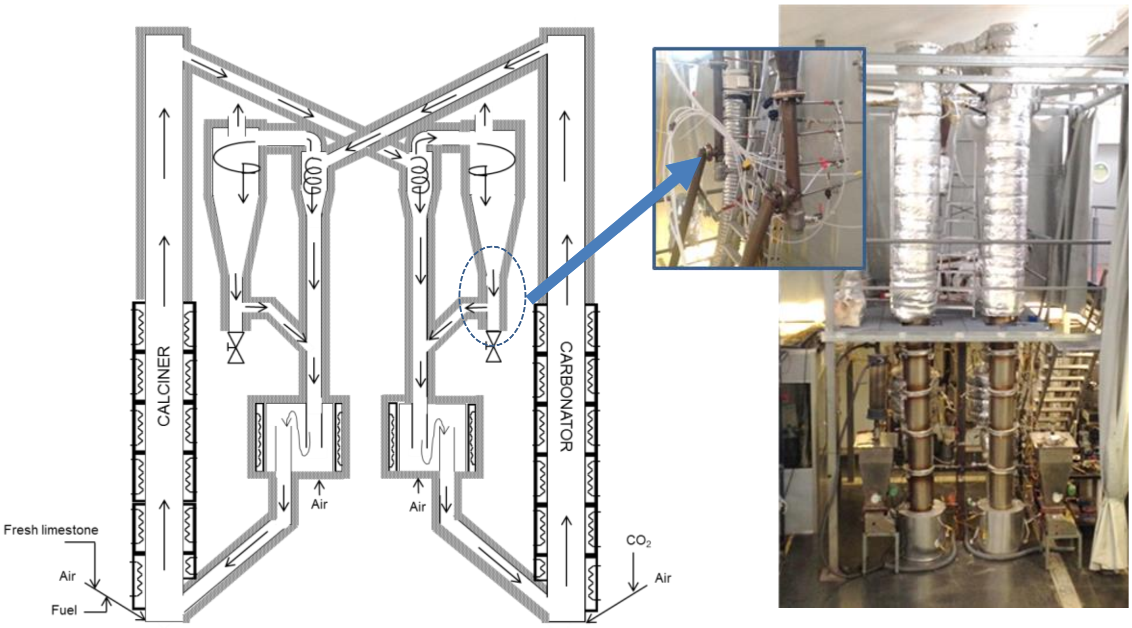

Figure 2.1. Scheme of the 30 kW$_{th}$ pilot after retrofitting a secondary recycle of solids.

The inventory of solids in the carbonator and calciner is estimated by measuring the pressure drop in each riser. There are also solid sampling ports at different locations in the pilot. The solid samples have been characterized to measure rate of reaction towards CO_2 and CO_2 maximum carrying capacity as well as particle size distribution and $CaSO_4$ content. The solid circulation between reactors in this facility can be estimated continuously, by solving an energy balance to the pipe connecting the loop seal and the riser of the carbonator using the temperature of the solids at the inlet and outlet as input. This estimated value was periodically checked using a bypass located below the loop seals, which allows diverting the solid flow to a dead volume during a certain period of time so that the average circulation of solids during the diversion period can be estimated.

2.2 Set up of the secondary recycle

New recycle loops have been installed in the 30 kW$_{th}$ pilot in an attempt to operate with finer particle size distribution in the calcium loop. These recycles are composed by a secondary cyclone to capture the particles leaving the primary cyclone, and a return leg in order to re-inject the fine particles into the stand pipes of the carbonator and calciner as depicted in Figure 2.1. Different configurations have been tested in order to connect the return leg of the secondary cyclones and the stand pipes. Initially, it was decided to use a connection based on an L-valve desing. For this purpose, an elbow was arranged between both elements (see Figure 2.2a). Initial test showed some gas leakeage from the stand pipes of the risers through this L-valve. This resulted in a drastic decrease of the secondary cyclone efficiency and a loss of material from the pilot. For this purpose, a restriction was installed in the inclined pipe connecting the stand pipe in order to minimize the gas lekeage.

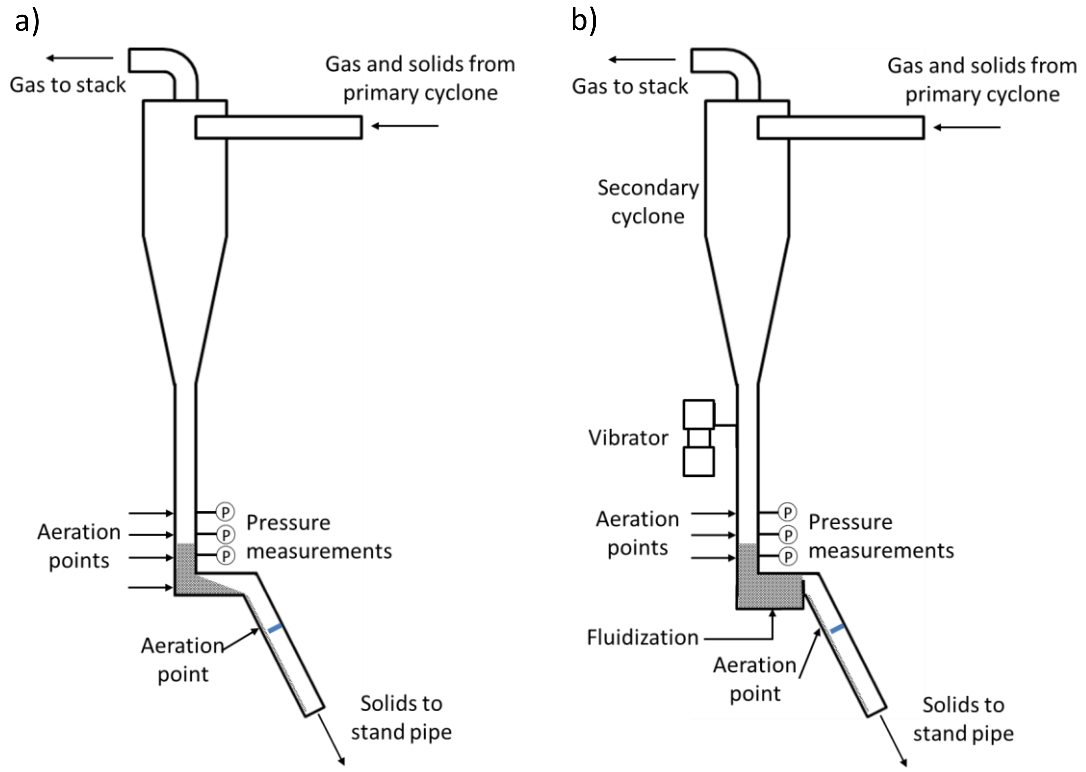

Figure 2.2. Configurations tested for the secondary recycle of solids: a) L-valve design, b) loop seal design.

Pressure measurements were also installed at different points in order to detect the height of the column of solids and possible blockages of solid. Despite, the different aeration points installed, it was not possible to achieve a stable solid circulation of fines through the recycle of solids using the L-valve configuration. However, it must be noted that this is likely to be the problem of the very small scale of the test rig (wall effects) and modest solid circulation.

Therefore, another configuration was tested and it is shown in Figure 2.2.b. In this case, the L-valve was substituted by a small “loop seal” formed by the introduction of a small sheet at the exit of the horizontal section of the standpipe. Initial tests using this configuration showed again the difficulties in fluidizing the fine powders retained in this set up, which lead to several solid pluggings in the secondary cyclone. This was partially solved by installing electric motor vibrators. Once these were introduced it allowed more stable operation and most of the test reported in Anex 2 were carried out under this configuration.

Figure 2.3 shows an example of typical particle size distribution present in the pilot during the tests presented in this work. Typically, the material circulating between reactors in the primary loop presents a larger particle size (dp_{50}=76 µm in this example). The moderate solid separation efficiency of the primary cyclones allows small particles escape towards the recycle loop, where a large fraction of the solids is captured by the secondary cyclones. As a result, the particles circulating through the recycle loops present a smaller particle size (dp_{50}=35 µm). Only solids with fine particle size (typically below 10 µm) leave the system through the stack. These represent a small fraction respect to the total inventory in the pilot and as a result, overall solid mass balance in each experiment can be closed with less than 10% of the total mass of solids lost from the system.

Ca-based materials with particle size below 30 µm are commonly handled in large scale cement plants (Telschow, Frandsen et al. 2012). CSIC received a batch of raw meal from an Italcementi plant in Bilbao (Arrigorriaga) but has been unable to operate the pilot with such fine materials because a highly unsteady solid circulation between reactors is established, due to a frequent plugging of the stand pipes (which are only 50 mm id in this pilot). This has prevented us from achieving CO_2 capture experiments with these materials and it was decided to avoid the operation with fine materials below 70 µm in the primary loop. In order to operate under these conditions, we made use of the recycle loops to purge the system from finest particles.

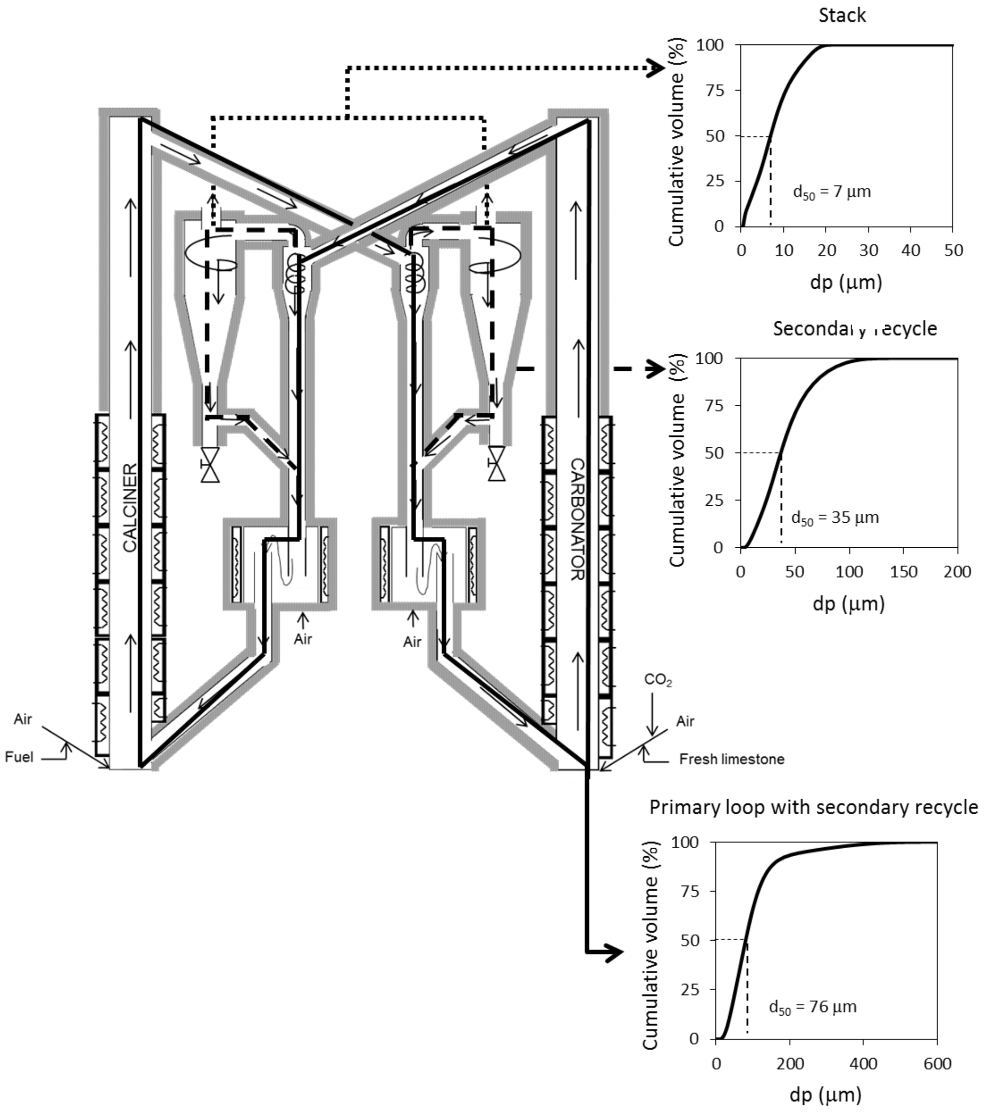

Figure 2.3. Average Particle Size Distributions (PSDs) during a CO_2 capture test with Imeco limestone.

3 EXPERIMENTAL RESULTS AND DISCUSSION

The range of the main operation conditions tested during these experiments is summarized in Table 3.1. A wide range of sorbent activities has been tested, from those of moderate limestone make-up flows up to those corresponding to fresh calcined limestones. Inlet CO_2 concentration up to 27% have been used, including experiments with and without steam. Despite the limitations on particle size (i.e. d_{p50} no less than 70 µm), experimental conditions tested can be considered representative of those expected in most of the CaL process schemes based on circulating fluidized bed reactors. Results presented in this work correspond to the data obtained during more than 85 hours of CO_2 capture tests, where a good closure of the overall carbon balances could be achieved (see discussion below and Annex II). Similarly, experiments with extensive plugging and/or instabilities or a poor closure of gas or solid mass balances were disregarded

Table 3.1. Range of the operating conditions and the main variables during the CO_2 capture tests.

Carbonator temperature (ºC)	T_{carb}	620-725
Carbonator inlet velocity (m/s)	u_{carb}	2.0-3.7
Inlet CO_2 volume fraction to the carbonator	ν_{CO2}	0.10-0.27
Inlet Steam volume fraction to the carbonator	ν_{H2O}	0-0.12
Inventory of solids in the carbonator (kg/m^2)	W_{carb}	15-590
Maximum CO_2 carrying capacity	X_{ave}	0.18-0.66
Solids circulation flowrate (kg/m^{2}s)	G_s	0.9-3.7
Calciner temperature (ºC)	T_{calc}	800-920
Calciner inlet velocity (m/s)	u_{calc}	1.5-3.3
Average particle size in the primary loop (µm)	d_{p50}	74-100
Molar ratio of fresh make-up to inlet CO_2	F_0/F_{CO2}	0-0.55
Experimental CO_2 capture efficiency (%)	E_{carb}	30-95

In order to analyze the effect of the different operating variables, screening experiments have been divided in relatively steady states periods of at least 20 min, where CO_2 inlet and outlet concentrations to the carbonator, temperature, bed inventory and solid circulation rates can be considered constant and can be measured independently. Different CO_2 mass balances are solved and closed in on each of these points in order to validate the consistency of the experimental information and the stability of the facility. In order to facilitate the interpretation of the results presented in this deliverable. Figure 3.1 shows a schematic of the experimental facility and the nomenclature used.

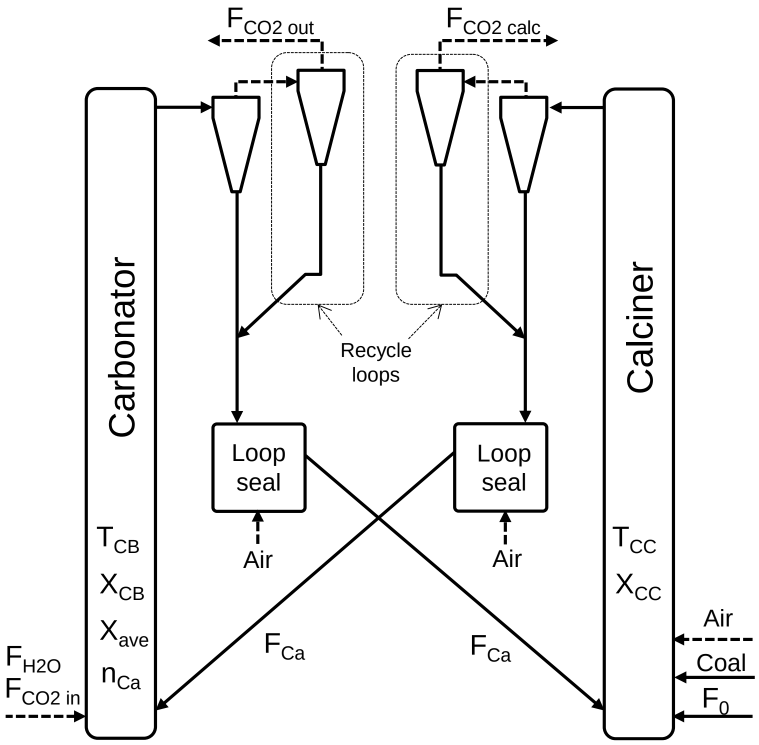

Figure 3.1. Schematics of the pilot plant facility and the main mass flows and operating variables involved in the test campaigns.

As an example of steady states considered, Figure 3.2 shows the results obtained during a particularly stable experimental period of 30 min. The average reactor temperature during this period was 655 ºC and 860 ºC in the carbonator and calciner, respectively. A flue gas flow with a CO_2 concentration of $12\%_v$ is fed to the carbonator, which operated with an inlet gas velocity of 2.0 m/s. In this case, a moderate make-up flow is fed to the calciner (F_0/F_{CO2}= 0.23), which led to a sorbent with a maximum CO_2 carrying capacity (X_{ave}) of 0.32. The average CO_2 capture efficiency during this experiment is 0.8 (normalized E_{carb} 0.85). CO_2 captured from the gas phase is calculated continuously as the CO_2 fed to the carbonator (F_{CO2in}) is known and the molar flow at the exit (F_{CO2out}) can be determined by knowing the flue gas flow leaving the reactor and its composition. Similarly, the CO_2 produced by calcination in the calciner can be calculated by discounting that produced by coal combustion. Figure 3.2b shows the calculated molar flow of CO_2 captured in the carbonator ($F_{CO2capt}$), the molar flow of CO_2 calcined in the calciner ($F_{CO2calc}$). Ideally, under steady state conditions and low make up flows of limestone, the CO_2 captured should be the same as the CO_2 calcined. Indeed, the difference observed in Figure 3.2b is due to the make-up flow of limestone fed into the calciner during this test period. The molar flow of CO_2 at the inlet and exit of the carbonator are used to calculate the capture efficiency, which is defined as follows:

$$E_{carb}=\frac{F_{CO2in}-F_{CO2out}}{F_{CO2in}} \tag{1}$$

When interpreting the performance of the carbonator reactor, it is important to take into account that the maximum CO_2 capture efficiency ($E_{carb\ eq}$) is limited by the minimum CO_2 molar fraction given by the equilibrium (Baker 1962).

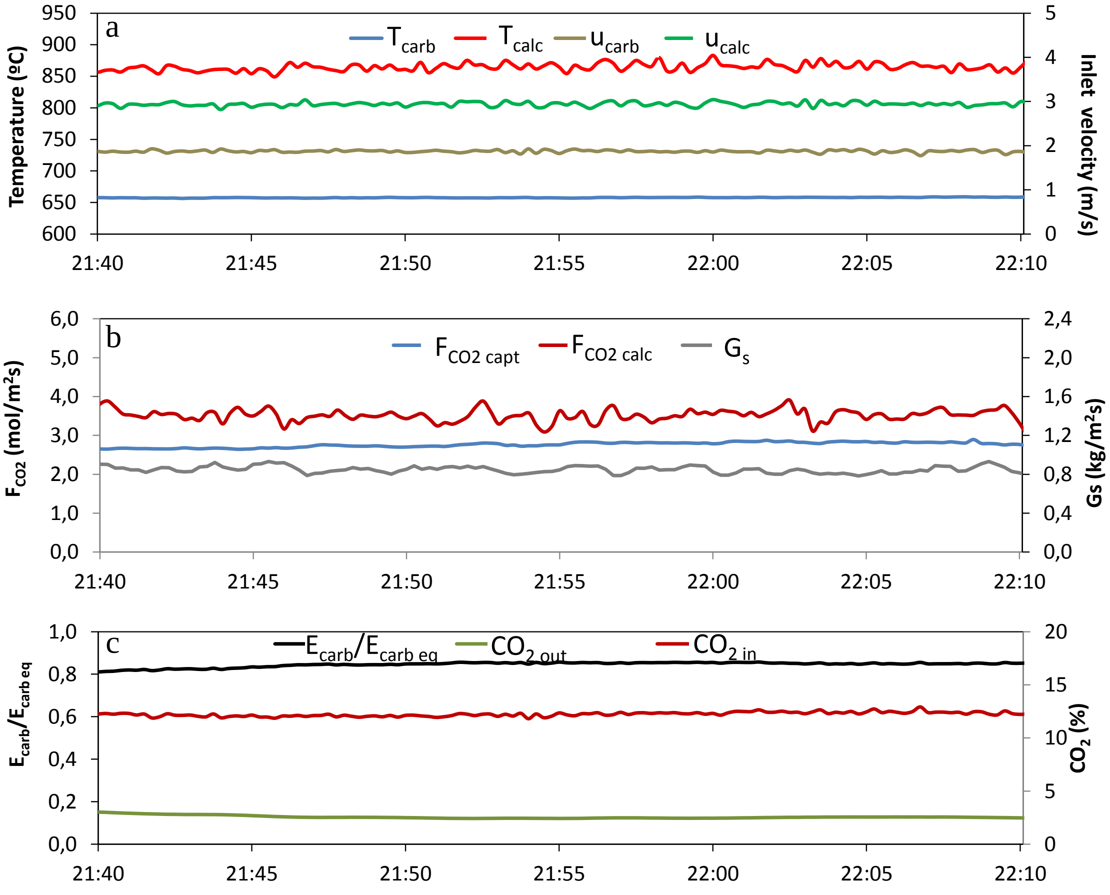

Figure 3.2. Example of a steady state in the 30 kW$_{th}$ experimental facility (W_{carb} = 600 kg/m^2, F_0/F_{CO2} = 0.23, X_{carb}=0.27, X_{calc}=0.08, X_{ave}=0.32, dp_{50} = 97 µm).

Another relevant mass balance that should be fulfilled is that corresponding to the molar flow of $CaCO_3$ formed in the circulating stream of solids through the carbonator which should be the same as the molar CO_2 captured from the gas phase. The molar flow of $CaCO_3$ can be calculated for each steady stated from the solid circulation between reactors and the carbonate content measured from the solids taken in the carbonator (X_{carb}) and calciner (X_{calc}). The calculated molar flow of $CaCO_3$ during the test presented in Figure 3.2b was 2.7 mol/m^{2}s, which matches the CO_2 capture from the gas phase.

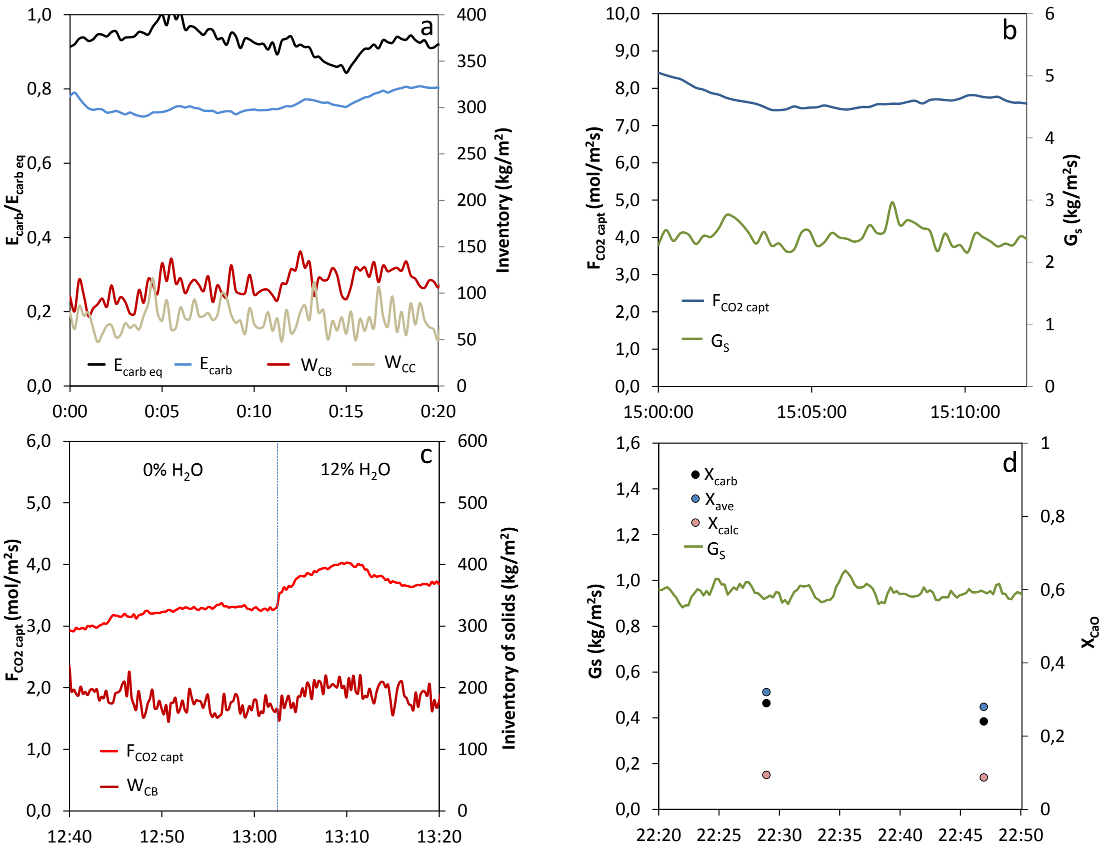

Figure 3.3. Example of experimental results a) Test operating with high activity materials (T_{carb}= 700 ºC, u_{carb} = 2.8 m/s, ν_{CO2} = 0.18, X_{ave}=0.47, G_s=2.7 kg/m^{2}s, W_{carb}=105 kg/m^2, dp_{50} = 75 µm); b) Test operating with a CO_2 concentration of 27% (T_{carb}= 704 ºC, u_{carb} = 2.6 m/s, ν_{CO2} = 0.26, X_{ave}=0.34, G_s=2.2 kg/m^{2}s, W_{carb}=117 kg/m^2, dp_{50} = 77 µm); c) Test showing the effect of steam on CO2 capture (T_{carb}= 673 ºC, u_{carb} = 2.5 m/s, ν_{CO2} = 0.14, X_{ave}=0.19, G_s=1.0 kg/m^{2}s, W_{carb}=190 kg/m^2, dp_{50} = 78 µm); d) Test operating with limited solid circulation between reactors (T_{carb}= 674 ºC, u_{carb} = 2.0 m/s, ν_{CO2} = 0.18, X_{ave}=0.32, Gs=0.9 kg/m^{2}s, W_{carb}=540 kg/m^2, dp_{50} = 86 µm).

Another example characteristic of CaL operating with a high activity sorbent is shown in Figure 3.3a. The X_{ave} during this test was 0.47 and with an average particle diameter (d_{p50}) of 75 µm. This fine solids results into a low inventory in the circulating fluidized bed reactors (around 100 kg/m^2 in the carbonator and 75 kg/m^2 in the calciner). Almost the maximum capture efficiency allowed by the equilibrium (around 80% when the carbonator is operating at 700 ºC) is achieved, even with limited very modest inventory of solids in the carbonator. Figure 3.3b shows a representative example of a CaL operating with high CO_2 load. The inlet concentration during this test was 26% and a CO_2 molar flow at the inlet of 9.6 mol/m^{2}s. An average CO_2 capture efficiency of 0.78 was achieved by sustaining a solid circulation of 2.2 kg/m^{2}s between reactors and a sorbent with a CO_2 carrying capacity of 0.34.

As indicated above, several tests were carried out by feeding steam with the flue gas. Figure 3.3c shows an experimental period of 40 minutes with an inlet CO_2 concentration of 14%$_v$. At 13:02, steam flow of 2.0 kg/h was injected with the flue gas while the air flow was reduced to maintain constant the other operation conditions (i.e., ν_{CO2}, gas velocity in the carbonator, inventory of solids). As can be seen, the presence of steam increases the flow of CO_2 captured in the carbonator from 3.3 mol/m^{2}s up to 3.8 mol/m^{2}s. This positive effect of steam on CaO carbonation has been reported in the literature by several authors (Manovic and Anthony 2010, Arias, Grasa et al. 2012, Donat, Florin et al. 2012, Manovic, Fennell et al. 2013).

In order to validate carbonator models, it is helpful to test operation conditions with low CO_2 capture efficiencies. As example, Figure 3.3d shows an experimental period where the CO_2 capture efficiency is limited by the solid circulation between reactors. The low circulation of solids (0.9 kg/m^{2}s) and the high inventory of solids in the carbonator (540 kg/m^2) led to a long residence time of the particles with almost reached their maximum conversion (X_{ave}=0.32).

In order to analyse the carbonator performance in a quantitative manner, a methodology similar to the one proposed in previous works when testing power plant configurations has been applied in this work. The key assumption is that the carbonator behaves as a perfect mixed reactor for the solids (Charitos, Rodriguez et al. 2011, Rodríguez, Alonso et al. 2011). In steady states, the CO_2 reacting with the inventory of CaO particles is the same as that being removed from the gas phase.

$$\begin{pmatrix} CO_2 \text{ removed} \\ \text{from the gas phase} \end{pmatrix} = \begin{pmatrix} CO_2 \text{reacting} \\ \text{with CaO in the bed} \end{pmatrix} \tag{2}$$

As indicated above, the molar flow of CO_2 entering and leaving the carbonator are continuously determined in the experiments. The molar flow of CO_2 reacting with the CaO particles in the carbonator bed can be calculated as the product to the average reaction rate of the solids at carbonator conditions and the active inventory of sorbent ($n_{Ca,\ active}$)

$$F_{CO2in} E_{carb} = n_{Ca,active} \left(\frac{dX}{dt} \right)_{reactor} \tag{3}$$

Regarding the average reaction rate of the solids, it can be assumed a constant rate until the particles achieve their maximum CO_2 carrying capacity (X_{ave}) (Alonso, Rodríguez et al. 2009). From this point, the reaction rate becomes too low and can be considered zero. More accurate reaction rate models could be applied (Martínez, Grasa et al. 2016); however this simple approach for the kinetics of carbonation is consistent with the experimental data available from TG tests (see for example (Grasa et al. 2008)) and consistent for the level of detail and modest accuracy of the experimental information concerning solids behaviour from this pilot. Thus, the particle reaction rate can be calculated as a function of the CO_2 carrying capacity of the sorbent (X_{ave}) and the average CO_2 concentration in the carbonator as follows:

$$\left(\frac{dX}{dt}\right)_{reactor} = k_s\,\varphi\,X_{ave}\left(\overline{\upsilon_{CO2} - \upsilon_{CO2eq}}\right) \tag{4}$$

where k_s is a constant reaction rate of the limestone used and φ is a gas-solid contacting factor as defined in previous works (Rodríguez, Alonso et al. 2011). The active inventory of sorbent is composed by those particles that have not reached their maximum CO_2 carrying capacity (X_{ave}). Assuming that the carbonator behaves as a perfect mix reactor, the fraction of active solids in the bed (f_a) can be calculated as the fraction of particles with a residence time lower than that required to increase the carbonate content of the particles from X_{calc} to X_{ave} under carbonator conditions (t*):

$$f_a = \left(1 - e^{\frac{-t^*}{n_{Ca}/F_{Ca}}}\right) \tag{5}$$

where n_{Ca} is the total inventory of calcium in the carbonator and F_{Ca} the molar flow of calcium between reactors. The characteristic reaction time (t*) can be estimated using the X_{calc} and X_{ave} values measured from the samples taken from the reactors and using the reaction rate define in Eq. 4.

$$t^* = \frac{X_{ave} - X_{calc}}{k_s\,\varphi\,X_{ave}\,(\upsilon_{CO2} - \upsilon_{CO2eq})} \tag{6}$$

By introducing Eqs. 4 and 5 in Eq. 3, all the CaL operation parameters are linked in the following expression:

$$F_{CO2}\,E_{Carb} = n_{Ca}\;f_{Ca}\,k_s\,\varphi\,X_{ave}\left(\overline{\upsilon_{CO2} - \upsilon_{CO2eq}}\right) \tag{7}$$

The apparent constant reaction rate ($k_s\varphi$) can be calculated as fitting parameter by comparing both terms of Eq. 7. A value of $k_s\varphi$=0.36 s^{-1} has been obtained using the new set of experimental results obtained under experimental conditions closer to those expected in cement plants. This value is consistent with that found in previous works, including those obtained in a 1.7 MW_{th} testing facility capturing CO_2 from a power plant flue gases (Charitos, Rodriguez et al. 2011, Arias, Diego et al. 2013).

Finally, in order to correlate the CO_2 capture efficiency with the main operation variables in the carbonator, Eq. 7 can be rearranged into the following expression:

$$E_{Carb} = \tau_{active}\, k_s\, \varphi \left(\overline{\upsilon_{CO2} - \upsilon_{CO2eq}}\right) \tag{8}$$

were τ_{active} is the active space time ($n_{Ca}f_{Ca}X_{ave}/F_{CO2}$) (Charitos, Rodriguez et al. 2011). Figure 3.4 shows the equilibrium normalized CO_2 capture efficiency (E_{carb}/E_{carbeq}) against the active space time.

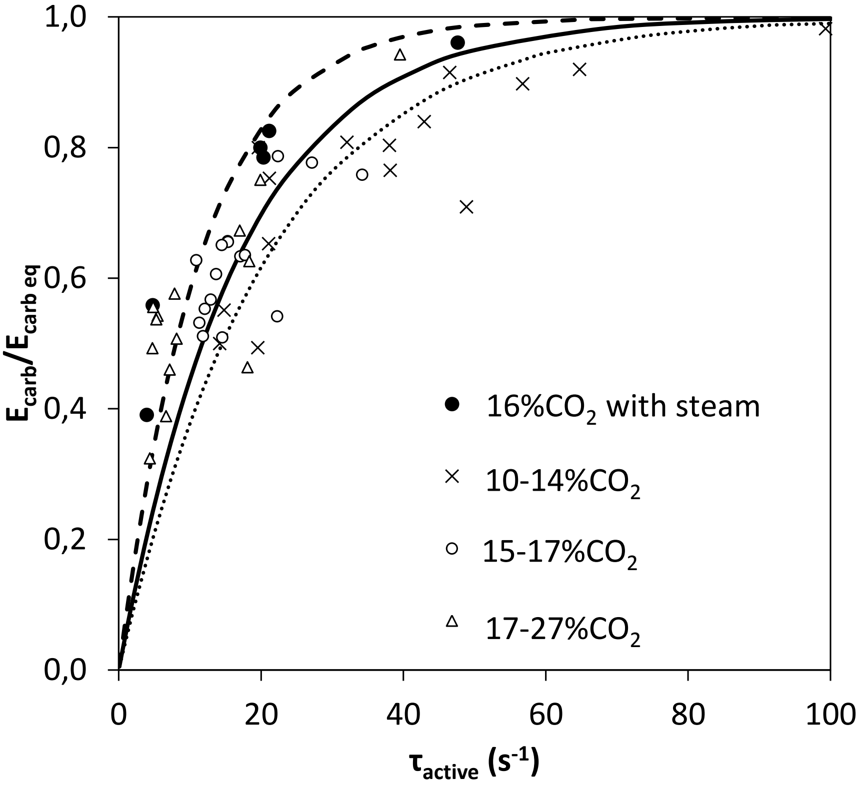

Figure 3.4. Normalized CO_2 capture efficiency as a function of the active space time (model lines: T_{carb}=655 ºC, $k_s\varphi$=0.36 s^{-1}, dot line υ_{CO2in}=0.13, solid line υ_{CO2in}=0.16 dash line υ_{CO2in}=0.23).

The solid line corresponds to the values calculated using Eq. 8 and the average values of the parameters found in the experimental data obtained for each series of data. Despite the dispersion, there is a reasonable agreement between the experimental results and those predicted by the model when grouping the data around three representative average partial pressures of CO_2 used to estimate the model curves with equation (8). The dispersion in data points of Figure 3.4 is due to the uncertainties in the experimental determination of τ_{active}, that is a combination of three experimental variables with inherent difficulties for more precise measurement in this small pilot (in particular solid circulation rates and a representative value of X_{ave} for the entire solid inventory in the carbonator). Regarding the effect of the steam on carbonator performance, we have not attempted to perform an exhaustive analysis of due limited experimental tests carried out. However, as can be seen in Figure 3.4, the experimental CO_2 capture efficiency achieved during the experiments with steam in the flue gas is systematically above the predicted values by the model (solid line). This confirms the positive effect of the steam on the carbonator performance observed in other pilot plants (Symonds, Lu et al. 2012, Dieter, Bidwe et al. 2014, Duelli Varela, Charitos et al. 2015).

4 CONCLUSIONS

CO_2 capture experiments by Calcium looping have been carried out in this work to screen experimental conditions resembling conditions closer to those in cement plants. For this purpose, a 30 kW_{th} pilot has been retrofitted to operate in conditions of higher carbonator CO_2 load, more active sorbent, and smaller particle sizes in the solid circulation loop. The use of materials with low particle sizes has resulted into a lower inventory of solids in the carbonator (as low as 75 kg/m2) at typical gas velocities in the carbonator reactor of the pilot (around 2.5 m/s). Under these conditions, and despite the high CO_2 load to the carbonator and low inventories, it is possible to achieve high capture efficiencies (close to those limited by the equilibrium) when the high sorbent activity, characteristic of cement application of calcium looping, are used. The apparent carbonation constant rate calculated from all experimental results in the pilot is $0.36s^{-1}$, which is consistent with the equivalent parameter found in previous works oriented to capture CO_2 from power plants. This reactivity constant increases (perhaps as much as 25%) when steam is present in the carbonator, in agreement with other results under power plant flue gas conditions. However, a drawback from these same findings is that the carbonation reaction rates (referred to a unit of active CaO in the particle) do not seem to improve significantly when reducing the particle size of the particles. Therefore, in order to achieve maximum capture efficiencies in future large pilot testing it is going to be important to operate the carbonator in order to retain a sufficiently large inventory of solids (at the expense of increased circulation rates and pressure drop of gases) and/or guaranty a very high activity of the material (i.e. minimising bellite formation in the CaL oxyfired calciner). Despite these remarks, the results presented in this work provide further confidence about the scalability of CaL technology for capturing CO_2 in cement plant, because the operation under conditions more relevant for cement application yields fundamental parameters very close to those developed for power plant configurations, that have been tested and validated at larger pilot level by a number of studies around the world.

5 NOTATION

E_{carb}		CO_2 capture efficiency
$E_{carb\ eq}$		maximum CO_2 capture efficiency allowed by the equilibrium
f_a		fraction of active particles in the carbonator bed
F_{Ca}	mol/m^{2}s	Ca molar flow circulating between reactors
$F_{CO2calc}$	mol/m^{2}s	molar flow of CO_2 produced by calcination leaving the calciner
F_{CO2in}	mol/m^{2}s	molar flow of CO_2 entering the carbonator
F_{CO2out}	mol/m^{2}s	molar flow of CO_2 leaving the carbonator
F_O	mol/s	make-up flow of limestone
G_s	kg/m^{2}s	solid flow circulation rate from carbonator to calciner
k_s	s^{-1}	constant reaction rate
n_{ca}	mol/m^2	total inventory of Ca in the carbonator bed
t*	s	time required to increase the carbonate content from X_{calc} to X_{ave}
T_{calc}	ºC	average calciner temperature
T_{carb}	ºC	average carbonator temperature
u_{calc}	m/s	calciner gas velocity
u_{carb}	m/s	carbonator gas velocity
W_{CC}	kg/m^2	total inventory of solids in the calciner
W_{CB}	kg/m^2	total inventory of solids in the carbonator
X_{ave}		average CO2 carrying capacity
X_{calc}		molar carbonate content of the solid in the calciner
X_{carb}		molar carbonate content of the solid in the carbonator
φ		gas-solid contacting effectivity factor

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7 ANNEX I: CHARACTERIZATION OF LIMESTONES USED

Two high purity limestones have been used in this work. The chemical composition shown in Table 7.1 has been measured by X-ray fluorescence (SRS 3000 Bruker). Figure 7.1 shows the decay in the CO_2 carrying capacity of both sorbent with the number of calcination/carbonation cycles. These tests have been carried out using an in-house thermogravimentric analyzer designed for long multicycle carbonation/calcination testing (more details can be found in M 12.2). Calcination was carried out in air at 950 ºC for 10 minutes and carbonation under 10% CO_2 in air at 650 ºC for 10 minutes. The activity decay of sorbent derived from Brecal limestone is more pronounced but both sorbents present a similar residual conversion after 50 cycles.

Table 7.1 Chemical composition of used limestones

%wt.	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SrO	CaO	TiO_2	Fe_2O_3	SO_3	LOI*
Imeco	0	0.82	0.43	0.91	0	0.03	54.20	0	0.38	0.07	43.21
Brecal	0	0.71	0.30	1.49	0	0.03	54.28	0	0.27	0.05	43.22

*LOI: Loss On Ignition

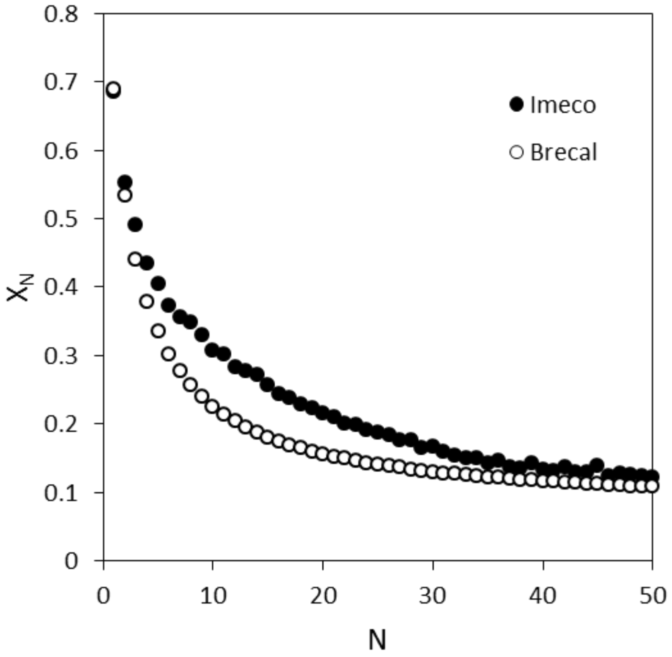

Figure 7.1. Evolution of the maximum conversion of CaO with the number of carbonation-calcination cycles.

8 ANNEX II: EXPERIMENTAL DATA SETS

This annex includes the experimental data sets corresponding to the campaigns carried out in the 30 kW$_{th}$ facility. Attrition tests carried out during the commissioning of the secondary recycle correspond to Tests 1-5. The CO_2 capture campaigns correspond to Tests 6-12. For each test, the evolution of the main variables affecting these tests is presented in several graphs. In addition, the composition of the samples taken during the experiments is included together with the particle size distribution of selected samples. This information is complemented by a description of the test conditions and main event taking place.

Test 1

This test was used as a reference for attrition measurements with no secondary recycle as the connections between secondary cyclones and the standpipes of the primary cyclones were blocked. The main objective of the test was measured the change in the particle size distribution (PSD) of the solids in the facility due to the circulation of solids without calcination and during the first calcination as it was known that the attrition is higher during this stage.

The limestone used was Brecal and around 20 kg of fresh limestone were fed at the beginning roughly half distributed between carbonator and calciner. A constant mass air flow rate of air of 15 Nm^3/h and 4 Nm^3/h was fed to the risers and loop-seals, respectively.

Figure 8.1 shows the main operating variables from the moment when the average temperature in both risers was around 560 ºC to the final of the test (i.e. when a molar calcium carbonate content around 0.05 was detected in the samples from calciner).

Figure 8.1 a. shows the average temperature of each riser as well as the inlet velocities. The average carbonator temperature was almost constant around 575 ºC maintained by the electrical ovens and the circulation of solids from the calciner. The average inlet velocity to the carbonator was constant and around 2.3 m/s. The average temperature in the calciner increased from 560 ºC to 725 ºC between 9:40 and 11:06. During this period, an average coal feed rate of 1.8 kg/h was fed in order to increase the temperature and the solids circulation rate without calcination. Then, the coal feed rate was increased to 3 kg/h in order to drive the calcination of the batch of $CaCO_3$ as fast as possible. As result, the average temperature of the calciner was raised to around 865 ºC which increased the inlet velocity in the calciner from 2.3 m/s to 3 m/s.

The solids inventory in the carbonator (Figure 8.1 b) was around 120 kg/m^2 during the entire test whereas the solids inventory in the calciner decreased from 130 kg/m^2 at 9:40 h to a negligible value at 11:35 h mainly due to the mass loss during calcination and the increase of the gas velocity. The solids circulation rate was 0.4 kg/m^{2}s at 9:40 and increased up to 0.75 kg/m^{2}s at 10:26 h due to the increase in velocity. After this point, it gradually decreased up to 0.05 kg/m^{2}s at the end of the test. The peaks observed on the solid circulation at 10:33 and 10:55 correspond with the measurements of the solids circulation rate and the extraction of samples.

The gas concentration at the exit of the calciner measured by the on-line analyzer is shown in Figure 8.1c. Between 9:48 and 11:04 h, during the heating without calcination, the average exit concentrations of O_2, CO_2 and CO were 13.3 vol.%, 7.8 vol.% and 172 ppmv respectively. Between 11:24 and 12:29 h, after increasing the coal feed rate, the average exit concentrations of O_2, CO_2 and CO were 6.07 vol.%, 16.1 vol%, and 161 ppmv respectively. In order to check that no reactions were taken place in the carbonator, the analyzer measured the exit gas concentration of the carbonator between 12:30 and 12:50 h. Finally, between 12:52 and 14:24 h the average exit O_2, CO_2 and CO concentrations were 6.3 vol.%, 14.1 vol% and 139 ppmv respectively. From these measurements, it is possible to estimate the CO_2 molar flow rate from calcination shown in Figure 8.1.d. Between 11:24 and 12:29 h the average CO_2 molar flow rate from calcination was 1.2 mol/m^{2}s, whereas between 12:52 and 14:24 h the average value decreased to 0.4 mol/m^{2}s due to the decreased in solids circulation rate.

After the test, all solids in the facility were removed, weighted and analyzed separately by the C/S analyzer and the final mass balance was closed at 90 % (Table 8.1). During the test, solid samples from carbonator (CB), calciner (CC), measurements of solids circulation rates (CIRC) and secondary cyclones (2CB and 2CC) were extracted with a frequency around 20 min for carbonate content analysis (Table 8.2) and PSD analysis (Figure 8.2).

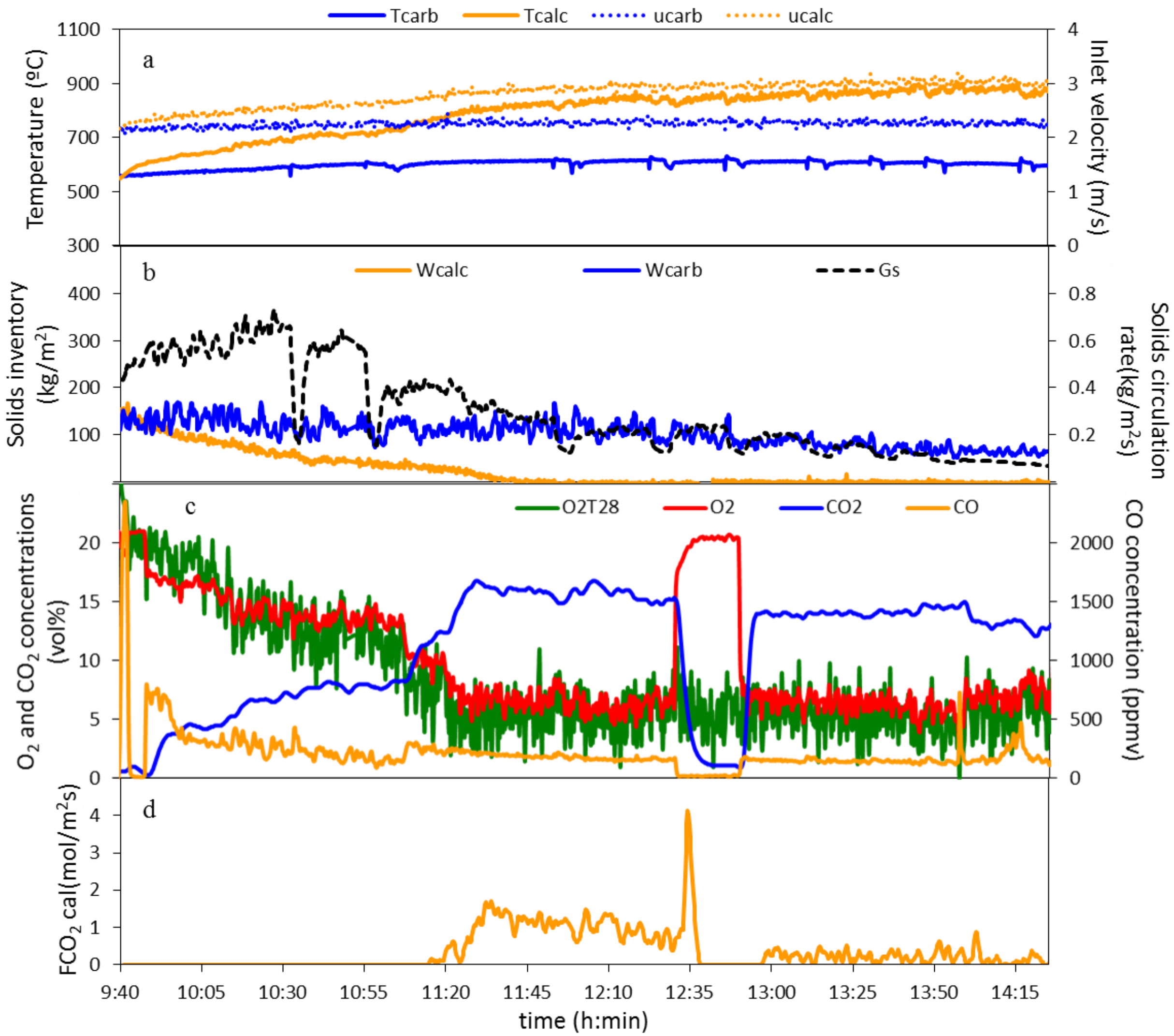

Figure 8.1. Experimental conditions during test 1. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in the risers and solids circulation rate. c. Gas concentrations measured by the on-line analyzer at the exit of calciner. d. Molar CO_2 flow rate from calcination.

Table 8.1. Final mass balance of test 1

Test 1							
Inlets				Outlets			
	Weight (kg)	C (wt%)	Ca (mol)		Weight (kg)	C (wt%)	Ca (mol)
Initial batch	19.4	11.8	190.8	Calciner	1.3	9.1	15.2
Initial silo	0	11.8	0	Carbonator	1.2	10.1	13.4
Final silo	0	11.8	0	LP-CC	2.6	6.3	35.3
Silo fed	0	11.8	0	LP-CB	2.0	5.3	28.6
				Circulation	0.5	3.7	7.1
				2nd Cyclones	4.4	10.1	48.4
				Samples	1.8	6.7	24.1
Total in			190.8	Total out	13.7		171.9
Global mass balance (%)				90			

Table 8.2. Analysis of samples extracted during test 1.

Sample	wC (%)	wS(%)	ID INCAR
9:33 2CB	11.7	0.144	
9:33 2CC	12.7	0.148	
10:33 CC	10.9	0.156	15-70153
10:33 CB	11.2	0.142	15-70152
10:33 CIRC	10.9	0.156	15-70154
10:33 2CB	11.3	0.141	15-70155
10:33 2CC	11.3	0.133	15-70156
10:55 CB	10.8	0.157	15-70157
10:55 CC	9.6	0.166	15-70158
10:55 CIRC	10.8	0.167	15-70159
10:55 2CB	11.1	0.158	15-70160
10:55 2CC	10.4	0.152	15-70161
11:53 CC	6.8	0.170	
11:53 CB	10.4	0.169	
11:53 CIRC	6.6	0.184	
11:53 2CB	8.9	0.159	
11:53 2CC	9.0	0.176	
12:23 CC	3.6	0.221	
12:23 CB	6.7	0.178	
12:23 CIRC	5.0	0.200	
12:23 2CB	7.6	0.186	
12:23 2CC	7.0	0.260	
12:45 CC	2.6	0.261	
12:45 CB	5.8	0.216	
12:45 CIRC	4.1	0.223	
12:45 2CB	6.6	0.260	
12:45 2CC	6.8	0.296	
13:12 CC	2.1	0.243	
13:12 CB	5.5	0.239	
13:12 CIRC	3.8	0.235	
13:12 2CB	6.0	0.275	
13:12 2CC	5.8	0.333	
13:30 CC	1.7	0.287	
13:30 CB	5.0	0.250	
13:30 CIRC	3.6	0.267	
13:30 2CB	5.6	0.278	
13:30 2CC	5.6	0.353	
13:47 CC	1.4	0.293	15-70163
13:47 CB	4.1	0.274	15-70162
13:47 CIRC	3.8	0.296	15-70164
13:47 2CB	6.4	0.280	15-70165
13:47 2CC	5.5	0.375	15-70166
14:16 CC	1.4	0.325	15-70168
14:16 CB	4.5	0.261	15-70167
14:16 CIRC	3.9	0.286	15-70169
14:16 2CB	4.9	0.334	15-70170
14:16 2CC	5.2	0.389	15-70171

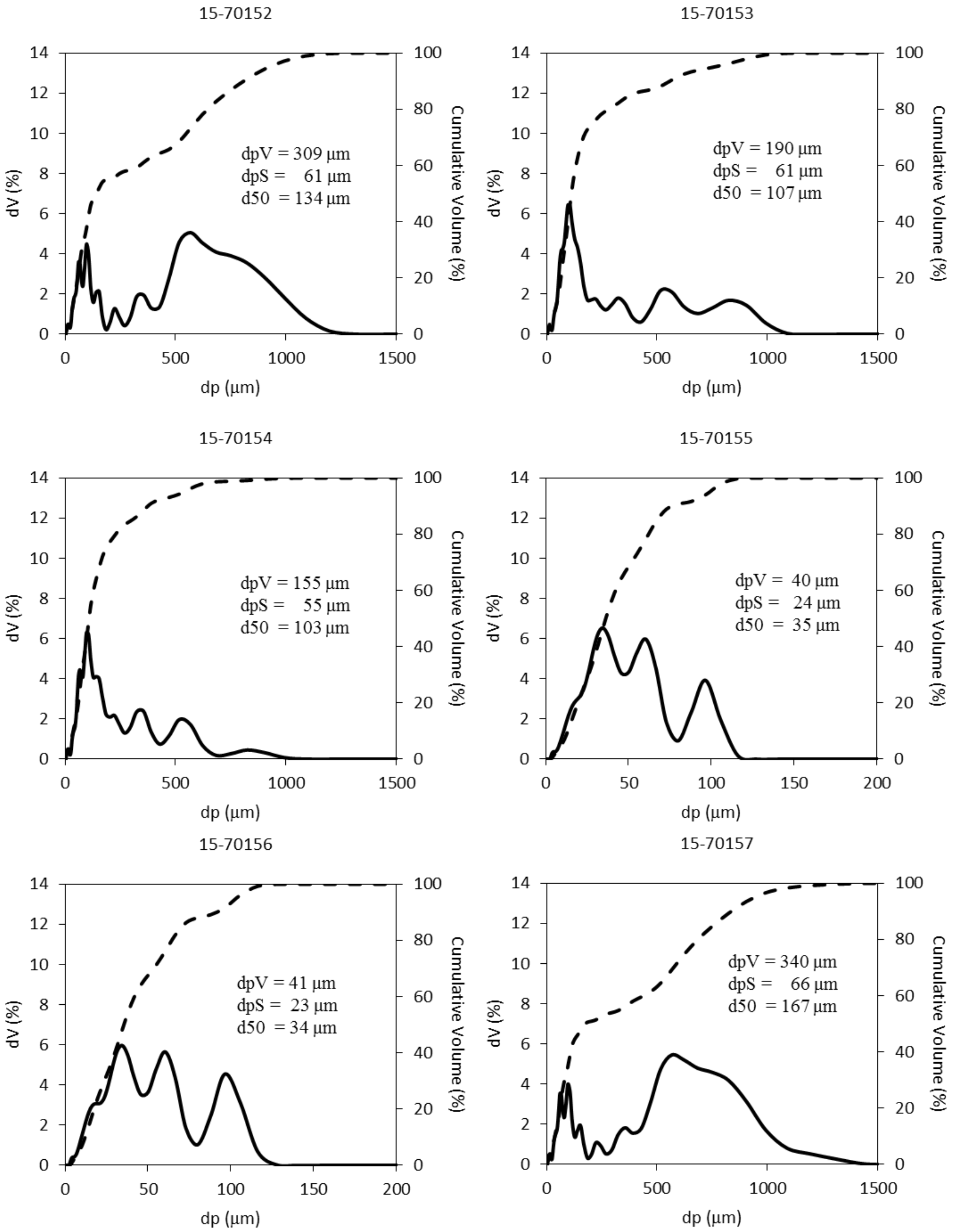

Figure 8.2. Particle size distributions of the samples extracted during test 1

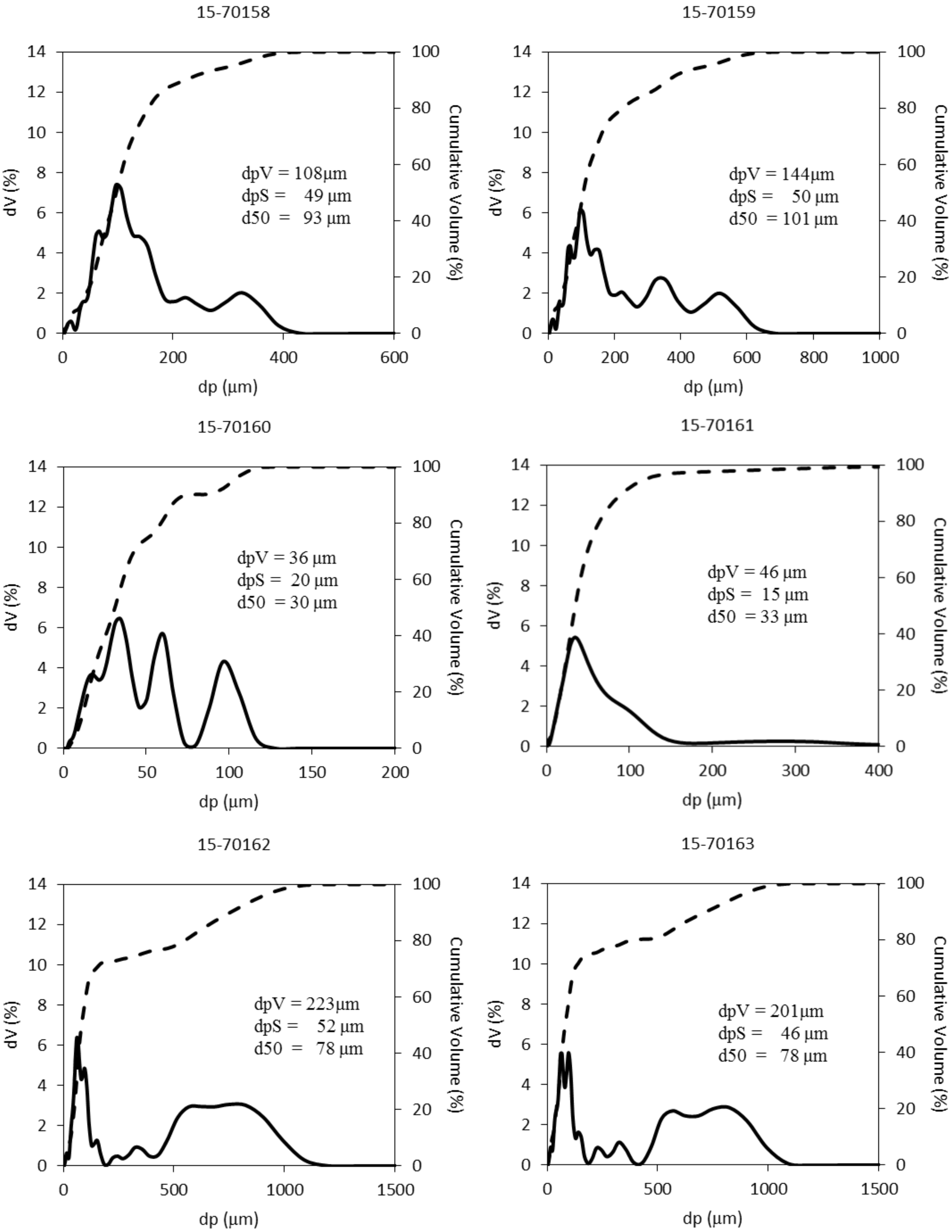

Figure 8.2. (cont.). Particle size distributions of the samples extracted during test 1

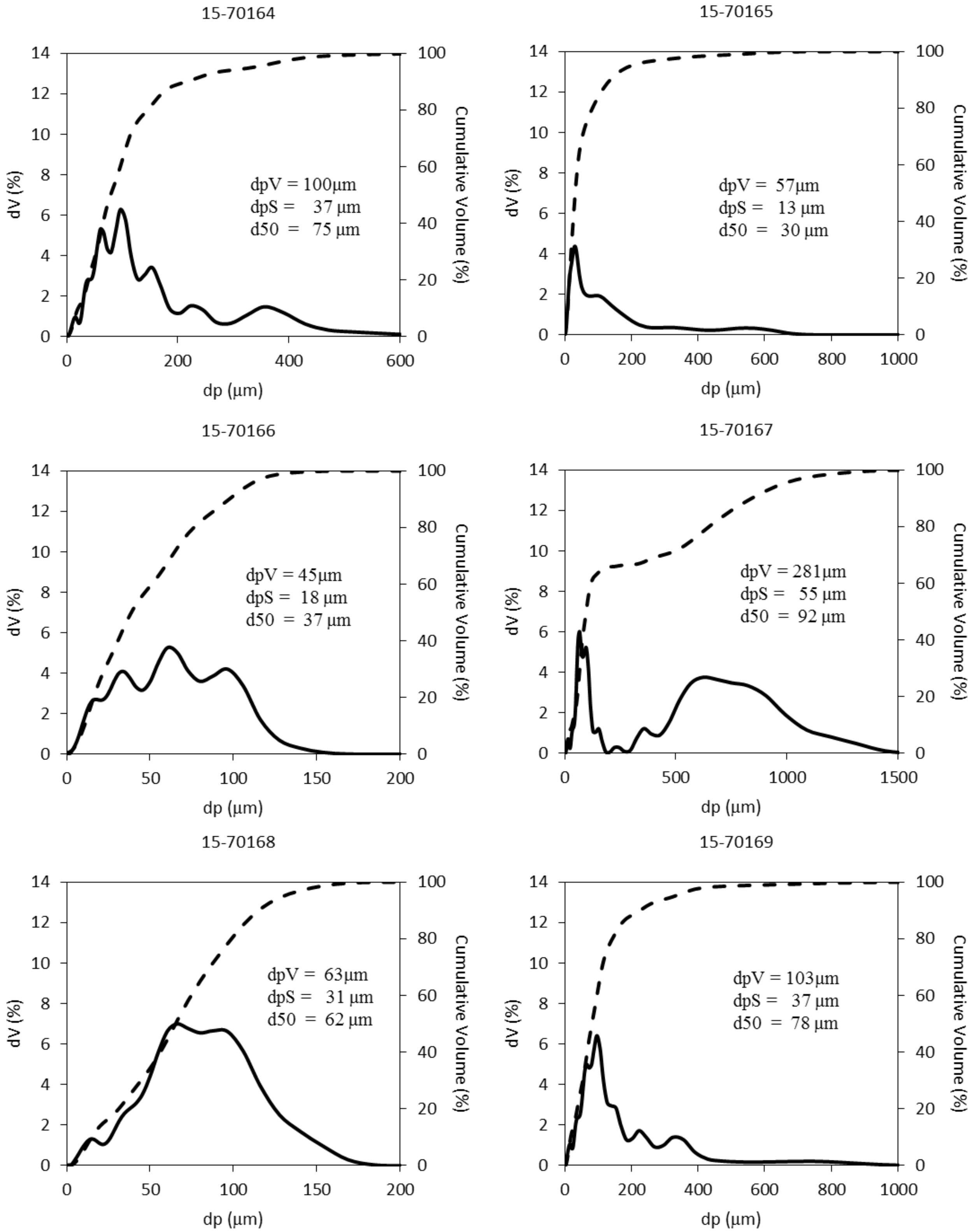

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Figure 8.2. (cont.). Particle size distributions of the samples extracted during test 1

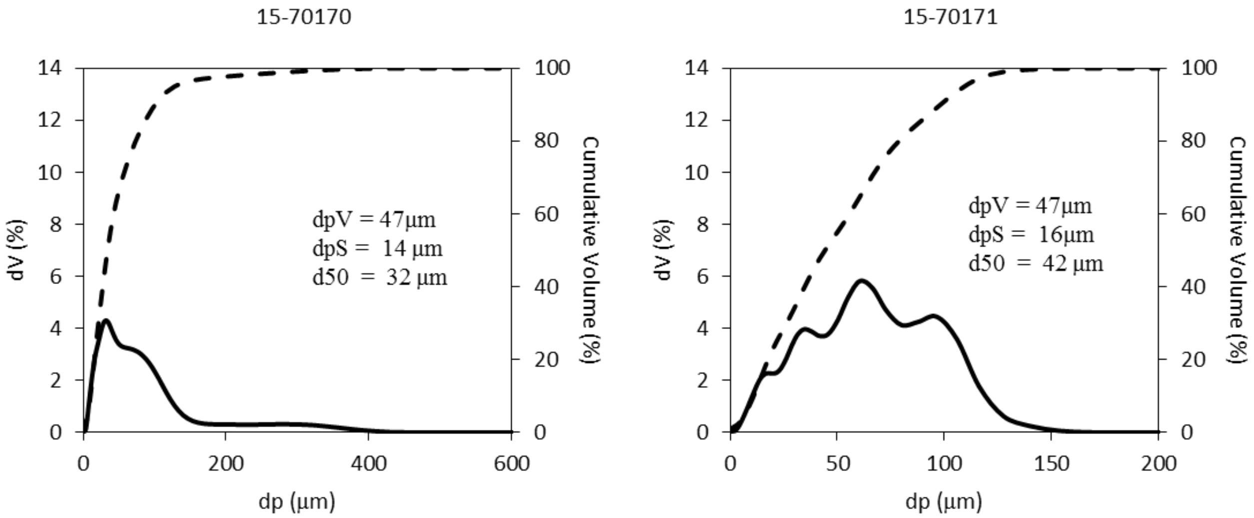


Figure 8.2. (cont.). Particle size distributions of samples extracted during test 1.

Test 2

This test was carried out with the secondary recycle active. The connections were of an L-valve type and they were fully opened without any restrictions (i.e. 50 mm). The objective was the same as in Test 1 (i.e. measure the change in the PSD due to the circulation of solids without calcination and during first calcination). During this test an important leakage of air through secondary loop from the stand pipes of risers was detected. This affected drastically to the efficiency of the secondary cyclones and a large part of the inventory of solids was lost for the facility.

Around 20 kg of fresh limestone was fed at the beginning roughly half distributed between carbonator and calciner. The experimental procedure was the same as in the previous test (i.e. a constant mass flow rate of air was fed to the risers and loop-seals, it was 15 Nm^3/h and 4 Nm^3/h respectively). Figure 8.3 shows the main operating variables from the moment when the coal started to be fed to the end of the test.

Figure 8.3 a. shows the average temperature of each riser as well as the inlet velocities. The average carbonator temperature was almost constant around 640 ºC maintained by the electrical ovens and the solids circulation rate. The average inlet velocity to the carbonator was constant and around 2.1 m/s. The average temperature in the calciner increased from 670 ºC at 11:30 h to 780 ºC at 12:29 h by burning an average coal feed rate of 1.3 kg/h in order to increase the temperature and the solids circulation rate without calcination. Then, the coal feed rate was increased up to 2.8 kg/h in order to increase the calciner temperature to carry out the calcination of the batch as fast as possible and the average temperature of the calciner increased up to around 900 ºC. As a consequence the inlet velocity in the calciner increased from 2.5 m/s to 3.2 m/s during the test. Between 15:54 and 16:48 the coal feeding was interrupted and the air flow rates were reduced in order to facilitate the feeding of solids directly to the carbonator and for checking the circulation path.

The solids inventory in the carbonator (Figure 8.3 b) decreased from 250 kg/m^2 at to values around 55 kg/m^2 even when additional solids were fed to the carbonator (as for example at 12:35 where an increase of the carbonator inventory can be seen). The solids inventory in the calciner decreased from 140 kg/m^2 at 11:30 h to values no detectable from 12:53 h to the final due to the calcination. The solids circulation rate was 1.4 kg/m^2s at 11:30 h and decreased to 0.35 kg/m^2s at the end of the test. The sharp peaks observed in this curve (for example at 12:00 h) correspond again with the measurements of the solids circulation rate.

The gas concentration at the exit of the calciner measured by the on-line analyzer was shown in Figure 8.3 c. Between 11:42 and 12:45h, when the coal was fed for heating without calcination, the average exit concentrations of O_2, CO_2, and CO were 13.2 vol.%, 8.8 vol.% and 118 ppmv respectively. Between 12:52 and 15:56 h, when the calcination took place, the average exit gas concentrations of O_2, CO_2 and CO were 8.7 vol%, 14.2 vol.% and 177 ppmv respectively. Between 15:55 and 16:48 the exit gas concentrations correspond with air, as the coal feeding was interrupted. Finally, between 17:10 and 18:43 h the average exit O_2, CO_2 and CO concentrations were 7.1 vol.%, 13.5 vol.% and 309 ppmv. The CO_2 molar flow rate from calcination is shown in Figure 8.3.d. During all test the average CO_2 molar flow rate from calcination was lower than 0.2 mol/m^2s.

After the test, all solids in the facility were removed, weighted and analyzed separately by the C/S analyzer and the final mass balance was closed at 67 % (Table 4.3). During the test, solid samples from carbonator (CCA), calciner (CBA), measurements of solids circulation rates (CIRC) and secondary cyclones (2CBA and 2CCA) were extracted with a frequency around 30 min for carbonate content analysis (Table 4.4) and PSD analysis (Figure 8.4).

From the analysis of PSD from secondary cyclones (15-69852, 15-69853, 15-69857, 15-69858) it was concluded that solids from the primary standpipes flowed to the secondary cyclones due to the connections of secondary recycle were full opened.

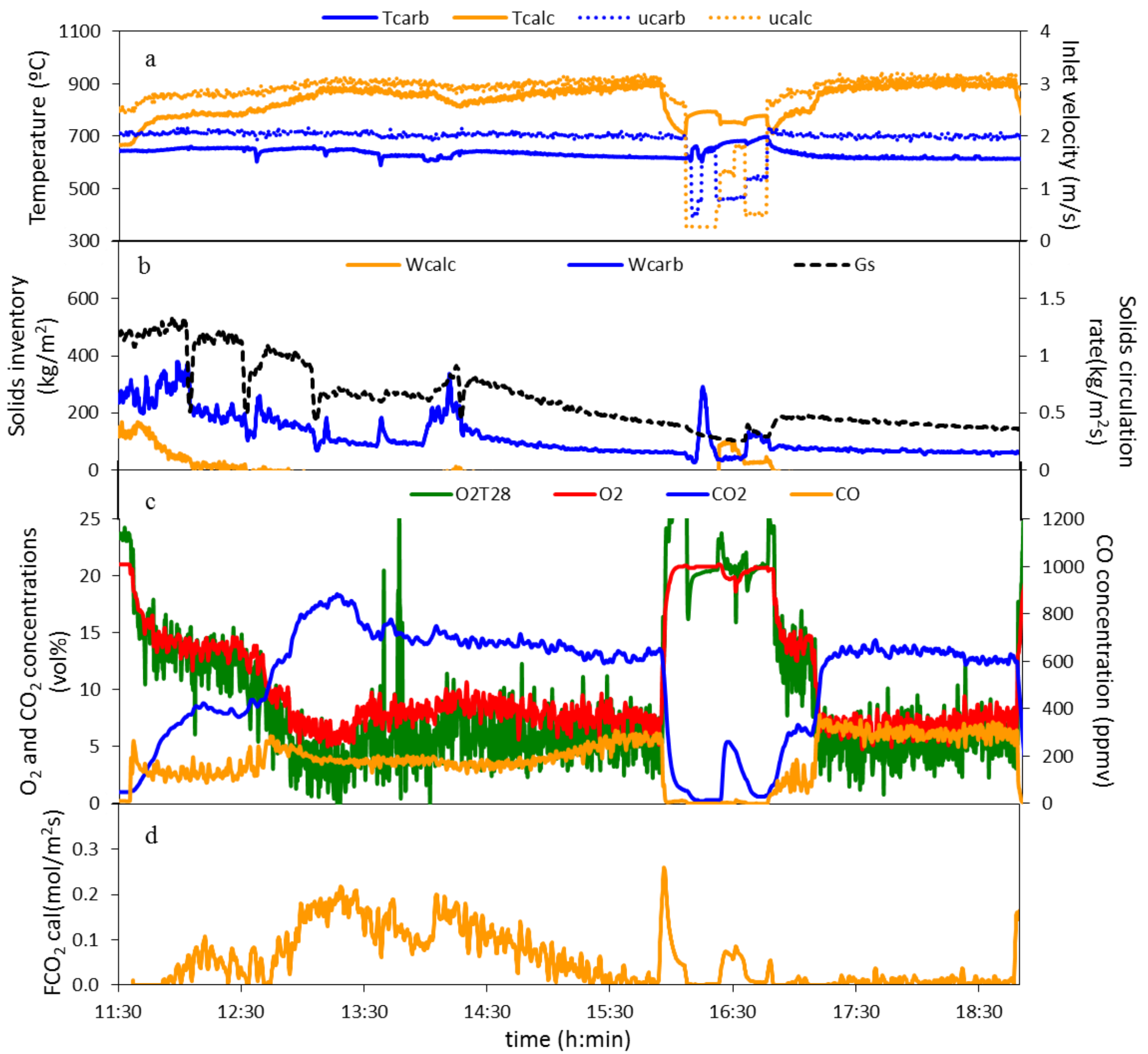


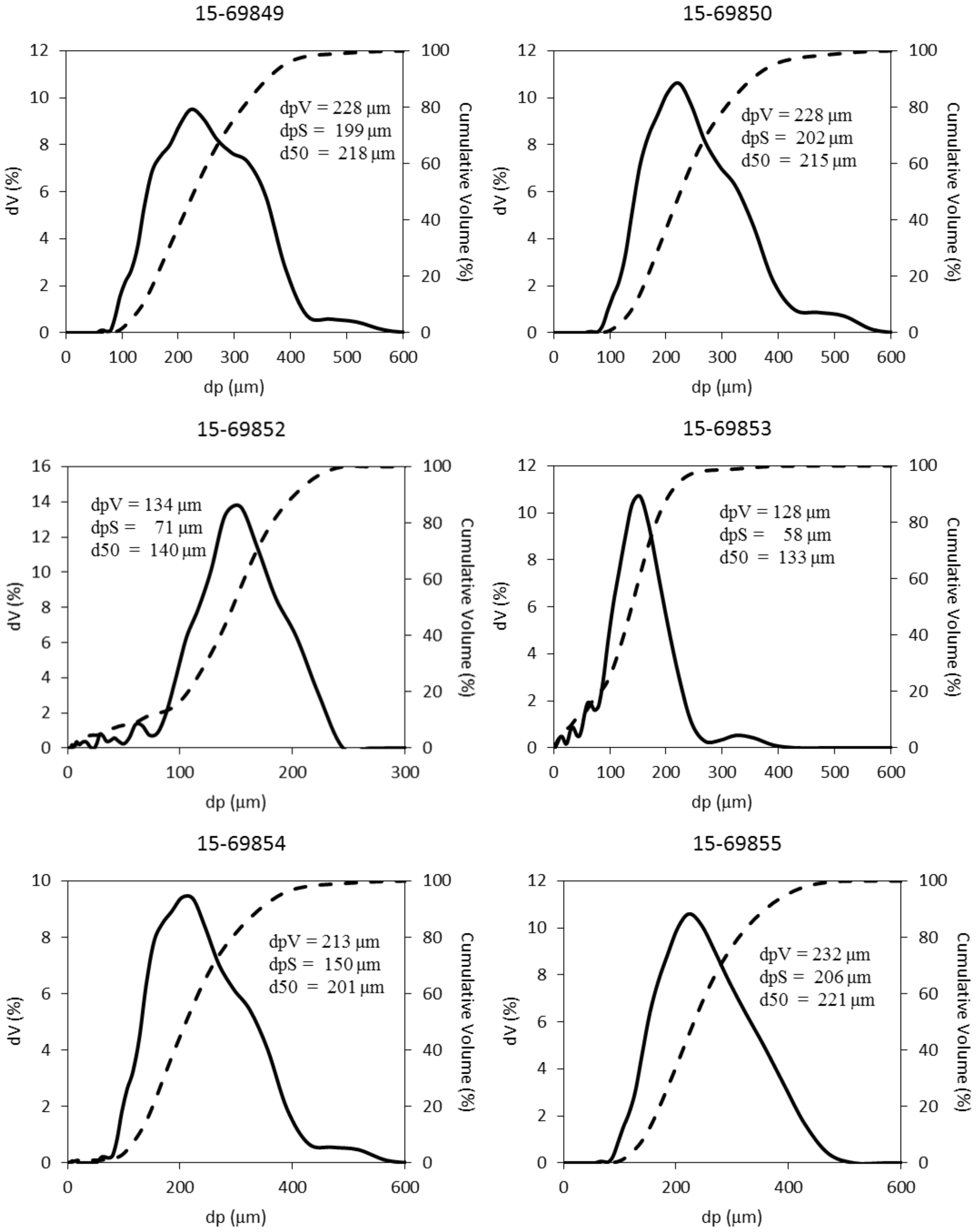
Figure 8.3. Experimental conditions during test 2. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in the risers and solids circulation rate. c. Gas concentrations measured by the on-line analyzer at the exit of calciner. d. Molar CO_2 flow rate from calcination

Table 8.3. Final mass balance of test 2

Test 2							
Inlets				Outlets			
	Weight (kg)	C (wt%)	Ca (mol)		Weight (kg)	C (wt%)	Ca (mol)
Initial batch	20	11.85	197.5	Calciner	1.3	10.1	15
Initial silo	0	11.85	0	Carbonator	1.1	8.9	13.6
Final silo	0	11.85	0	LP-CC	3.1	3.9	46.6
Silo fed	4.4	11.85	43.7	LP-CB	3.4	3.7	53.1
				Circulation	1.4	6.7	18.4
				2nd Cyclones	0.2	4.2	3.5
				Samples	0.8	6.3	11
Total in	24.4		241.2	Total out	11.4		161.1
Global mass balance (%)				67			

Table 8.4. Analysis of samples extracted during test 2

Sample	wC (%)	wS(%)	ID INCAR
12:02 CCA	11.9	0.163	15-69849
12:02 CBA	10.9	0.153	
12:02 2CCA	11.5	0.149	15-69853
12:02 2CBA	11.5	0.136	15-69852
12:02 CIRC	11.3	0.147	15-69850
12:30 CCA	11.1	0.141	15-69854
12:30 CIRC	10.0	0.146	15-69855
12:30 CBA	10.5	0.161	15-69856
12:30 2CBA	10.6	0.167	15-69857
12:30 2CCA	10.3	0.165	15-69858
13:03 CCA	10.1	0.154	
13:03 CIRC	7.5	0.186	
13:03 CBA	9.2	0.160	
13:03 2CBA	9.3	0.170	
13:03 2CCA	9.3	0.164	
14:15 CIRC	9.2	0.160	
17:00 CCA	6.5	0.156	
17:00 CBA	3.3	0.206	
17:32 CCA	2.9	0.211	
17:32 CBA	2.1	0.256	
18:02 CCA	2.7	0.246	15-69860
18:02 CBA	1.6	0.279	15-69859
18:35 CCA	2.3	0.270	15-69862
18:35 CBA	1.8	0.307	15-69861


15-69849

15-69850

15-69852

15-69853

15-69854

15-69855

Figure 8.4. Particle size distributions of samples extracted during test 2.

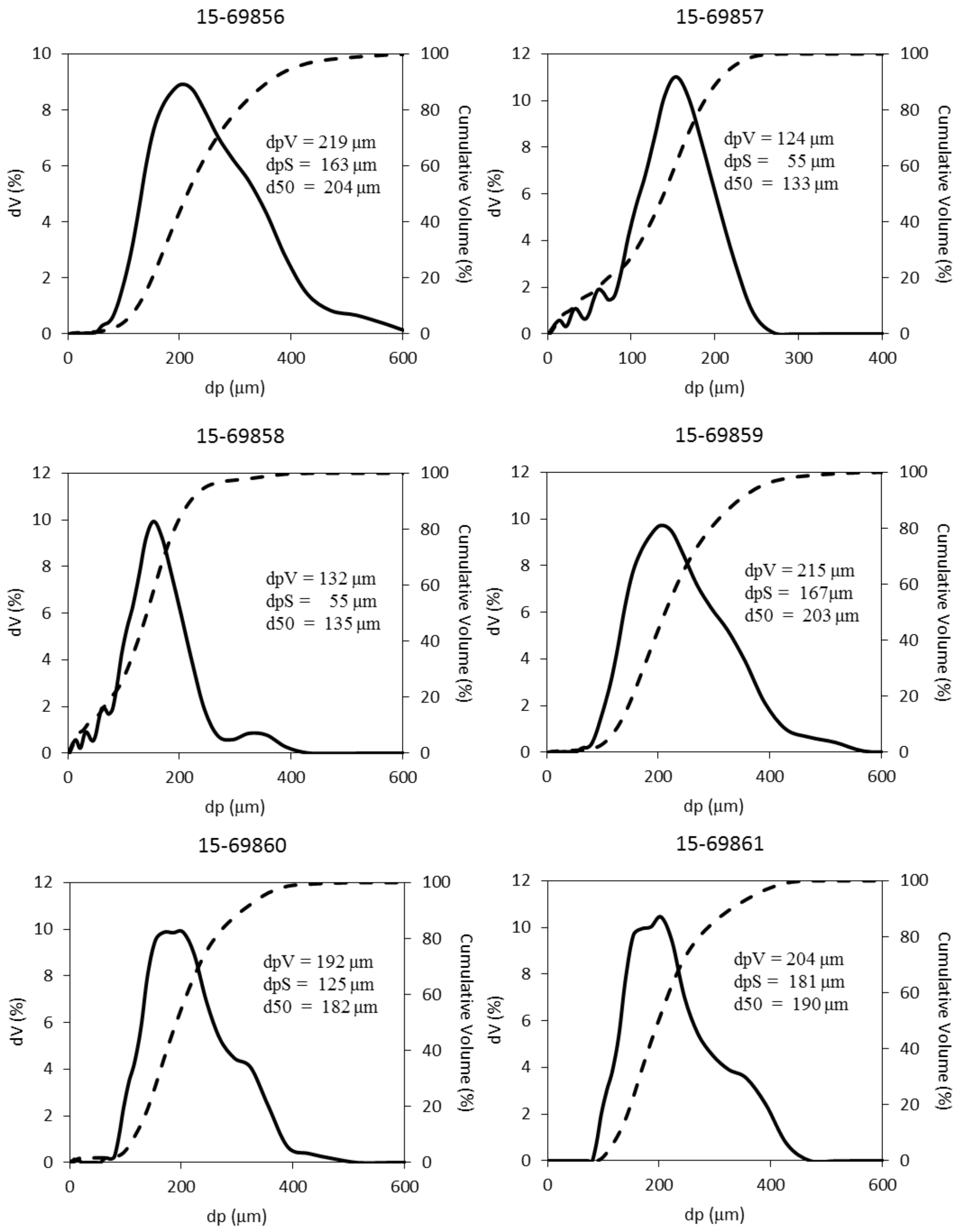


Figure 8.4 (cont.). Particle size distributions of samples extracted during test 2.

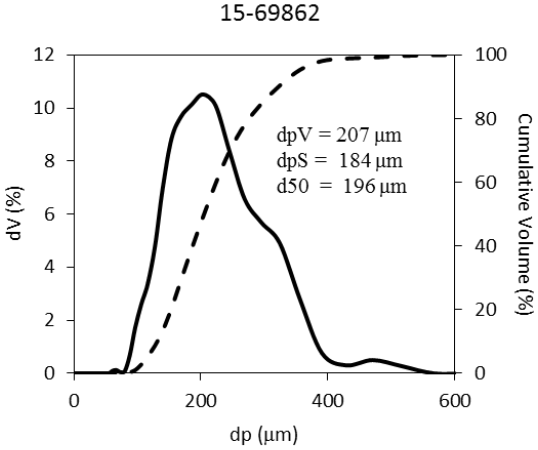


Figure 8.4 (cont.). Particle size distributions of samples extracted during test 2.

Test 3

This test was carried out with modified L-valves (i.e. L-valves with orifice of 6 mm) in order to prevent the leakage of solids from primary cycle to secondary cyclones. The objective of the test was to check the feasibility of the solids circulation and determine the air flowrate needed in the aeration ports for stable circulation in the facility at temperatures around 600 ºC.

Around 20 kg of fresh limestone was fed at the beginning roughly half distributed between carbonator and calciner. A constant mass flow rate of air was fed to the risers and loop-seals it was 15 Nm^3/h and 4 Nm^3/h respectively. Figure 8.5 shows the main operating variables after the air started to be fed to the end of the test.

Figure 8.5 a. shows the average temperature of each riser as well as the inlet velocities. Both temperatures and gas velocities were similar as no reactions taken place in the reactors. The temperatures increased from 350 ºC at 8:34 h to 600 ºC at the end of the test maintained by the electrical ovens and the solids circulation rate whereas the velocity increased from 1.6 m/s at 8:40 h to 2.4 m/s at the end due to the increase in the temperature.

The solids inventories in the carbonator and calciner (Figure 8.5 b) were around 250 kg/m^2 and 350 kg/m^2 respectively at the beginning however they decreased during the test to values around 100 kg/m^2 at 13:57 h. At 14:00 h and 14:17 h two batches of solids were fed to the carbonator increasing the solids inventory in the calciner and the solids circulation rate. At 14:35 the air flow to aeration ports was stopped in order to check secondary cyclones and inventories in both reactors increased. However, the inventories decreased even when the aeration was re-started.

After the test, all solids in the facility were removed and weighted. The final mass balance was closed at 90 % (Table 8.5) it indicates that the previous unusual losses of solids from the facility to the stack were corrected. However, the aeration was insufficient as there were many solids accumulated in the secondary recycle.

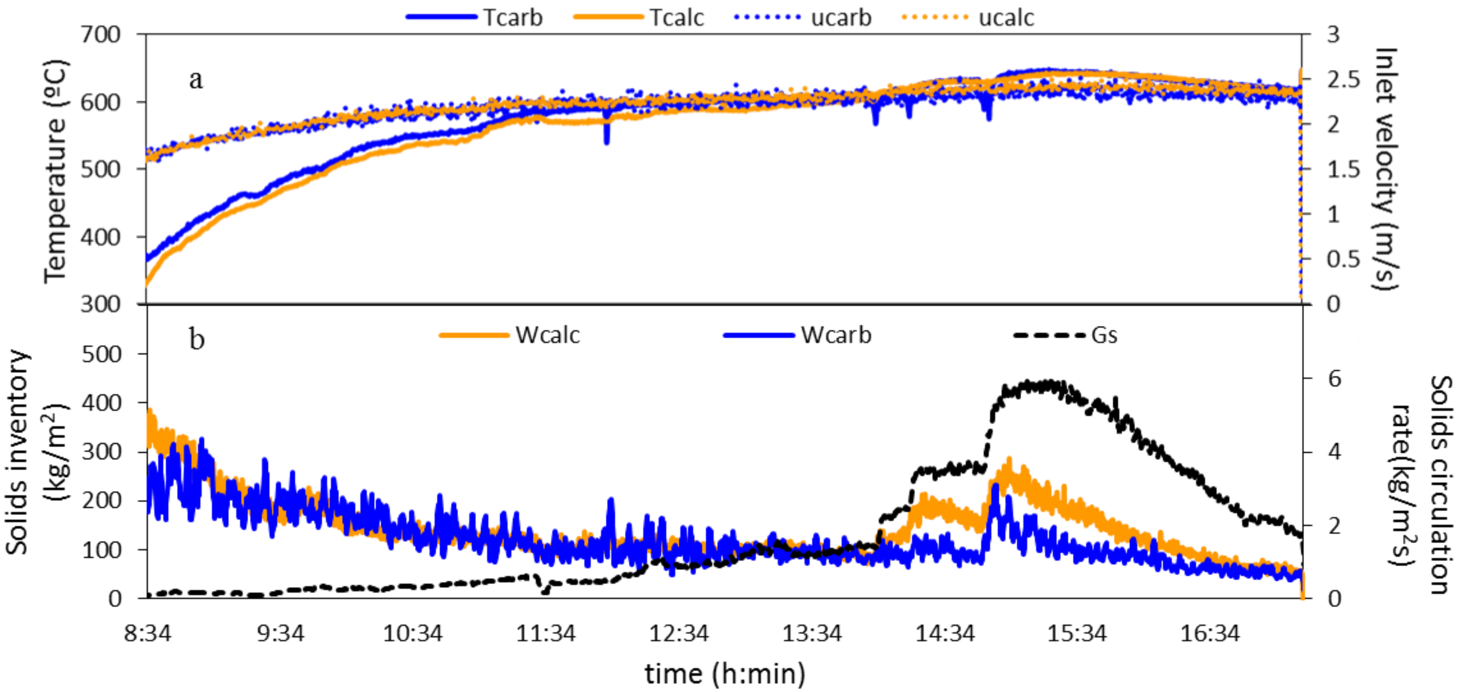


Figure 8.5. Experimental conditions during test 3. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in the risers and solids circulation rate.

Table 8.5. Final mass balance of test 3.

Test 3							
Inlets				Outlets			
	Weight (kg)	C (wt%)	Ca (mol)		Weight (kg)	C (wt%)	Ca (mol)
Initial batch	20	12	200	Calciner	2.4	12	21
Initial silo	0	12	0	Carbonator	2.4	12	24
Final silo	0	12	0	LP-CC	3.5	12	35
Silo fed	1.5	12	15.3	LP-CB	4.0	12	40
				Circulation	1.0	12	10
				2nd Cyclones	5.9	12	59
				Samples	0.1	12	0.7
Total in	21.5		215.3	Total out	19.3	12	192.7
Global mass balance (%)				90			

Test 4

This test was carried out with the same previous L-valve configuration (i.e. L-valves with orifice of 6 mm) but adding aeration ports close to the orifice. The objective of the test was to check the feasibility of the solids circulation at normal conditions (i.e. temperatures around 900 ºC) by burning coal in both reactors during the initial period of the test to calcine the initial batch of limestone.

Around 20 kg of fresh limestone was fed at the beginning roughly half distributed between carbonator and calciner. A constant mass flow rate of air was fed to the risers and loop-seals it was 15 Nm^3/h and 4 Nm^3/h respectively. The experimental procedure was to increase the temperature in both reactors up to calcination temperatures and then reduce the temperature in the carbonator in order to reach the carbonation temperatures. Figure 8.6 shows the main operating variables after the air started to be fed to the end of the test.

Figure 8.6 a. shows the average temperature of each riser as well as the inlet velocities. Between 8:45 and 10:09 h the temperature in both reactors increased from 400 ºC to 580 ºC due to the electrical ovens and the solids circulation rate whereas the velocities increased from 1.8 m/s to 2.2 m/s. At 10:09 h, a coal flow rate of 1.5 kg/h were fed to each riser in order to reach an average temperature around 900 ºC and the inlet velocities increased to 3 m/s at 11:15 h. At 13:35 h the coal flow rate was reduced to 2 kg/h in both risers in order to avoid temperatures higher than 910 ºC and the inlet velocities were increased to 3.4 m/s by increasing the air flow rates to the loop seals in order to increase the solids inventories in the risers. At 14:00h the electrical ovens and the coal flow rate of the carbonator were switched off in order to reach temperatures around 650 ºC. Due to the low inventories and solids circulation rates, the average temperature in the carbonator decreased to values of 530 ºC at the end of the test.

The solids inventories in the carbonator and calciner (Figure 8.6 b) were around 150 kg/m^2 at the beginning. They decreased to values almost no detectable at 11:22 h whereas the solid circulation rate increased to 1.2 kg/m^{2}s. At this time, the secondary recycled was checked and no solids circulation was detected, then the standpipe of carbonator plugged and the solids circulation rate decreased to 0.2 kg/m^{2}s. The standpipe was discharged by injecting air and a small inventory was detected in both risers and the solids circulation rates increased to 0.7 kg/m^{2}s at 12:05 h. At 12:22 h a batch of solids was fed to the calciner, however the solids inventories remained very low, it was concluded that solids were accumulated around the orifice even when the aeration was increased. When the temperature in the carbonator decreased to values around 530 ºC, a batch of solids was fed to the reactor and the solids inventory increased to 205 kg/m^2 at 14: 21 h but it decreased to values of around 40 kg/m^{2}s at 14:30 h. It was detected that the solids were accumulated near the orifice. Two batches of solids were fed to carbonator at 14:35 h and 15:00 h with the similar result. It was concluded that the orifice is two small in order to control the solids circulation at normal operating conditions.

After the test, all solids in the facility were removed, weighted and analyzed by the C/S analyzer. The final mass balance was closed at 97 % (Table 8.6) it indicates that there were no unusual losses of solids from the facility to the stack. During the test, the calcination of the solids were checked by samples extracted (Table 8.7).

Table 8.6. Final mass balance of test 4.

Test 4							
Inlets				Outlets			
	Weight (kg)	C (wt%)	Ca (mol)		Weight (kg)	C (wt%)	Ca (mol)
Initial batch	20	11.7	195.0	Calciner	1.3	9.4	15.0
Initial silo				Carbonator	2.1	11.0	22.0
Final silo				LP-CC	2.0	9.3	23.2
Silo fed	5.3	11.7	51.7	LP-CB	1.3	5.2	18.7
				Circulation	0.7	1.2	11.9
				2nd Cyclones	11.3	7.1	147.9
				Samples	0.1	6.9	1.3
Total in	25.3		246.7	Total out	18.8		240.0
Global mass balance (%)				97			

Table 8.7. Analysis of samples extracted during test 4

Sample	wC (%)	wS(%)	ID INCAR
13:04 CBA	4.9	0.176	
13:04 CCA	8.0	0.140	
13:47 CIRC	0.8	0.250	

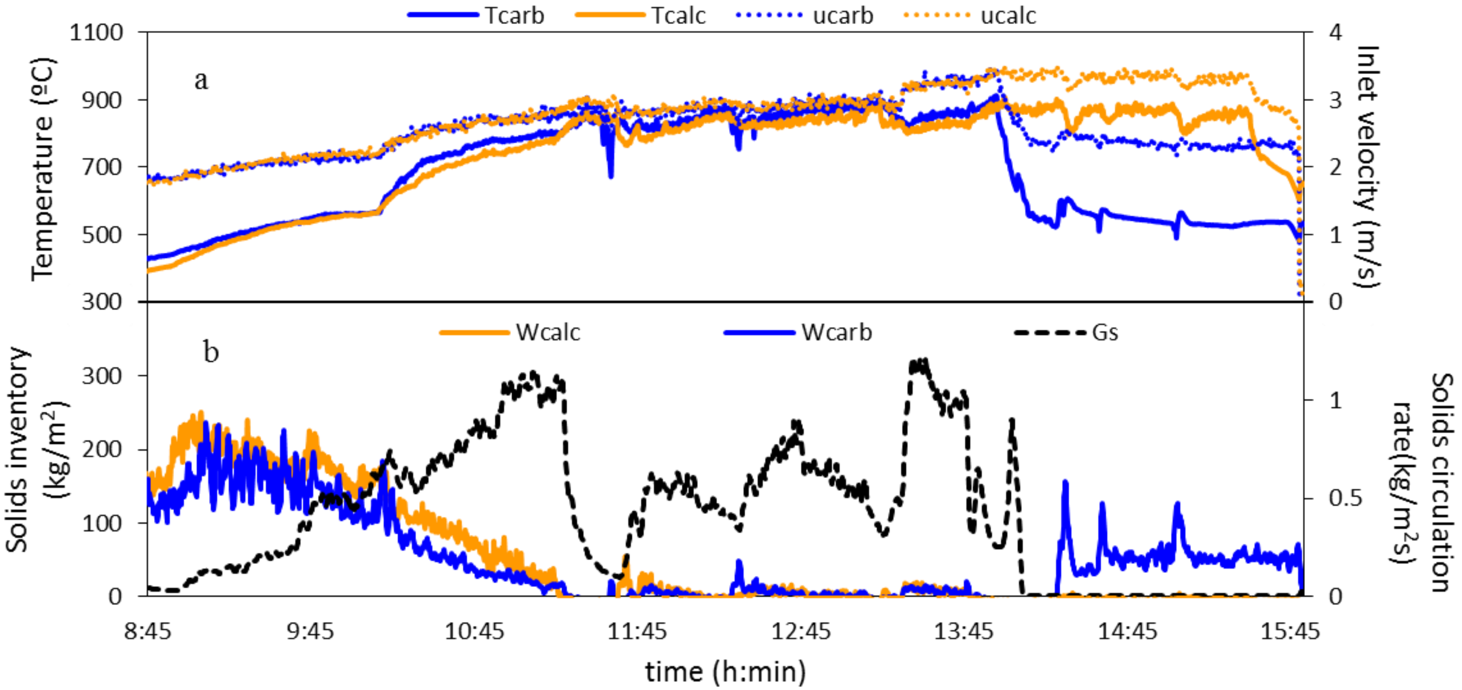


Figure 8.6. Experimental conditions during test 4. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in the risers and solids circulation rate.

Test 5

This test was carried out with L-valves but with orifice of variable area and several points of aeration and pressure taps. The objective of the test was to check the feasibility of the solids circulation at normal conditions (i.e. temperatures around 900 ºC).

Around 20 kg of fresh Imeco limestone was fed at the beginning roughly half distributed between carbonator and calciner. A constant mass flow rate of air was fed to the risers and loop-seals, it was 15 Nm^3/h and 4 Nm^3/h respectively. The experimental procedure was to increase the temperature in the calciner to calcination temperatures with the new valves. Figure 8.7 shows the main operating variables after the air started to be fed to the end of the test.

Figure 8.7 a. shows the average temperature of each riser as well as the inlet velocities. Between 8:40 and 11:05 h the temperature in both reactors increased from around 450 ºC to 635 ºC due to the electrical ovens and the solids circulation rate whereas the velocities increased from 1.9 m/s to 2.4 m/s. At 11:05 h a coal flowrate of 2 kg/h was fed to the calciner and an average temperature of around 840 ºC was reached at 11:29 h. The inlet velocity in the calciner increased to 3 m/s at the same time whereas in the carbonator the average temperature increased to 695 ºC remaining the inlet velocity around 2.6 m/s. Between 11:30 h and 11:45 h the coal and air flow rates were stopped due to a leakage in the exit of primary cyclone of calciner. Once the leakage was stopped, the air flowrates were re-started at 11:45 h and the coal flow rate was re-started at 12:31 h. The average calciner temperature increased to 850 ºC at 13:05 h and the inlet velocity increased to 3 m/s at the same time. In the carbonator the average temperature increased from 650 ºC at 11:45 h to 700 ºC at 13:05 h and the inlet velocity was around 2.6 m/s at this time. Between 13:45 and 15:02 h the air and coal flowrates were stopped again due to the standpipe of carbonator was plugged. From 15:02 h to the end of the test no coal flowrate was used. It was tried to circulate solids in the system and the average temperatures of both risers stabilized at a value around 650 ºC due to electrical ovens and solids circulation. The average inlet velocity of the carbonator was 2.5 m/s whereas the inlet velocity of the calciner increased from 2.5 m/s at 15:02 to 3.1 m/s at 16:31 h due to the increase in the air flowrate to this riser for checking the solids circulation.

The solids inventories in the carbonator and calciner (Figure 8.7 b) were around 320 kg/m^2 until 11:30 h when the air and coal feeding were stopped. Once the air flowrate was re-started, a large amount of solids was detected in the secondary cyclone of calciner and no circulation from the secondary cyclones to the primary standpipes was detected. As a consequence a limestone flowrate of 10 kg/h was fed to the calciner at 12:12 h and the solids inventory in the calciner increased from 100 kg/m^2 at 11:45 h to around 300 kg/m^2 at 12:45 h when the limestone flowrate was stopped. In the carbonator, the solids inventory increased from 180kg/m^2 at 11:45 h to 430 kg/m^2 at 12:49 h. Once the limestone feeding was stopped, both inventories decreased to values around 250 kg/m^2 at 13:40 h and problems in the standpipe of carbonator were detected. Once the air flowrates were re-started at 15:02 h, limestone was fed to the calciner at a rate of 10 kg/h until 15:38 h and the solids inventory in the calciner increased from 190 kg/m^2 at 15:05 to 450 kg/m^2 at 15:40 h when the limestone feeding was stopped. The solids inventory in the carbonator increased from 230 kg/m^2 at 15:05 h to values around 490 kg/m^2 at 16:03 h. However, from this point, the solids inventory in the carbonator decreased continuously to values below 100 kg/m^2 and the tendency of the inventory of solids in the calciner was similar. At the end of the test a high accumulation of solids in the secondary recycle of the calciner was detected. The solids circulation rate was 4 kg/m^{2}s at its maximum value and fluctuated along the test due to the changes described previously.

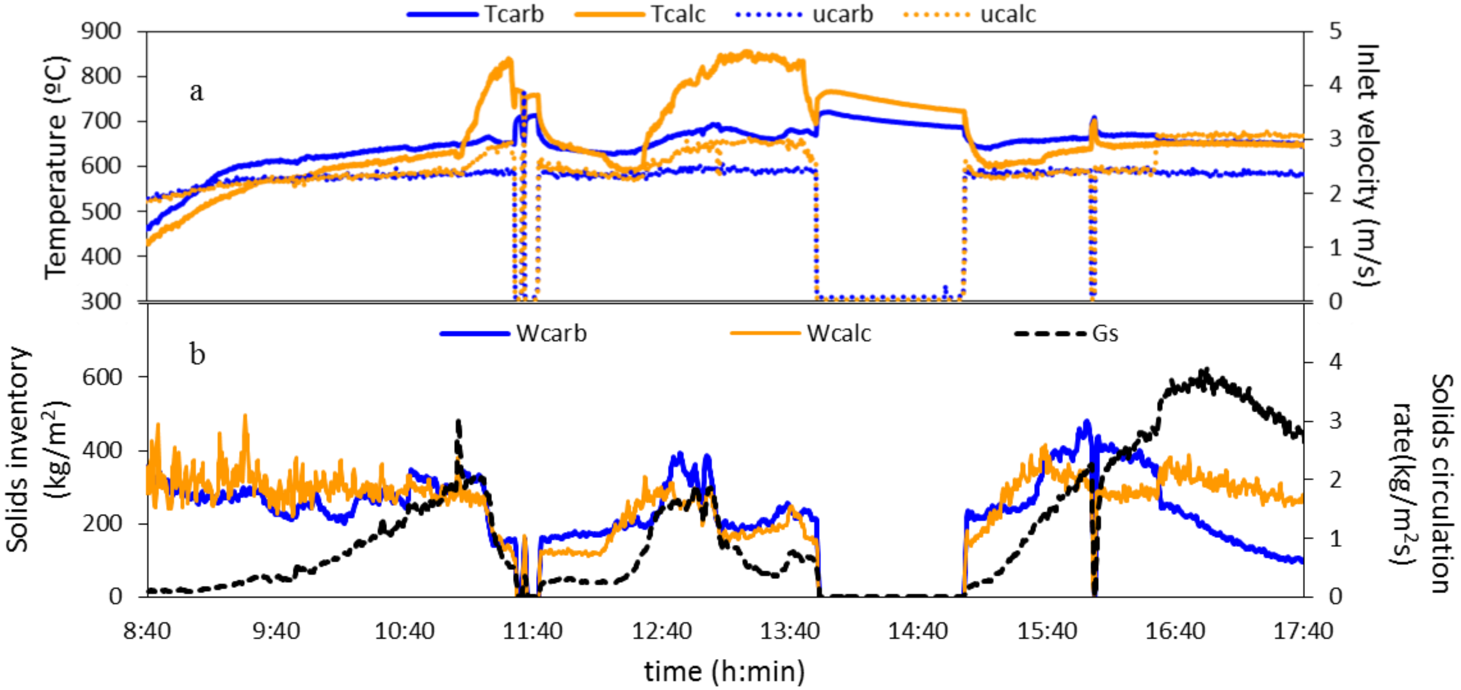


Figure 8.7. Experimental conditions during test 5. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in the risers and solids circulation rate.

Test 6

This test was carried out with L-valves with variable area orifice and several points of aeration and pressure taps. The objective of the test was to carry out a CO_2 capture test with continuous limestone feeding.

Around 20 kg of fresh limestone was fed at the beginning roughly half distributed between carbonator and calciner. A constant mass flow rate of air was fed to the calciner and its loop-seal, it was 15 Nm^3/h and 4 Nm^3/h respectively. Figure 8.8 shows the main operating variables from the coal flowrate started to be fed to the calciner until the end of the test.

The average temperature in the carbonator (Figure 8.8.a) was mostly between 645 ºC and 685 ºC during the test. Between 16:22 h and 17:02 h it decreased to 585 ºC due to a shutdown of the loop-seal. The average temperature in the calciner increased from 640 ºC at the beginning to values around 880 ºC at 12:20 h and then remained between 825 ºc and 900 ºC during the test. The inlet velocity of the carbonator was between 2 and 2.4 m/s except during two periods: between 12:46 and 14:10 h and between 16:22 and 17:02 h. At these periods changes in the air inlet flowrate was made in order to move solids from carbonator to the calciner and/or to restore the seal in the standpipe. The inlet velocity of the calciner was 2 m/s at the beginning and remained between 2.4 and 2.8 m/s during the test.

The solids inventory in the calciner (Figure 8.8 b) decreased from values around 210 kg/m^2 at 11:00 h to values around 50 kg/m^2 at 12:55 h remaining around this value until the end of the test. The solids inventory in the carbonator was around 300 kg/m^2 between 11:00 h and 13:20 h when solids from this riser were removed as it was no possible to move them by changing air flowrates. At 14:10 h when the air flowrates were reestablished and solids removed, a limestone flowrate of 10 kg/h was fed to the carbonator and the solids inventory increased from 90 kg/m^2 to values around 210 kg/m^2 at 15:13 h and remained around a value of 180 kg/m^2 until the end of test. The solids circulation rate was lower than 1 kg/m^2s until 17:00 h and quite unstable then it increased to values between 1.2 and 2.1 kg/m^2s from 17:00 h to the end. Figures 8.8.c and 8.8.d shown the gas concentrations measured by the on-line analyzers at the exit of carbonator and at the exit of the calciner respectively. The average carbonator exit O_2 concentration was 18.8 vol% from 14:00 h to the end of the test, whereas the average exit CO_2 concentration varied from 4.5 to 15.3 vol% depending on the inlet CO_2 flowrate and the solids circulation rate. Between 17:22 and 18:50 and average exit CO concentration of 0.06 vol.% was detected. At the exit of the calciner the average O_2 concentration was around 6.4 vol% from 12:20 h to the end of the test whereas the average CO_2 concentration was around 19.8 vol%. The average exit CO concentration varied between 174 and 1100 ppmv during the test. The molar flow of capture CO_2 was unstable between 14:00 and 17:00 h (Figure 8.8.d) and varied between 5.8 mol/m^2s and zero due to the unstable circulation. After 17:00 h both calcined and captured molar CO_2 flowrates tended to be similar and around 2.8 mol/m^2s. Accordingly the CO_2 capture efficiency (Figure 8.8.e.) was varied between 86% and zero between 14:00 and 17:00. From 17:00 h the CO_2 capture efficiency increased to values around 75% at the end of the test.

After the test, all solids in the facility were removed, weighted and analyzed by the C/S analyzer. The final mass balance was closed at 91 % (Table 8.8). During the test, solid samples from carbonator (CB), calciner (CC), measurements of solids circulation rates (CIRC) and secondary cyclones (2CB and 2CC) were extracted for carbonate content analysis and maximum carrying capacity (Table 8.9).

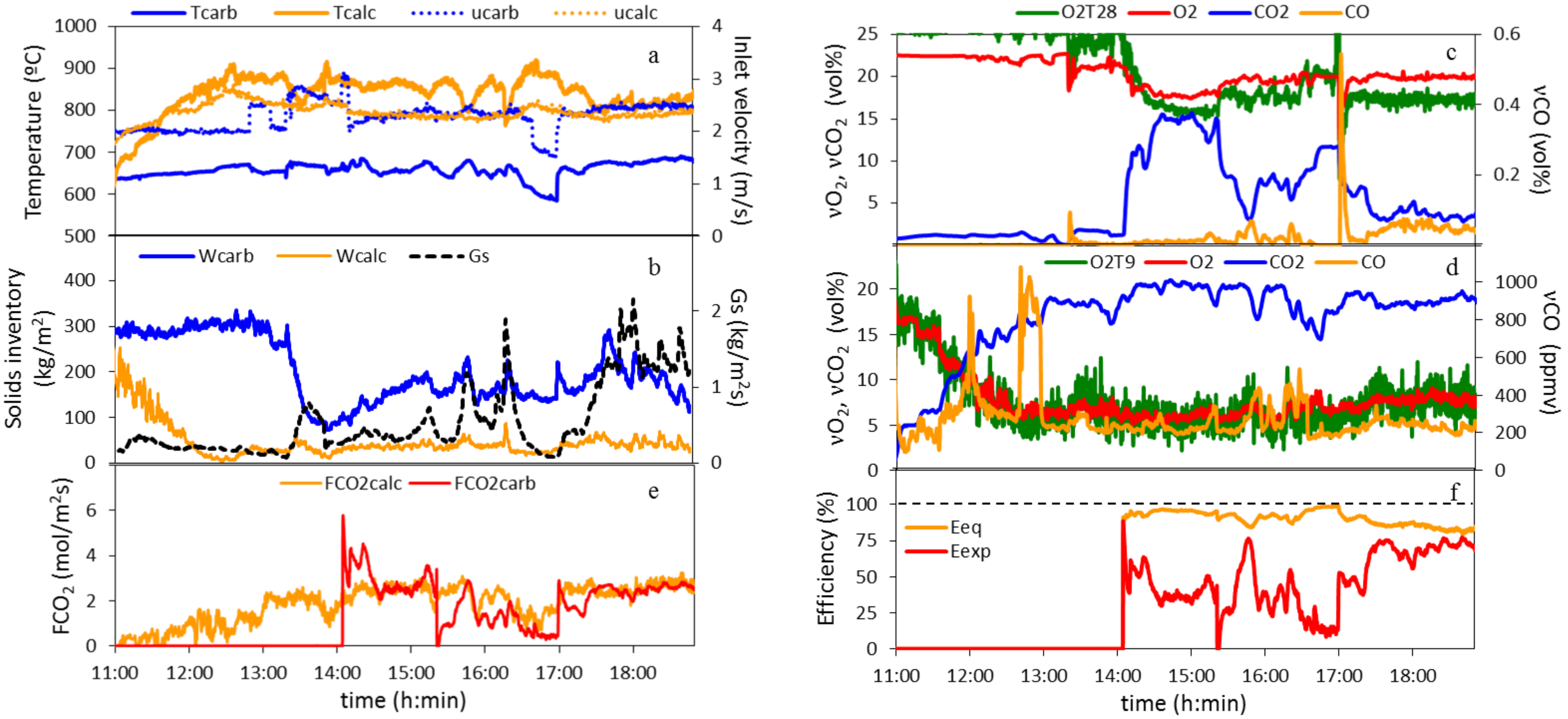


Figure 8.8. Experimental data during test 6. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. d. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.8. Final mass balance of test 6.

Test 6							
Inlets				Outlets			
	Weight (kg)	C (wt%)	Ca (mol)		Weight (kg)	C (wt%)	Ca (mol)
Initial batch	20.0	12.1	201.7	Calciner	3.1	10.3	34.6
Initial silo	73.5	12.1	741.1	Carbonator	2.8	7.6	36.2
Final silo	37.2	12.1	375.1	LP-CC	3.6	5.9	50.6
Silo fed	36.3	12.1	366.0	LP-CB	4.0	5.4	57.4
				Circulation	1.5	9.1	17.9
				2nd Cyclones	24.0	7.7	308.7
				Samples	0.8	7.2	10.5
Total in	56.3		567.7	Total out	39.8		516.0
Global mass balance (%)				91			

Table 8.9. Analysis of samples extracted during test 6.

Sample	wC (%)	wS(%)	ID INCAR	Xcarb$_{TG}$	Xave
12:55 CC	5.2	0.172	15-70683	0.32	0.61
13:15 2CC	11.0	0.156			
13:50 CIRC	6.1	0.169			
14:20 CB	8.0	0.169			
14:20 CC	5.6	0.165	15-70684	0.32	0.60
14:23 CB	6.5	0.195			
14:23 CC	7.4	0.178			
15:15 CB	8.6	0.153			
15:15 CC	7.0	0.187	15-70685	0.47	0.63
15:15 2CB	7.9	0.157			
15:15 2CC	6.4	0.182			
15:51 LP-CB	9.1	0.169			
18:06 CB	8.1	0.167			
18:06 CC	6.6	0.212	15-70686	0.40	0.53
18:48 CB	6.9	0.187			
18:48 CC	5.2	0.189	15-70687	0.28	0.44

Test 7

This test was carried out with an L-valve with variable area orifice in the recycle from carbonator and the loop seal configuration in the secondary recycle from calciner. The objective of the test was to carry out a CO_2 capture test with limestone feeding. The solids used came from test 5.

Figure 8.9 shows the main operating variables from the starting of CO_2 feeding to the carbonator until the end of the test.

The average temperature in the carbonator (Figure 8.9.a) was between 620 ºC and 685 ºC whereas the average temperature in the calciner varied between 780 and 845 ºC during the period shown the figure. The air inlet velocity to the carbonator was 3.2 m/s and when CO_2 was fed this velocity increased to 3.6 m/s. The inlet velocity to the calciner varied between 2.7 m/s and 3.3 m/s due to changes in the air flow rates.

The solids inventory in the calciner (Figure 8.9 b) remained at values around 50 kg/m^2 during the period shown in the figure. The solids inventory in the carbonator was around 440 kg/m^2 at 11:30 h and decreased to values around 65 kg/m^2 at 12:42 h when the limestone feeding was re-started. As a consequence, the solids inventory increased to 255 kg/m^2 at 13:10 h when the system was shut down due to a rupture of the primary standpipe of calciner. The solids circulation rate decreased from values around 5.8 kg/m^2s at 11:30 h to values of around 2.8 kg/m^2s at 13:10 h. The carbonator exit gas concentrations measured by the on-line analyzer 2 are shown in Figure 8.9.c. It was noticeable the high CO concentration measured, and it was concluded that there was an appreciable combustion in the loop-seal that fed this reactor as the CO_2 feeding was stopped to check this possibility between 11:42 and 12:25 h. Moreover, in order to check these measurements on-line gas analyzer 1 was measured the carbonator exit gas concentrations between 11:35 and 11:55 h and the concentrations measured by this analyzer were similar to the other (see Figure 8.9.d.). The rest of time the analyzer 1 was measured the exit gas concentrations of calciner. Between 11:55 and 13:10 h the average concentrations of O_2 and CO_2 measured by this analyzer were 4 vol.%, 24.5 vol.%. The CO concentration varied between 240 and 1000 ppmv during the same period. Two periods of CO_2 capture were obtained during this test. Between 11:32 and 11:42 h when the molar flow of CO_2 captured (Figure 8.9.e.) decreased from 4.7 mol/m^2s to 1.8 mol/m^2s and between 12:26 and 13:10 h when varied between 3.8 and 6.2 mol/m^2s. The molar flow of CO_2 calcined increased from 3.2 mol/m^2s at 12:00 to average values of 5.2 mol/m^2s at 12:30 h. Accordingly the CO_2 capture efficiency (Figure 8.9.e.) decreased from 62% to 21% during the first period and decreased from 86% to 56% during the second period.

During the test, solid samples from carbonator (CCA), calciner (CBA), and secondary recycle (R-CBA, R-CCA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.10, Figure 8.10).

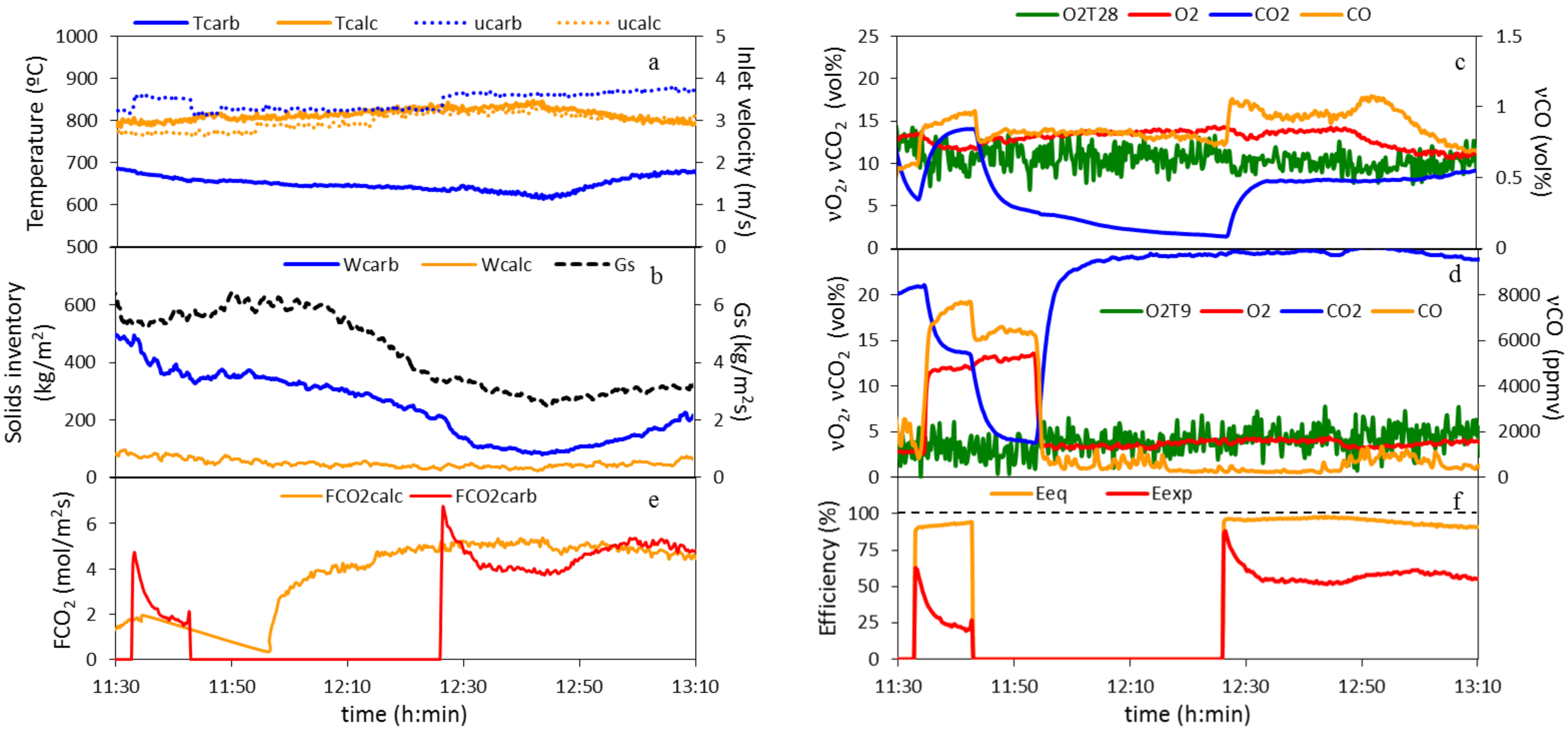


Figure 8.9. Experimental data during test 7. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. d. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.10. Analysis of samples extracted during test 7.

Sample	wC (%)	wS(%)	ID INCAR	Xcarb_{TG}	Xave
10:42 CBA	11.0	0.159	15-70761	0.81	0.84
10:42 CCA	11.1	0.123	15-70762	0.83	0.85
11:25 CBA	10.4	0.148	15-70763	0.79	0.81
11:25 CCA	10.6	0.144			
12:12 CBA	9.0	0.186			
12:12 CCA	9.7	0.141			
12:39 CBA	6.4	0.205	15-70764	0.37	0.55
12:39 CCA	8.4	0.190			
12:59 CBA	7.4	0.239	15-70765	0.43	0.57
12:59 CCA	8.9	0.218			
13:03 R-CBA	9.4	0.151	15-70758		
13:03 R-CCA	8.5	0.184	15-70759		

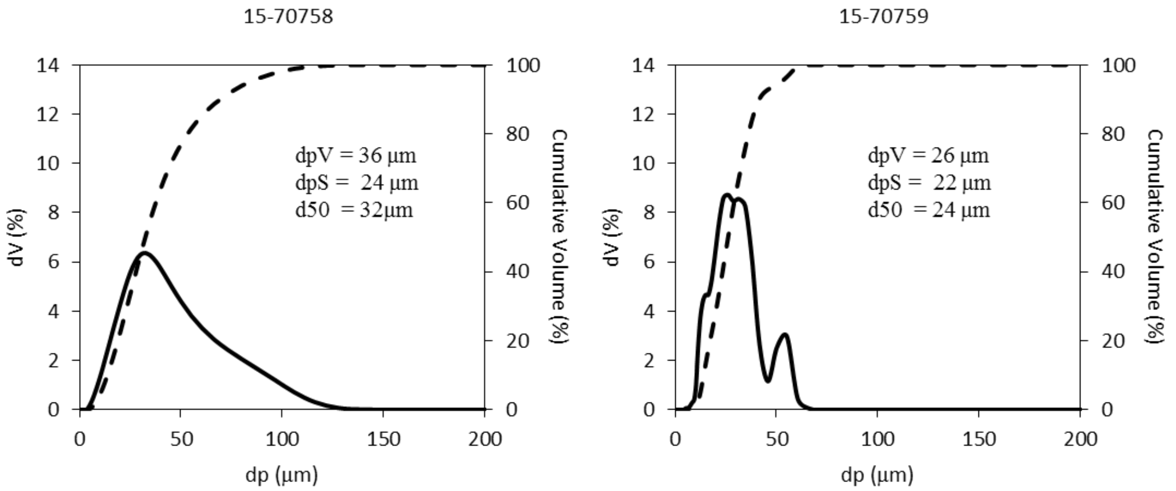


Figure 8.10. Particle size distributions of samples from the secondary recycled extracted during test 7.

Test 8

This test was carried out with an L-valve configuration with variable area orifice in the recycle from carbonator and the loop seal configuration in the secondary recycle from calciner. The solids used came from test 7. Figure 8.11 shows the main operating variables after feeding coal to the calciner until the end of the test.

Between 10:15 h and 12:50 h the secondary cyclone of calciner and or the secondary recycle from this riser was plugged. The air flow rates and the limestone feeding were changed several times during this period. As a consequence, the average temperatures (Figure 8.11.a) in the risers were between 630 and 740 ºC for carbonator and between 595 and 860 ºC for calciner. The inlet velocities were between 0.4 and 2.4 m/s for both risers. Between 12:50 h and 15:18 h, it was tried to move solids from one reactor to the other without burning coal in order to check the circulation of solids in the secondary recycle. The average temperature and the inlet velocity were similar in both reactors and around 670 ºC and 2.2 m/s respectively. Between 15:18 h and 17:41 h the coal was fed to the calciner and it was tried to check the circulation in the system during calcination. It was detected combustion in the loop-seal that fed to the carbonator. As a consequence, the average temperature in the carbonator increased from 670 ºC at 15:18 h to 750 ºC at 17:41 h. During the same period, the average temperature in the calciner increased from 670 ºC to 880 ºC while the air flowrates were changed in order to maintained the inlet velocities to both risers similar and around 2.3 m/s. Between 17:41 h and 18:30 h, CO_2 was fed to the carbonator. The average temperature in the carbonator varied between 620 ºC and 680 ºC whereas the average temperature in the calciner varied between 810 and 880 ºC during this period. The inlet velocity to the carbonator was 2.8 m/s when CO_2 was fed whereas the inlet velocity to the calciner was reduced to 1.9 m/s due to changes in the air flowrates.

The solids inventories in both reactors (Figure 8.11 b) oscillated between 50 kg/m^2 and 400 kg/m^2 in the carbonator and between 7 and 360 kg/m^2 in the calciner. These oscillations were related with the limestone feeding and the discharges from the secondary recycle. The solids circulation rate was unstable and mostly it varied between 1.2 and 5.8 kg/m^2s. The on-line analyzer 1 measured the calciner exit gas concentration during the period of time shown (Figure 8.11.c.). Between 10:15 and 12:50 h, the average exit O_2 concentration varied between 5.8 and 21 vol.%, the average CO_2 concentration varied between 0 to 20.1 vol% and the average CO concentration varied between 0 and 1100 ppmv due to the changes in the air and coal flowrates. Between 12:50 and 15:18 h no coal was fed to the calciner and the exit concentrations corresponded with air. Finally, between 15:18 and 18:26 h the average exit concentrations of O_2, CO_2 and CO varied between 2 and 7.5 vol.%, 14 and 25 vol.% and between 205 and 3000 ppmv respectively. The on-line gas analyzer 2 was measured the carbonator exit gas concentrations during the test (Figure 8.11.d.). Between 15:22 and 17:45 h it was noticeable the combustion in the loop-seal as the average O_2, CO_2 and CO concentrations were 15.1 vol.%, 7.1 vol.% and 0.01 vol.% respectively. Then CO_2 was fed at 17:48 h, and the average exit O_2 was around 14.6 vol%. The average CO_2 concentration increased from 6.6 vol.% at 17:48 h to 12.9 vol.%. The increase in CO concentration measured in both risers during the CO_2 injection (around 3000 ppmv) was related with the calciner temperature and the appreciable combustion in the loop-seal that fed to the carbonator. Between 17:48 and 18:15 h the molar flow of CO_2 captured (Figure 8.11.e.) decreased from 7.3 mol/m^2s to 5.4 mol/m^2s whereas the molar flow of CO_2 was around an average value of 2.2 mol/m^2s. The CO_2 capture efficiency (Figure 8.11.e.) was around 75% whereas the maximum allowed by the equilibrium at the same time was around 80%.

During the test, solid samples from carbonator (CCA), calciner (CBA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.11 and Figure 8.12).

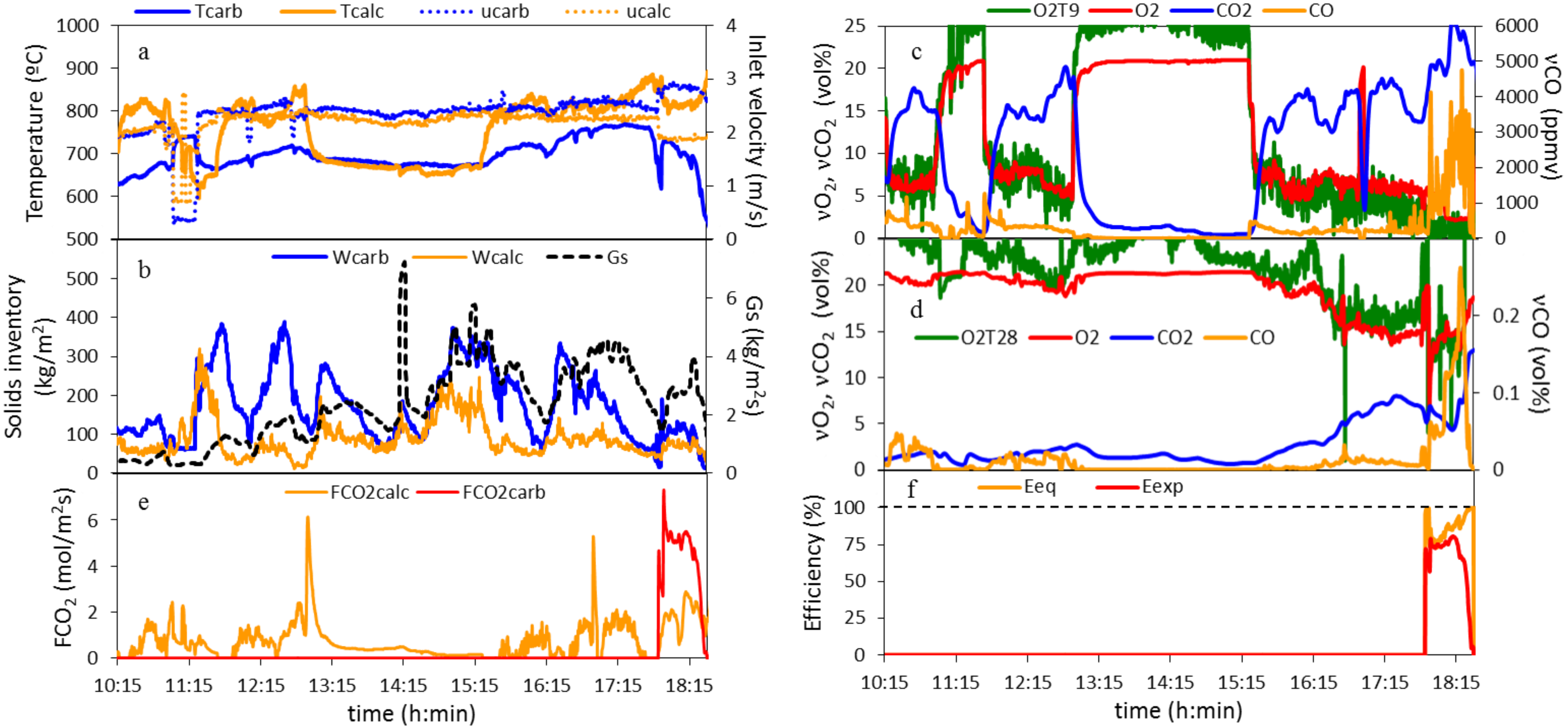


Figure 8.11. Experimental data during test 8. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. d. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.11. Analysis of samples extracted during test 8.

Sample	wC (%)	wS(%)	ID INCAR	Xcarb$_{TG}$	Xave
16:01 CBA	6.33	0.226			
16:01 CCA	5.69	0.214			
16:47 CBA	6.51	0.192			
16:47 CCA	6.26	0.190			
17:18 CBA	4.15	0.259			
17:18 CCA	3.44	0.232			
17:39 CBA	3.09	0.253			
17:39 CCA	1.19	0.238			
18:02 CBA	5.08	0.256	15-70889	0.27	0.41
18:02 CCA	5.41	0.248	15-70890	0.31	0.42
18:18 CBA	6.40	0.249	15-70891	0.37	0.48
18:18 CCA	6.78	0.231	15-70892	0.39	0.48

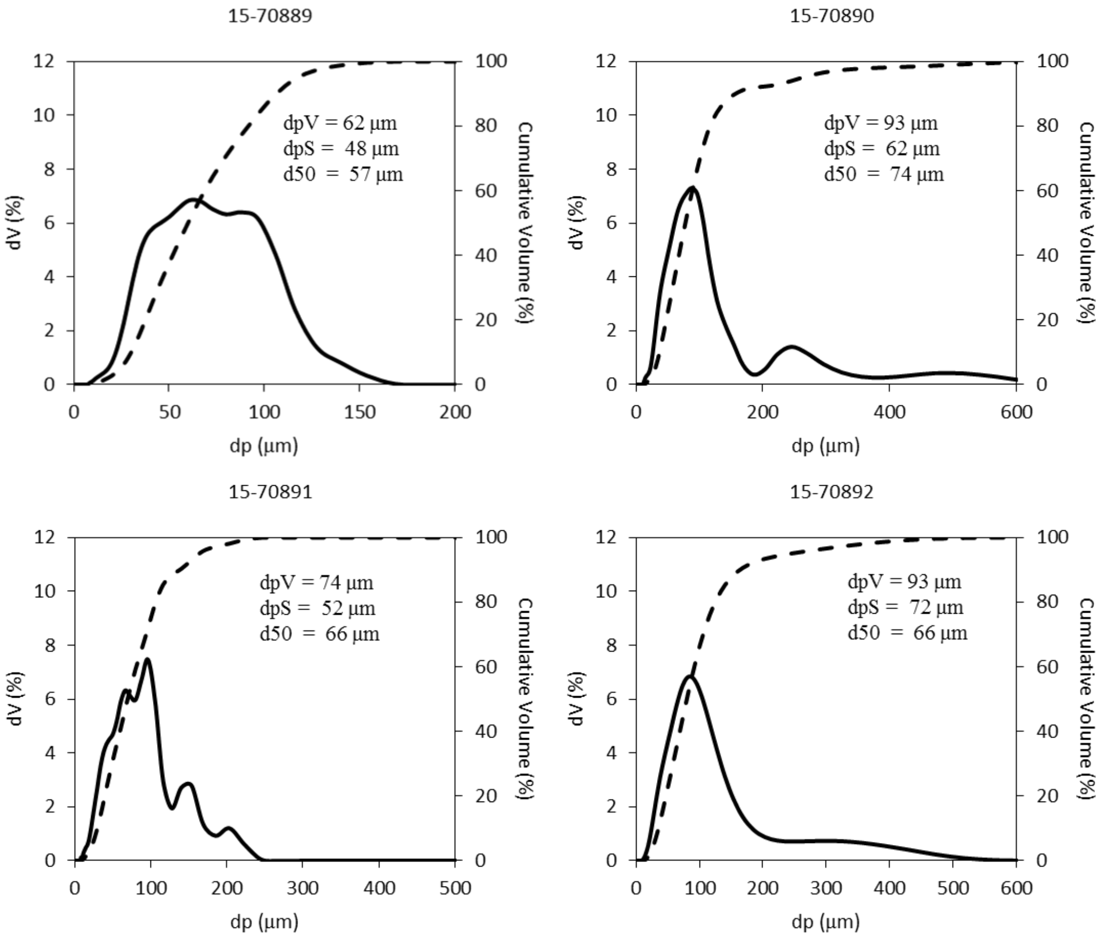


Figure 8.12. Particle size distributions of some selected samples from test 8.

Test 9

This test was carried out with an L-valve configuration with variable area orifice in the recycle from carbonator and a loop seal configuration in the secondary recycle from calciner. Additional aeration in the standpipes of secondary cyclones was installed. The initial solids used came from test 8. Figure 8.13 shows the main operating variables after feeding coal to the calciner until the end of the test.

Between 11:00 h and 13:30 h the secondary cyclone of calciner, the secondary recycle from this riser and the primary standpipe of carbonator were plugged. Changes in the air flowrates, limestone feeding and flowrates of aerations were made several times during this period. As a consequence, the average temperatures (Figure 8.13.a.) in the risers were between 640 and 710 ºC for carbonator and between 710 and 840 ºC for calciner. The inlet velocities were between 1.2 and 2.3 m/s for both risers. Between 13:30 h and 19:22 h, it was tried to check the circulation of solids and to detect the plugins through the pressure taps and thermocouples installed in the secondary cyclones. The average temperature was similar in both reactors and around 680 ºC. The inlet velocity in both risers was similar and varied between 1.5 and 2 m/s. Between 19:22 h and 21:30 h, the coal was fed to the calciner and the average temperature increased from 680 ºC to an average of 830 ºC at 20:15 h and mostly remained around this value until the end. The average temperature in the carbonator varied between 643 ºC and 730 ºC from 19:22 h to the end of test. The inlet velocity to the carbonator varied between 2.1 m/s and 2.8 m/s depending mainly on the CO_2 flowrate fed to the carbonator whereas the inlet velocity to the calciner was 1.6 m/s between 19:22 and 22:50 h and it was increased to 2.5 m/s at 23:42 h to the end in order to increase the calcination rate.

The solids inventories in both reactors (Figure 8.13 b) oscillated between 60 kg/m^2 and 590 kg/m^2 in the carbonator and between 7 and 340 kg/m^2 in the calciner. As in the previous test, these oscillations were related with the limestone feeding and the discharges from the secondary recycle when it was increased the aerations and blown. The solids circulation rate was unstable and oscillated between 0.3 kg/m^{2}s and 3.3 kg/m^{2}s. The on-line analyzer 1 measured the calciner exit gas concentration during the period of time shown (Figure 8.13.c.). Between 11:00 and 13:04 h the average exit O_2, CO_2 and CO concentrations were 4.4 vol.%, 20 vol.% and 375 ppmv respectively. Between 13:04 and 19:17, no coal was fed to the calciner. Finally, from 19:17 h to the end, the average exit concentrations of O_2, CO_2 and CO were 3.9 vol.%, 22 vol.% and 142 ppmv respectively. The on-line gas analyzer 2 was measured the carbonator exit gas concentration during the test (Figure 8.13.d.) except between 22:32 and 22:52 h when it was measured at the inlet gas concentration to the carbonator. Between 21:31 h and 22:05 h, an inlet CO_2 concentration of 14 vol.% (without combustion) was fed to the carbonator and the exit CO_2 concentration measured by the analyzer decreased from 3.4 to 0.1 vol%. Between 22:05 h and 22:53 h, the CO_2 mass flowrate was 10.6 kg/h (i.e. inlet CO_2 concentration of 24 vol.% without combustion) and the exit CO_2 concentration increased up to 15.1 vol% at 22:28 h. Then, at 22:55 h the inlet CO_2 mass flowrate was reduced to 5.5 kg/h and the average exit CO_2 concentration was around 8.9 vol%. Between 21:31 h and 22:05 h, the molar flow of CO_2 captured (Figure 8.13.e.) was around 4.2 mol/m^{2}s whereas between 22:05 and 22:39 h it decreased from 8.3 to 3.3 mol/m^{2}s. Between 23:33 and 0:42 h, the molar CO_2 captured and calcined were similar and around 3.5 mol/m^{2}s. The CO_2 capture efficiency (Figure 8.13.e.) increased from 85% to 96% between 21:31 and 22:05 h and it was similar to the equilibrium. Then it decreased to 45 % and it was around 60% between 23:33 and 0:42 h.

During the test, solid samples from carbonator (CCA), calciner (CBA), measurements of circulation (CIRC) and secondary recycles (3CBA, 3CCA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.12 and Figure 8.14).

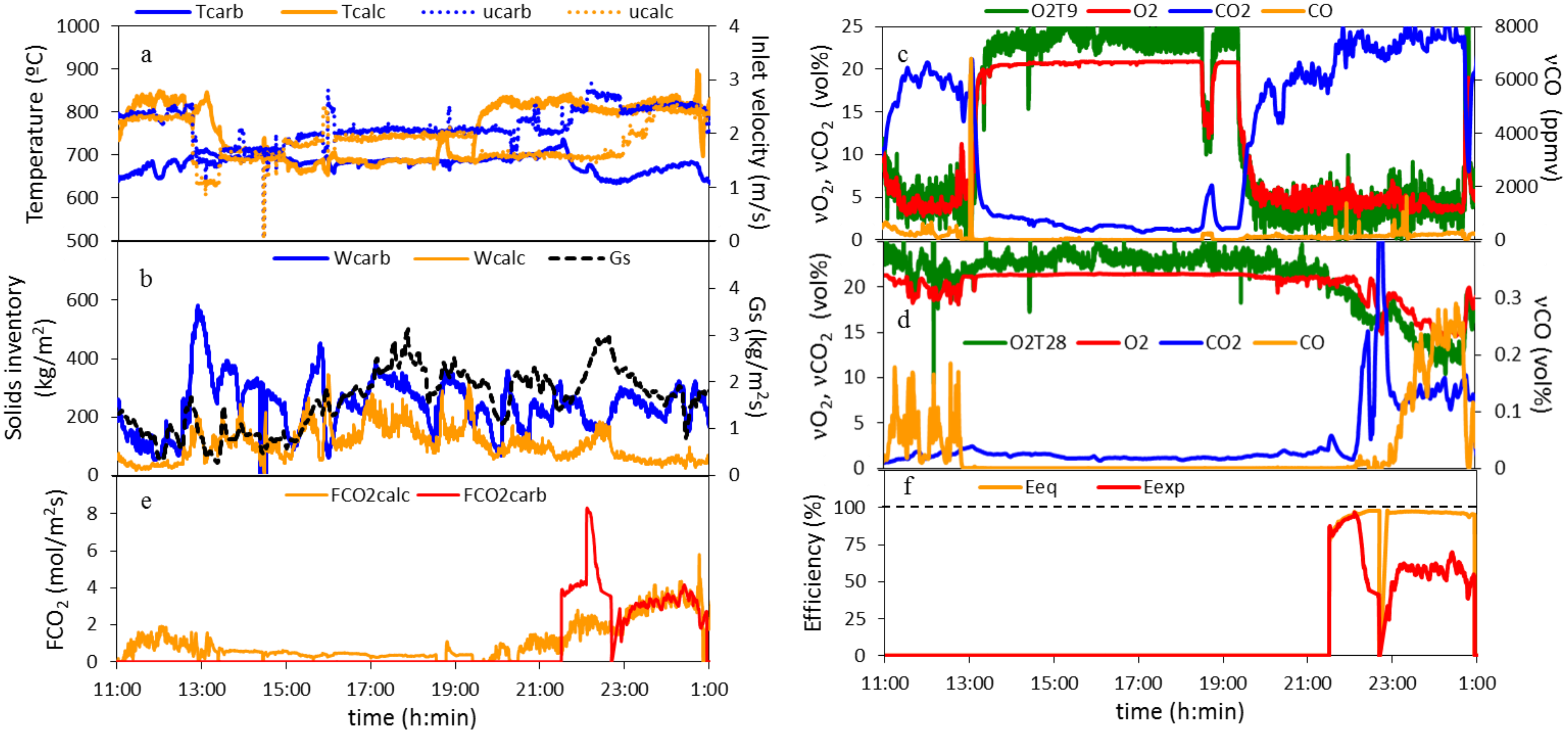


Figure 8.13. Experimental data during test 9. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. d. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.12. Analysis of samples extracted during test 9.

Sample	wC (%)	wS(%)	ID INCAR	$Xcarb_{TG}$	Xave
18:28 CIRC	5.07	0.227			
20:11 CCA	6.20	0.255			
20:11 CBA	6.36	0.218			
20:41 CCA	4.80	0.199			
20:41 CBA	5.25	0.195			
21:18 CCA	2.03	0.221			
21:18 CBA	3.42	0.208			
21:45 CCA	3.83	0.233			
21:45 CBA	2.94	0.222			
21:56 CCA	4.16	0.234			
21:56 CBA	3.58	0.232	15-71310	0.22	0.5
22:05 CCA	4.74	0.232	15-71311	0.25	0.49
22:05 CBA	3.67	0.217			
22:17 CCA	6.37	0.214	15-71312	0.26	0.47
22:17 CBA	5.65	0.217			
22:23 CBA	6.17	0.214			
22:23 CCA	6.58	0.218	15-71313	0.35	0.46
22:40 CBA	6.12	0.224			
22:40 CCA	6.39	0.219	15-71314	0.39	0.47
22:52 CBA	6.23	0.224			
22:52 CCA	6.43	0.191	15-71315	0.36	0.45
23:05 CBA	6.11	0.203	15-70927	0.34	0.44
23:05 CCA	6.26	0.231	15-70928	0.34	0.41
23:18 CBA	5.85	0.231	15-70919	0.32	0.41
23:18 CCA	6.10	0.236	15-70920	0.35	0.41
23:24 3CBA	7.28	0.209	15-70921		
23:24 3CCA	6.50	0.213	15-70922		
23:55 CBA	4.22	0.242	15-70923	0.23	0.34
23:55 CCA	5.44	0.241	15-70924	0.27	0.34
23:58 3CBA	6.71	0.217	15-70925		
23:58 3CCA	5.93	0.236	15-70926		
0:38 CBA	4.68	0.263	15-70929	0.23	0.35
0:38 CCA	5.90	0.237	15-70930	0.32	0.37
0:37 CIRC	5.56	0.270			
0:47 CIRC	5.91	0.259			

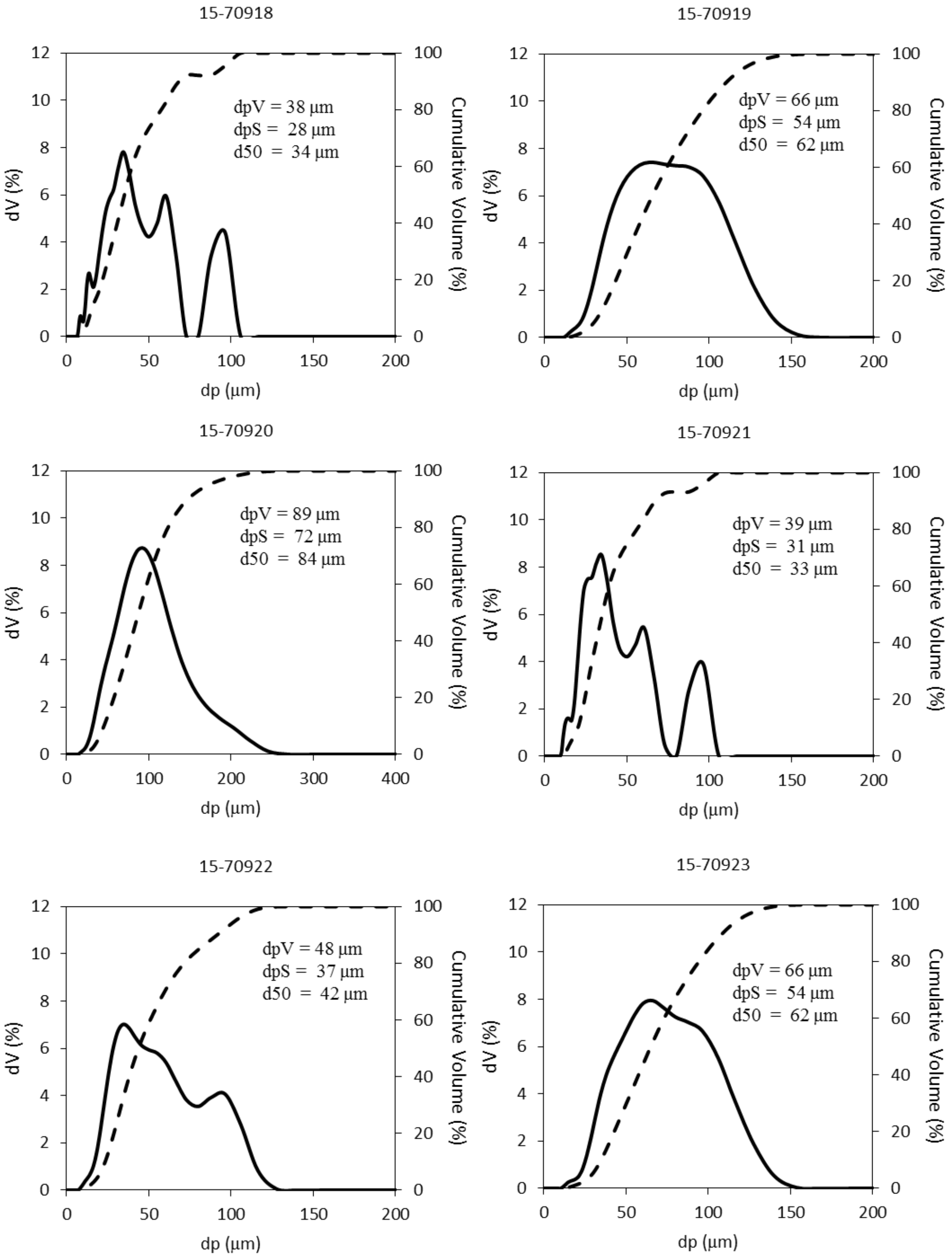


Figure 8.14. Particle size distributions of selected samples during test 9.

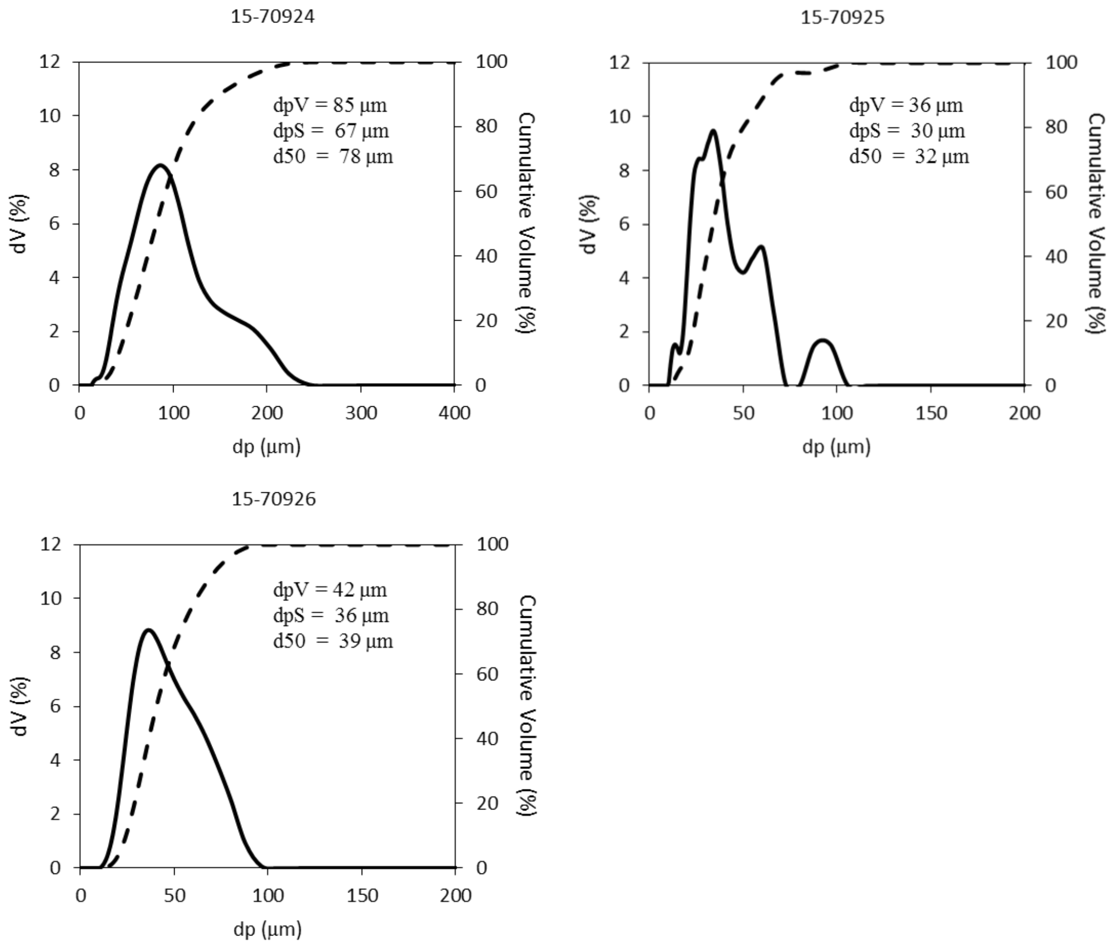


Figure 8.14. (cont.). Particle size distributions of selected samples during test 9.

Test 10

This test was carried out with the loop seals configuration in the secondary recycles. Also, small electrical motor vibrators were installed in the secondary cyclones of both reactors. The objective of the test was to carry out a CO_2 capture test with small particle sizes. The initial solids used came from test 9.

Figure 8.15 shows the main operating variables after feeding coal to the calciner until the end of the test.

Between 10:24 h and 11:45 h, the average temperatures in the carbonator (Figure 8.15.a.) was increased from 614ºC to 640 ºC due to circulation of solids and electrical ovens. The average temperature of calciner increased from 600 ºC to 820 ºC at the same period due to the coal combustion and the average inlet velocities were around 2.5 m/ and 3.0 for carbonator and calciner respectively at 11:45 h. Due to a breakage in the seal of the calciner loop, the coal feeding was stopped at 11:45 h and it was re-start at11:55 h, as a consequence the average calciner temperature dropped to around 660 ºC. Between 11:55 h and 13:08 h, the average temperature of calciner rose up to 910 ºC whereas the average carbonator temperature varied between 665 ºC and 732 ºC. The inlet velocity of calciner varied between 2.6 and 3.3 m/s whereas the inlet velocity to carbonator varied between 2.6 and 2.2 m/s due to the change in the temperatures. At 13:08 the coal feeding was stopped due to the lack of solids in the primary loop. At this time, the loop-seal of carbonator was stopped in order to facilitate the feeding of fresh limestone and re-seal the standpipe with solids. As a consequence, the average temperature of calciner dropped to similar values of the average temperature of carbonator around 650 ºC. The inlet velocity of calciner dropped to values of 2.2 m/s whereas the inlet velocity of carbonator was around 1.5 m/s due to the loop-seal was stopped. At 13:40 the coal feeding was re-started and the vibrators were switched on continuously. The average temperature of the calciner increased up to 885 ºC at 15:44 h whereas the carbonator temperature increased from around 660 ºC to 763 ºC at 15:02 h and then decreased to around 650 ºC at 15:44 h when CO_2 was fed to the carbonator. The inlet velocity to calciner increased from 2.2 m/s to 3.2 m/s due to the change in temperature and the inlet velocity of carbonator decreased from 2.4 m/s to 1.6 m/s when CO_2 was injected. Between 15:47 and 16:16, limestone was fed to the calciner, the average temperature of calciner decreased to 825 ºC whereas the carbonator temperature maintained an average temperature around 650 ºC. At 16:16 h the coal, CO_2 and limestones feedings were stopped due to the secondary cyclone of calciner was plugged.

The solids inventories in both reactors (Figure 8.15 b) oscillated between 44 kg/m^2 and 420 kg/m^2 in the carbonator and between 21 and 270 kg/m^2 in the calciner. These oscillations were related with the limestone feeding and the discharges from the secondary recycle due to the vibrators. The solids circulation rate was unstable and oscillated between 0.1 kg/m^2s and 6 kg/m^2s. The on-line analyzer 1 measured the calciner exit gas concentration during the period of time shown (Figure 8.15.c.). During the periods when coal was fed the average O_2, CO_2 and CO concentrations were 7.1 vol.%, 16.6 vol.% and 127 ppmv respectively. The on-line gas analyzer 2 was measured the carbonator exit gas concentration during the test (Figure 8.15.d.). Between 10:24 and 15:02 it was detected certain combustion in the loop-seal of carbonator as the analyzer measured a CO_2, CO and O_2 concentrations that varied from 0 to 6.8 vol.%, from 0 to 0.1 vol% and from 21 to 13.5 vol.% respectively whereas no CO_2 was fed during this period. Between 15:02 h and 15:55 h a CO_2 inlet concentration of 24 vol% (without combustion) was fed to the carbonator and the exit CO_2 concentration measured by the analyzer increased from 5.3 to 21 vol.%. at 15:38 h and then decreased to values around 7.5 vol.% when the inlet CO_2 concentration was reduced to 10 vol% (without combustion) at 16:14 h. The molar CO_2 flow calcined (Figure 8.15.e.) varied between 0 to 4.9 mol/m^2s along the test whereas the molar flow of CO_2 captured reached an average maximum value of around 7.9 mol/m^2s at 15:12 h and then decreased to an average value of around 2.8 mol/m^2s between 15:16 h to 16:14 h. The CO_2 capture efficiency (Figure 8.15.e.) was around 80% between 15:02 and 15:16 h and it was similar to the equilibrium. Then it decreased to 40 % between 15:23 and 16:14 h.

During the test, solid samples from carbonator (CCA) and calciner (CBA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.13 and Figure 8.16).

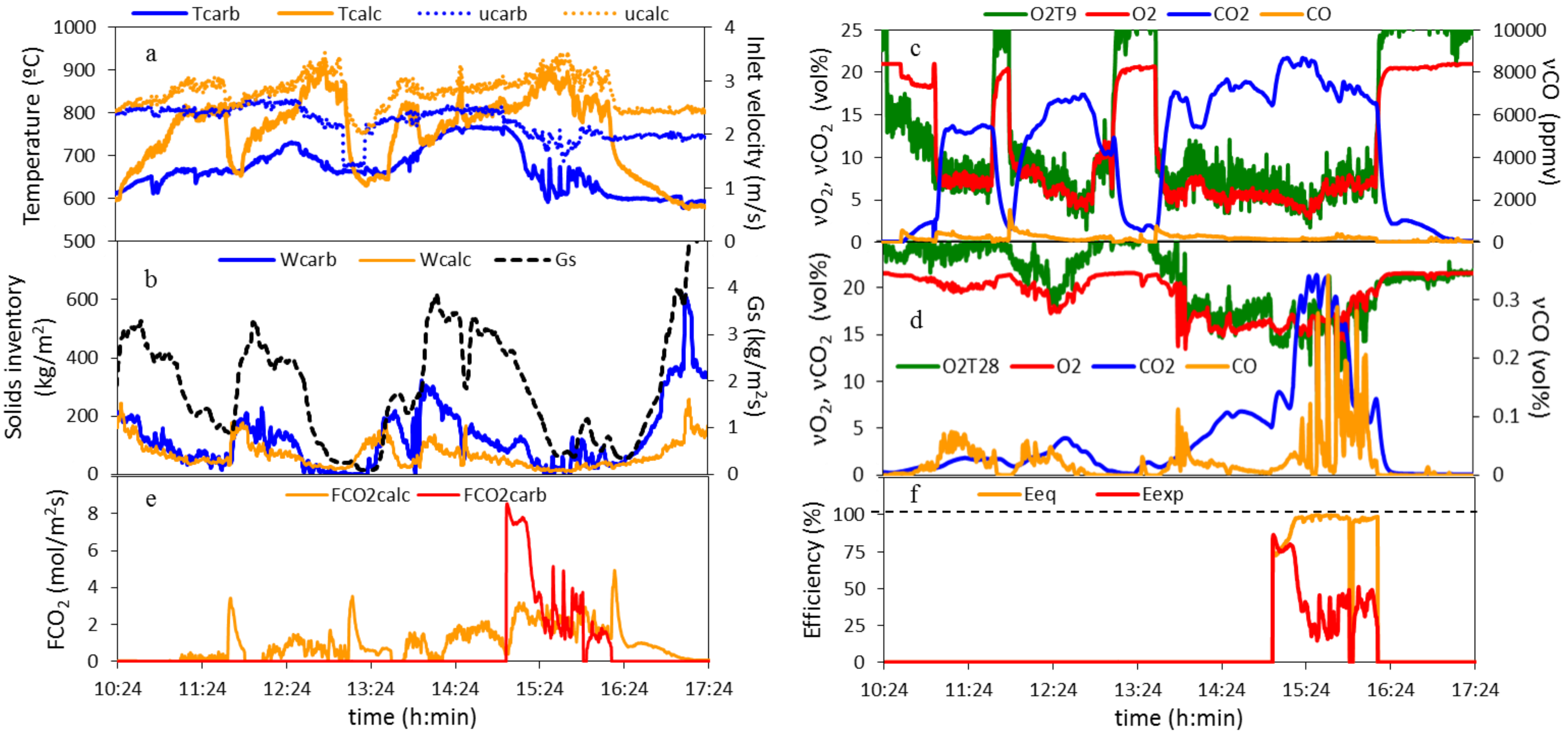


Figure 8.15. Experimental data during test 10. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. d. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.13. Analysis of samples extracted during test 10.

Sample	wC (%)	wS(%)	ID INCAR	$Xcarb_{TG}$	Xave
14:22 CCA	3.50	0.161	15-71203	0.24	0.42
14:54 CCA	1.67	0.223	15-71204	0.12	0.38
15:13 CCA	3.49	0.182	15-71205	0.23	0.34
15:13 CBA	2.74	0.220			
17:28 CCA	4.74	0.133	15-71206	0.3	0.41

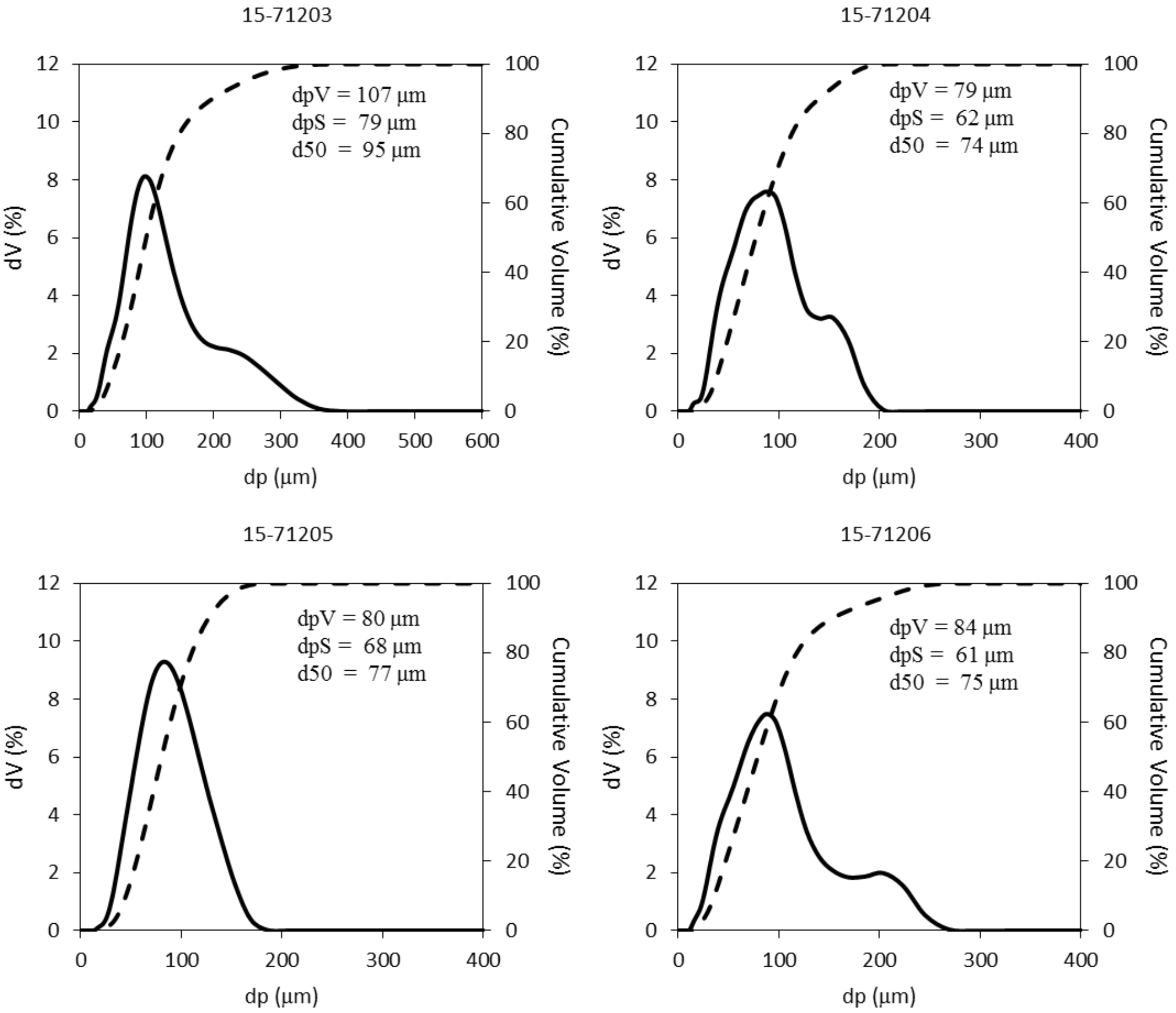


Figure 8.16. Particle size distributions of samples extracted during test 10.

Test 11

This test was carried out with the loop seal configuration in the secondary recycles and the small vibrators in the secondary cyclones. However, due to the problems of circulation in the test before, the fine material was extracted in order to control the built up of them in the primary loop. The initial solids used came from test 10. Figure 8.17 shows the main operating variables after feeding coal to the calciner until the end of the test.

The average temperature in the carbonator (Figure 8.17.a.) was between 640ºC and 720 ºC during the test. The small temperature decreases detected (i.e. at 10:27 h) corresponds with the feed of small batches of solids to the carbonator. The average temperature in the calciner was between 762 and 880 ºC and it was controlled by the coal feeding. The inlet velocity to the calciner was almost constant during the period shown and around 2.8 m/s. In the carbonator, the inlet velocity varied between 2.0 and 2.7 m/s due to changes in the air flow rates fed to the riser. The solids inventories in the calciner (Figure 8.17 b) were constant and around 50 kg/m^2 during the period shown whereas the solids inventory in the carbonator oscillated between 30 and 620 kg/m^2. These oscillations were related with the batches of solids fed to the carbonator and with limestone feeding to the calciner. The solids circulation rate varied between 0.9 kg/m^{2}s and 2 kg/m^{2}s and it was more stable than in previous tests. The on-line analyzer 2 measured the carbonator exit gas concentration during the period of time shown (Figure 8.17.c.) except between 16:21 h and 17:35 h when it was measured the exit gas concentrations of calciner. In the same way, the on-line gas analyzer 1 was measured the calciner exit gas concentration during the test (Figure 8.17.d.) except between 16:21 h and 17:35 h when it was measured the exit gas concentrations of carbonator. The average exit concentration of O_2 at the exit of carbonator was 18.2 vol%. Between 11:40 and 12:22 h, an inlet CO_2 concentration of 21 vol.% was fed to the carbonator and the average exit CO_2 concentration increased from 3 vol.% to 15 vol.%. Between 12:23 and 13:27 h, the inlet CO_2 concentration was decreased to 12 vol.% and the average exit CO_2 concentration increased from 2.5 vol.% to 6.5 vol.%. Between 13:28 and 16:20 h, the inlet CO_2 concentration was increased to 18 vol.% and the average exit CO_2 concentration increased from 6.6 vol.% to 9.1 vol.%. Between 19:06 and 22:14 h, the inlet CO_2 concentration was 12 vol.% and the average exit CO_2 concentration decreased from 6.3 vol.% to 2.5 vol.%. Between 22:15 and 22:49 h, an inlet CO_2 concentration of 18 vol.% was fed to the carbonator and the average exit CO_2 concentration was 7.6 vol.%. Finally, from 22:52 to the end the inlet CO_2 concentration was decreased to 15 vol.% and the average exit CO_2 concentration was 4.7 vol.%. The signal of the exit CO_2 concentration in each riser oscillated around a value with an amplitude of 2 or 3 points in percentage. These oscillations were due to the apertures of the secondary cyclones that induced a leakage of gas from the loop-seals to the cyclones. As a consequence, the CO_2 concentration at the exit of calciner decreased and the CO_2 concentration at the exit of carbonator increased until the leakages were closed (by solids deposition in the secondary cyclones). These oscillations were traduced in oscillations of the molar flow rates of CO_2 calcined and captured (Figure 8.17.e). The average molar flowrates captured and calcined were 3.4 mol/m2s between 12:34 and 16:15 h. Between 18:54 to the end the average molar flowrate of CO_2 captured was 2.7 mol/m^{2}s whereas the average molar flow rate of CO_2 calcined was 3.7 mol/m^{2}s. The CO_2 capture efficiency (Figure 8.17.f) varied between 62 and 80 % between 12:34 and 16:15 h. Between 18:54 and 22:15 h the CO_2 capture efficiency increased from 75 % to 82 % and decreased to an average value of 64 % at 22:52 h.

During the test, solid samples from carbonator (CCA), calciner (CBA), measurements of solids circulation rate (CIRC) and secondary cyclones (2CBA, 2CCA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.14 and Figure 8.18).

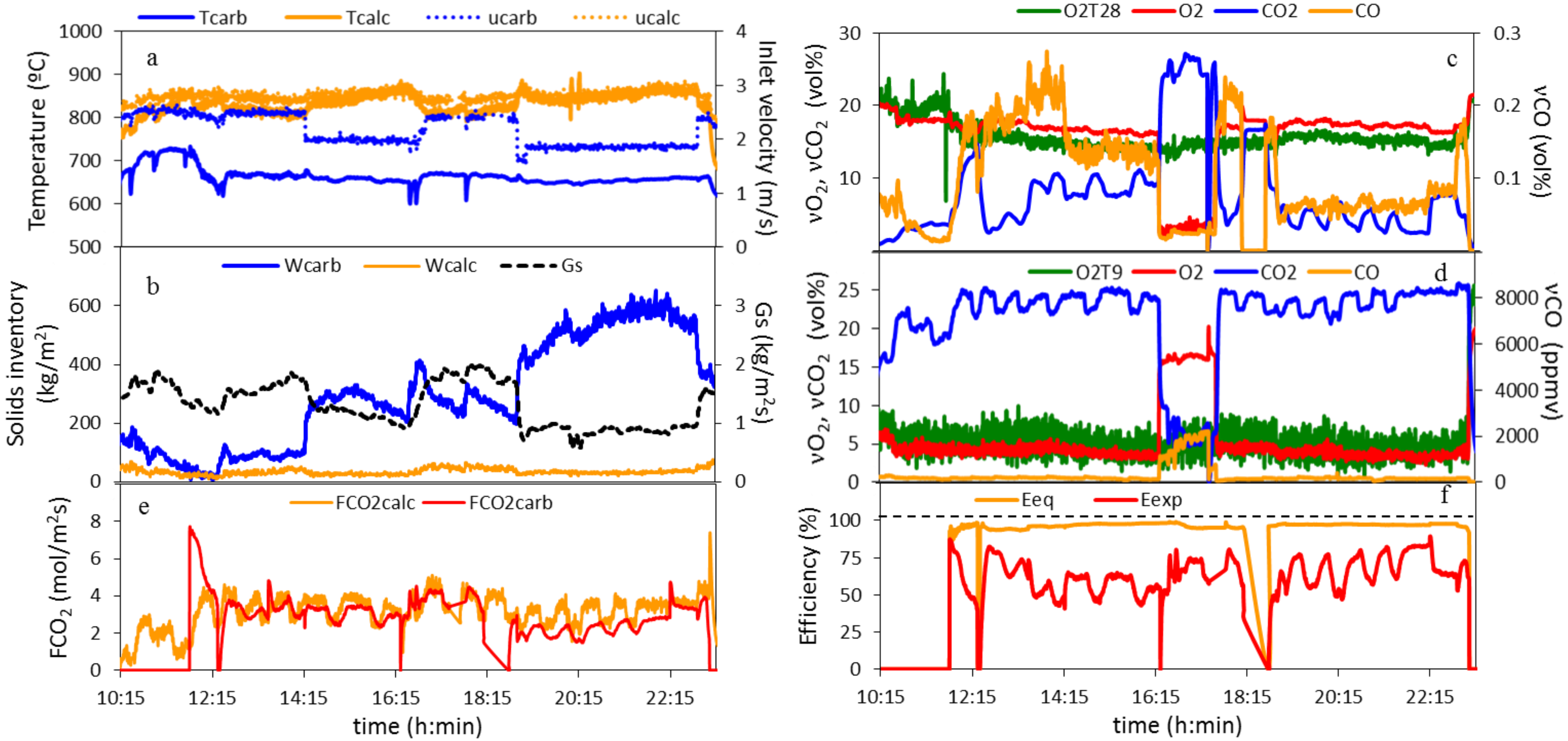


Figure 8.17. Experimental data during test 11. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Solids inventories in both reactors and solids circulation flowrate. c. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. d. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.14. Analysis of samples extracted during test 11.

Sample	wC (%)	wS(%)	ID INCAR	Xcarb$_{TG}$	Xave
9:20 2CCA	5.92	0.165	15-71207	0.37	0.45
9:20 2CBA	6.22	0.190	15-71208	0.38	0.45
9:52 2CCA	6.68	0.151			
9:52 2CBA	6.99	0.148			
10:20 2CCA	7.33	0.124			
10:20 2CBA	6.85	0.142			
10:51 2CCA	6.33	0.165	15-71209	0.40	0.47
10:51 2CBA	6.84	0.154	15-71210	0.43	0.48
11:22 2CCA	4.02	0.188			
11:22 2CBA	4.39	0.186			
11:22 CBA	1.37	0.293			
11:47 2CCA	2.68	0.237			
11:47 2CBA	2.74	0.224			
11:55 CCA	3.78	0.249	15-71212	0.21	0.33
11:55 CBA	2.02	0.319			
12:13 2CCA	3.59	0.236			
12:13 2CBA	2.86	0.273			
12:18 CCA	4.48	0.200	15-71213	0.27	0.38
12:18 CBA	1.54	0.362			
12:38 CCA	3.29	0.302	15-71214	0.20	0.28
12:38 CBA	1.94	0.336			
12:57 CCA	3.35	0.292	15-71215	0.20	0.27
12:57 CBA	2.49	0.329			
13:19 CCA	3.80	0.304	15-71216	0.21	0.27
13:19 CBA	2.68	0.344			
13:38 CCA	3.62	0.324	15-71217	0.22	0.29
13:38 CBA	3.06	0.354			
13:58 CCA	3.96	0.315	15-71218	0.22	0.29
13:58 CBA	3.12	0.344			
14:26 CCA	3.99	0.294	15-71219	0.25	0.30
14:26 CBA	2.92	0.349	15-71220	0.16	0.27
14:41 2CCA	5.57	0.210	15-71221	0.34	0.38
14:41 2CBA	4.78	0.254	15-71222	0.26	0.34
15:04 CCA	4.41	0.318	15-71223	0.26	0.31
15:04 CBA	2.65	0.361			
15:18 CCA	4.13	0.346	15-71224	0.25	0.29
15:18 CBA	2.51	0.406			
16:08 CCA	3.24	0.361	15-71225	0.19	0.21
16:08 CBA	1.00	0.520	15-71226	0.07	0.21
16:29 CCA	2.77	0.437	15-71227	0.16	0.21
16:29 CBA	0.66	0.562			

Sample	wC (%)	wS(%)	ID INCAR	$Xcarb_{TG}$	Xave
17:03 CCA	3.77	0.367	15-71228	0.21	0.26
17:03 CBA	2.62	0.461			
18:00 CCA	3.35	0.361	15-71229	0.20	0.25
18:00 CBA	2.33	0.458	15-71230	0.14	0.23
18:50 CCA	2.85	0.436	15-71231	0.17	0.22
18:50 CBA	1.58	0.579			
19:19 CCA	3.47	0.413	15-71232	0.20	0.25
19:19 CBA	1.84	0.519			
19:44 CCA	4.16	0.354	15-71233	0.24	0.28
19:44 CBA	2.40	0.432	15-71234	0.14	0.26
20:05 CIRC	4.10	0.389	15-71235	0.24	0.29
20:15 CIRC	4.37	0.340			
21:00 CCA	4.74	0.326	15-71236	0.28	0.32
21:00 CBA	2.61	0.373			
21:25 CBA	2.15	0.396			
21:25 CCA	4.59	0.328	15-71237	0.26	0.30
21:57 CCA	4.44	0.342	15-71238	0.27	0.31
21:57 CBA	1.77	0.439			
22:29 CCA	4.67	0.316	15-71239	0.29	0.32
22:29 CBA	1.88	0.463	15-71240	0.12	0.25
22:47 CCA	4.15	0.384	15-71241	0.24	0.28
22:47 CBA	1.75	0.469			
23:04 CCA	3.50	0.420	15-71242	0.21	0.27
23:04 CBA	2.25	0.453			

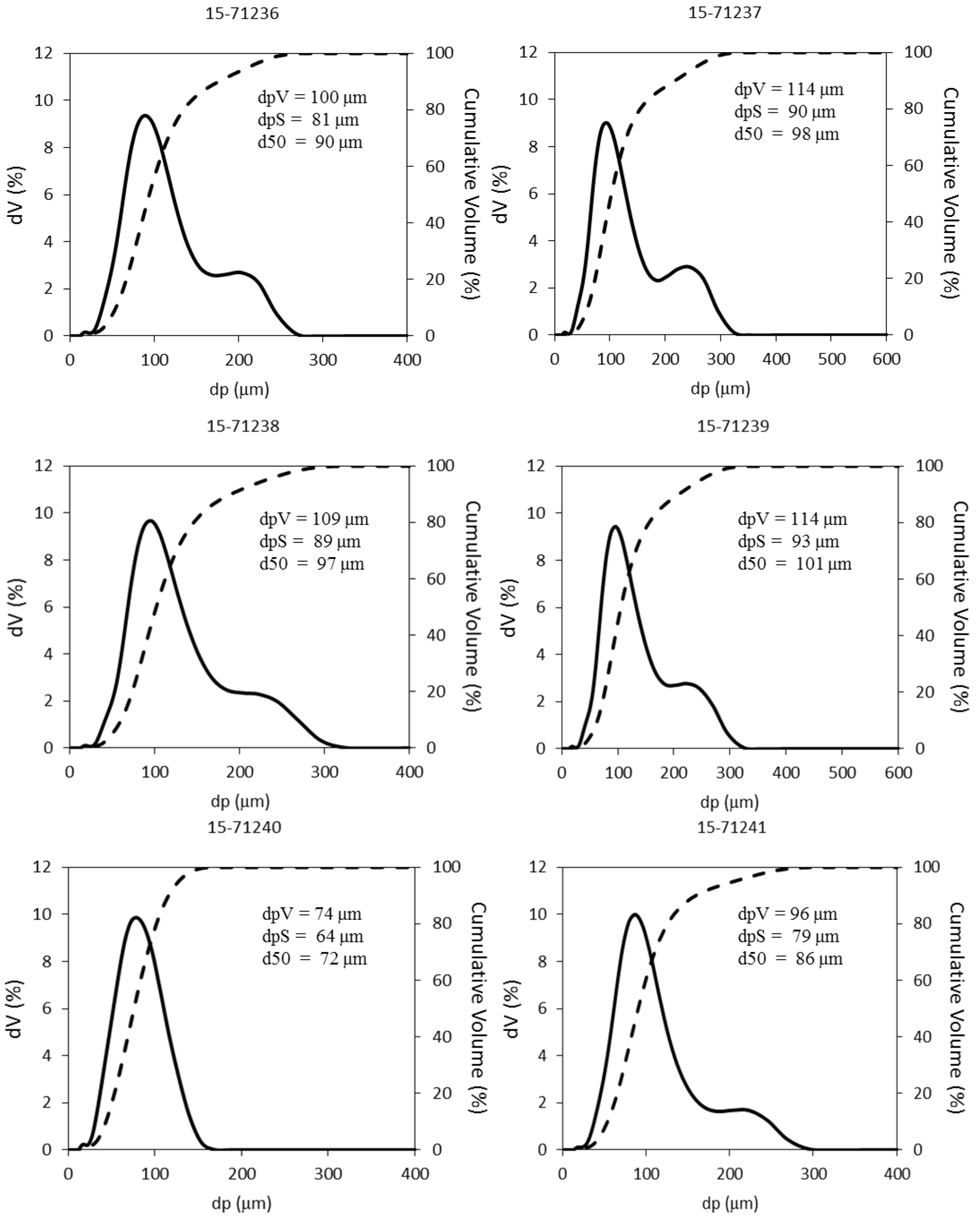


Figure 8.8. Particle size distributions of selected samples from test 11.

Test 12

This test was carried out with the loop seal configuration in the secondary recycles and it was installed a double valve at the exit of each secondary cyclones in order to prevent the gas leakage of previous test. As in the test before the fine material was extracted in order to control the built up of them in the primary loop. The initial solids used came from test 11. Figure 8.19 shows the main operating variables just before CO_2 injection in the carbonator to the calciner until the end of the test.

The average temperature in the carbonator (Figure 8.19.a.) was between 600ºC and 730 ºC whereas the average temperature in the calciner was between 775 and 905 ºC. The inlet velocity to the calciner was maintained around 2.7 m/s. In the carbonator, the inlet velocity varied between 2.1 and 3.2 m/s due to changes in the inlet flow rates fed to the riser (i.e. air, CO_2 and steam). The solids inventories in the calciner (Figure 8.19 b) were between 30 kg/m^2 and 160 kg/m^2 during the period shown whereas the solids inventory in the carbonator oscillated between 30 and 360 kg/m^2. These oscillations were related with the batches of solids fed to the carbonator (i.e. the increase from 90 kg/m^2 to 310 kg/m^2 at 11:52 h) and with limestone feeding to the calciner (i.e. the increase from 165 kg/m^2 to 375 kg/m^2 at 14:28 h). The solids circulation rate varied between 0.9 kg/m^{2}s and 2.1 kg/m^{2}s. The on-line analyzer 2 measured the carbonator exit gas concentration during the period of time shown (Figure 8.19.c.). The average exit O_2 concentration varied between 16.3 vol.% and 19.3 vol.% due to the different inlet CO_2 concentration and the combustion in the loop-seal that fed this reactor. The average exit CO_2 concentration varied between 1.1 vol% and 18.7 vol.%. There were five periods when the CO_2 was not injected: between 14:28 and 16:03 h, between 16:27 h and 16:53 h, between 17:23 and 17:40 h, between 18:00 and 18:58 h and between 19:36 and 20:08 h. During these periods only calcination took place. The on-line gas analyzer 1 was measured the calciner exit gas concentration during the test (Figure 8.19.d.). The average exit O_2 concentration varied between 3.6 and 6 vol.% whereas the average exit CO_2 concentration varied between 15 and 25.5 vol.%. The molar flow of CO_2 calcined (Figure 8.19.e) varied between 0.5 and 4.5 kg/m^{2}s whereas the molar flow of CO_2 captured varied between 2.8 and 8.8 mol/m^{2}s depending on the inlet CO_2 and steam fed to the carbonator. The maximum carbonation efficiency varied between 80% and 98% (Figure 8.19.f). Between 11:30 h and 12:00 h, the inlet CO_2 concentration was 22 vol% and no steam was fed, the CO_2 capture efficiency decreased from 93 % to an average value around 57%. Between 12:02 and 12:20 h the inlet CO_2 concentration was increased to 28 vol% and the CO_2 capture efficiency decreased to 48 % at 12:20 h. Between 12:20 and 13:03 h the inlet CO_2 concentration was decreased to 15 vol.% and the CO_2 capture efficiency increased to values around 66%. Then, steam was fed to the carbonator at inlet concentration of 14.4 vol% while the inlet CO_2 concentration was maintained, the CO_2 capture efficiency increased to 73% at 13:20 h when the steam feeding was stopped and the CO_2 capture efficiency decreased to values around 54 %. Between 16:03 and 16:15 h, inlet CO_2 and steam concentrations of 15 vol% and 14.3 vol% respectively were fed to the carbonator, the CO_2 capture efficiency was around 84%, then the CO_2 inlet concentration was increased to 28 vol.% until 16:30 h and the CO_2 capture efficiency decreased to 78%. Between 16:53 and 17:03, h an inlet CO_2 concentration around 26 vol.% was fed to the carbonator without steam, the CO_2 capture efficiency decreased from 96% to 56 %, then the inlet CO_2 concentration was decreased to 11% until 17:14 h and the CO_2 capture efficiency increased to 84 % at 17:14 h. After that, the CO_2 inlet concentration was increased to 21 vol.% and the CO_2 capture efficiency decreased to 48 %. Between 17:42 and 17:56 h inlet concentrations of CO_2 and steam of 25 vol% and 13.4 vol% respectively were fed to the carbonator. The CO_2 capture efficiency decreased from 98 % to 40 %, then the steam flowrate was stopped and the CO_2 capture efficiency dropped to 31%. Between 19:02 and 19:36 h, an inlet CO_2 concentration of 27 vol.% without steam was fed to the carbonator, the CO_2 capture efficiency decreased from 96% to 54%. Between 20:06 and 20:32 h, inlet concentrations of CO_2 and steam of 25 vol.% and 13.8 vol.% were fed to the carbonator and the CO_2 capture efficiency dropped from 95 % to 55%. Finally, at 20:32 h the steam feeding was stopped and the CO_2 capture efficiency decreased to 46% at 20:40 h.

During the test, solid samples from carbonator (CCA), calciner (CBA), and secondary cyclones (2CBA, 2CCA) were extracted for carbonate content analysis and selected samples were analyzed for measuring maximum carrying capacity and PSD (Table 8.15 and Figure 8.20).

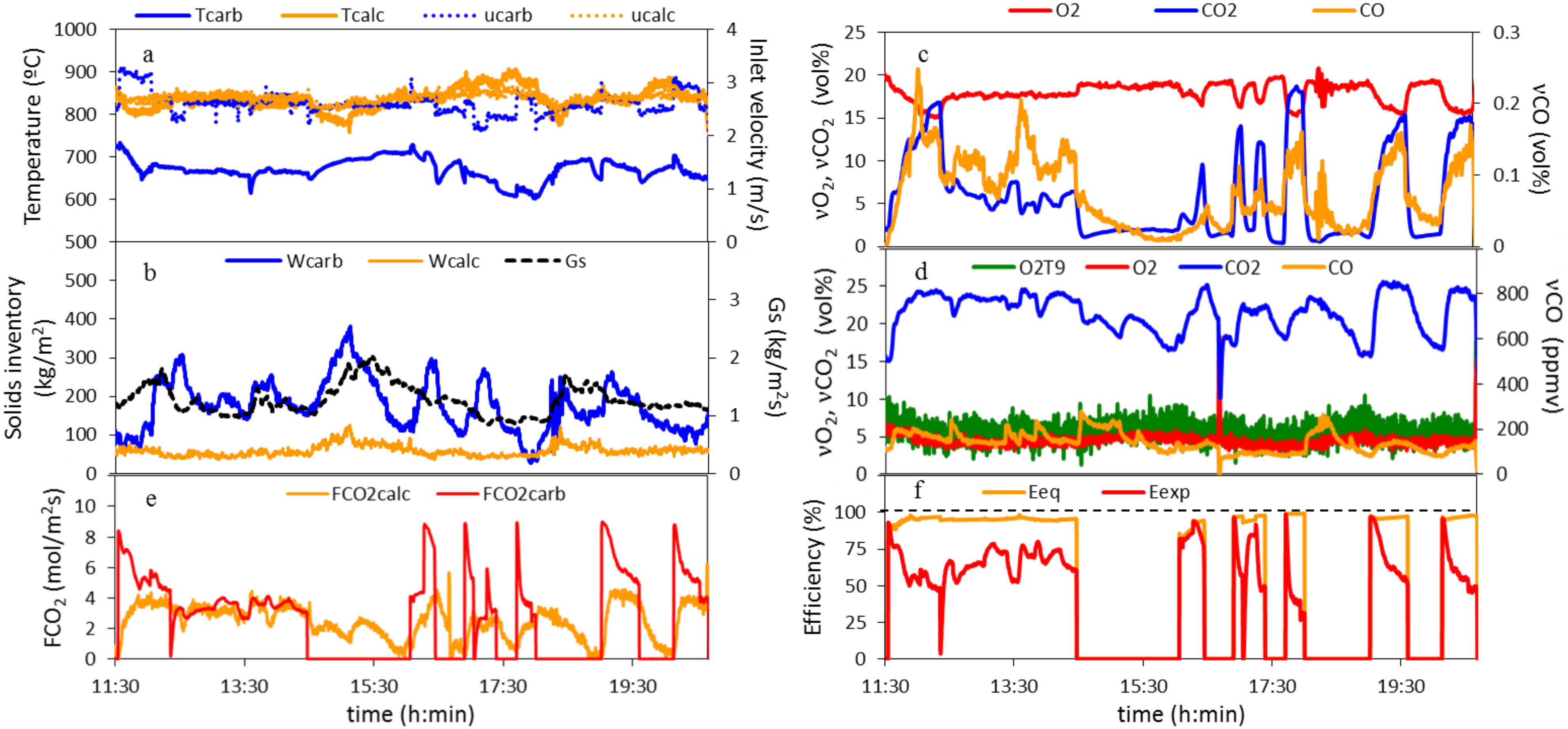


Figure 8.9. Experimental data during test 12. a. Average temperatures and velocities in the carbonator (carb) and calciner (calc). b. Gas concentration measurements by the on-line analyzer 1 at the exit of calciner. c. Solids inventories in both reactors and solids circulation flowrate. d. Gas concentration measurements by the on-line analyzer 2 at the exit of carbonator. e. CO_2 molar flowrate captured and calcined. f. Maximum CO_2 capture efficiency (Eeq) allowed by the equilibrium and experimental CO_2 capture efficiency (Eexp).

Table 8.15. Analysis of samples extracted during test 12.

Sample	wC (%)	wS(%)	ID INCAR	Xcarb$_{TG}$	Xave
10:16 2CCA	4.58	0.220	15-71649		
10:16 2CBA	4.66	0.234			
10:58 CCA	1.31	0.491	15-71650	0.09	0.25
10:58 CBA	2.25	0.469	15-71651		
11:02 2CCA	5.11	0.256			
11:02 2CBA	5.52	0.244			
11:19 CCA	0.40	0.512	15-71652	0.05	0.24
11:19 CBA	0.63	0.530			
11:37 2CCA	3.27	0.311			
11:37 2CBA	3.37	0.268			
11:50 CCA	2.75	0.473	15-71653	0.17	0.25
11:50 CBA	1.58	0.525	15-71655		
12:00 CCA	2.70	0.461	15-71657	0.16	0.23
12:00 CBA	2.31	0.471	15-71658	0.15	0.27
12:06 2CCA	2.12	0.354			
12:06 2CBA	3.51	0.300			
12:19 CCA	2.65	0.451		0.16	0.22
12:19 CBA	1.56	0.548	15-71659	0.1	0.21
12:28 2CCA	2.40	0.306			
12:28 2CBA	3.58	0.346			
12:44 CCA	2.09	0.535	15-71660	0.13	0.2
12:44 CBA	0.99	0.591	15-71661	0.07	0.19
13:12 CCA	2.37	0.514	15-71662	0.13	0.18
13:12 CBA	0.52	0.633	15-71663		
13:22 CCA	2.37	0.570	15-71666	0.14	0.19
13:22 CBA	0.63	0.659			
13:19 2CCA	2.93	0.314	15-71664		
13:19 2CBA	2.73	0.418	15-71655		
13:31 CCA	2.19	0.566	15-71667	0.13	0.18
13:31 CBA	0.59	0.648	15-71668	0.05	0.16
13:45 CCA	2.62	0.546	15-71669	0.14	0.2
13:45 CBA	1.31	0.583			
14:10 CCA	2.44	0.619	15-71670	0.14	0.18
14:10 CBA	0.92	0.750	15-71671		
14:26 CCA	1.80	0.665	15-71693	0.13	0.18
14:26 CBA	0.55	0.748			
15:44 CBA	0.56	0.568	15-71673		
16:11 CCA	1.72	0.477	15-71674	0.11	0.24
16:11 CBA	0.66	0.599	15-71654		
16:23 CCA	3.18	0.522	15-71675	0.2	0.24
16:23 CBA	1.16	0.607	15-71676		

Sample	wC (%)	wS(%)	ID INCAR	$Xcarb_{TG}$	Xave
16:46 CCA	0.37	0.612	15-71672	0.06	0.23
16:46 CBA	0.21	0.639			
16:56 CCA	1.94	0.616	15-71677	0.12	0.22
16:56 CBA	0.16	0.684		0.04	0.21
17:12 CCA	1.94	0.640	15-71678	0.12	0.2
17:12 CBA	0.00	0.763	15-71679		
17:22 CCA	1.79	0.590	15-71680	0.11	0.19
17:22 CBA	0.12	0.713			
17:44 CCA	1.66	0.643	15-71682	0.11	0.19
17:44 CBA	0.37	0.709			
17:52 CCA	1.78	0.622	15-71681	0.11	0.18
17:52 CBA	0.17	0.788			
18:48 CBA	0.10	0.550	15-71683		
19:04 CCA	2.37	0.526	15-71684	0.14	0.22
19:04 CBA	0.50	0.606			
19:34 CCA	2.19	0.521	15-71685	0.14	0.21
19:34 CBA	1.12	0.640	15-71686		
20:00 CBA	0.05	0.688	15-71687	0.03	0.18
20:11 CCA	2.27	0.613	15-71688	0.13	0.19
20:11 CBA	0.24	0.642	15-71689		
20:30 CCA	2.00	0.619	15-71690	0.12	0.18
20:30 CBA	0.60	0.711			

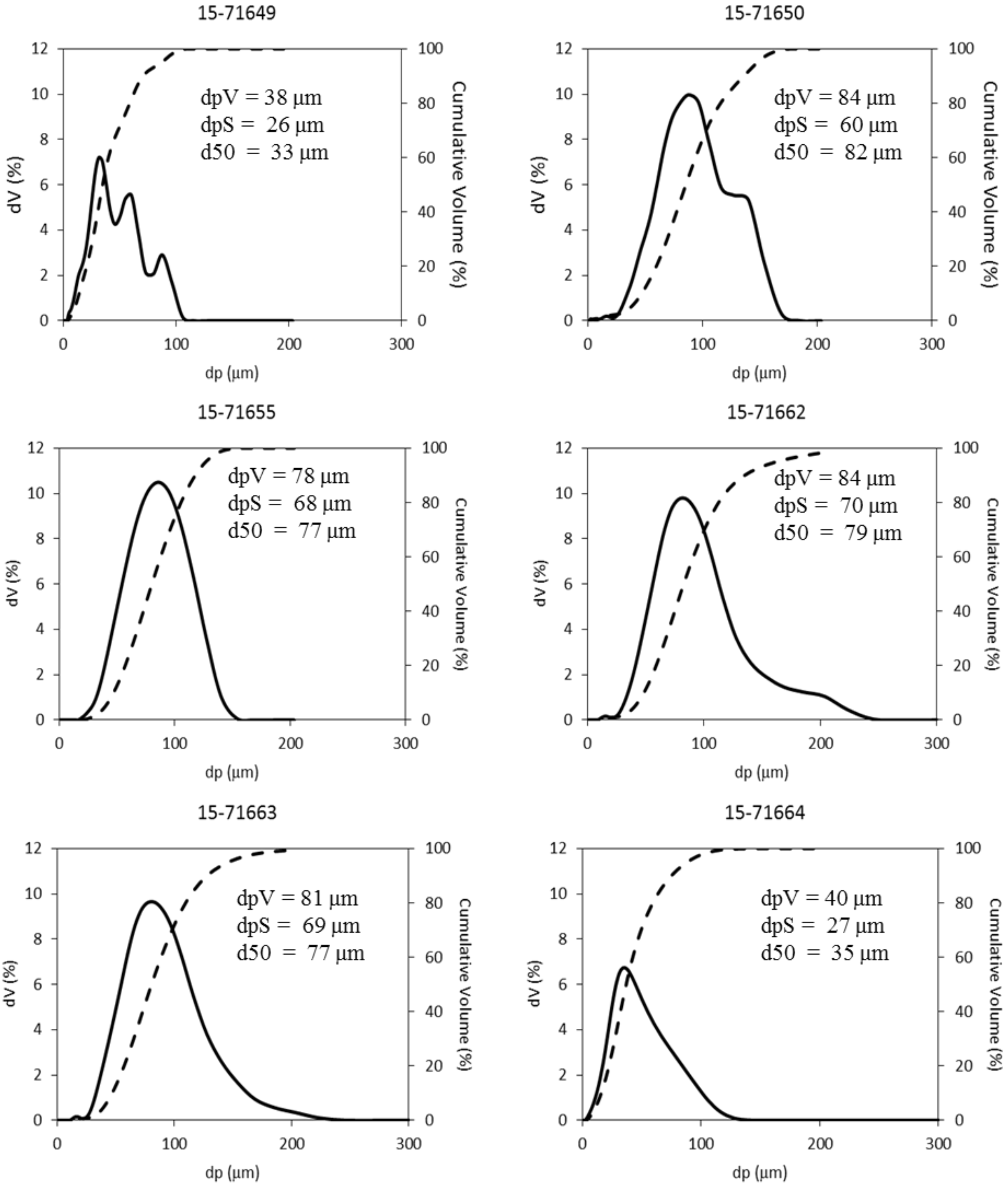


Figure 8.20. Particle size distributions of selected samples extracted during test 12.

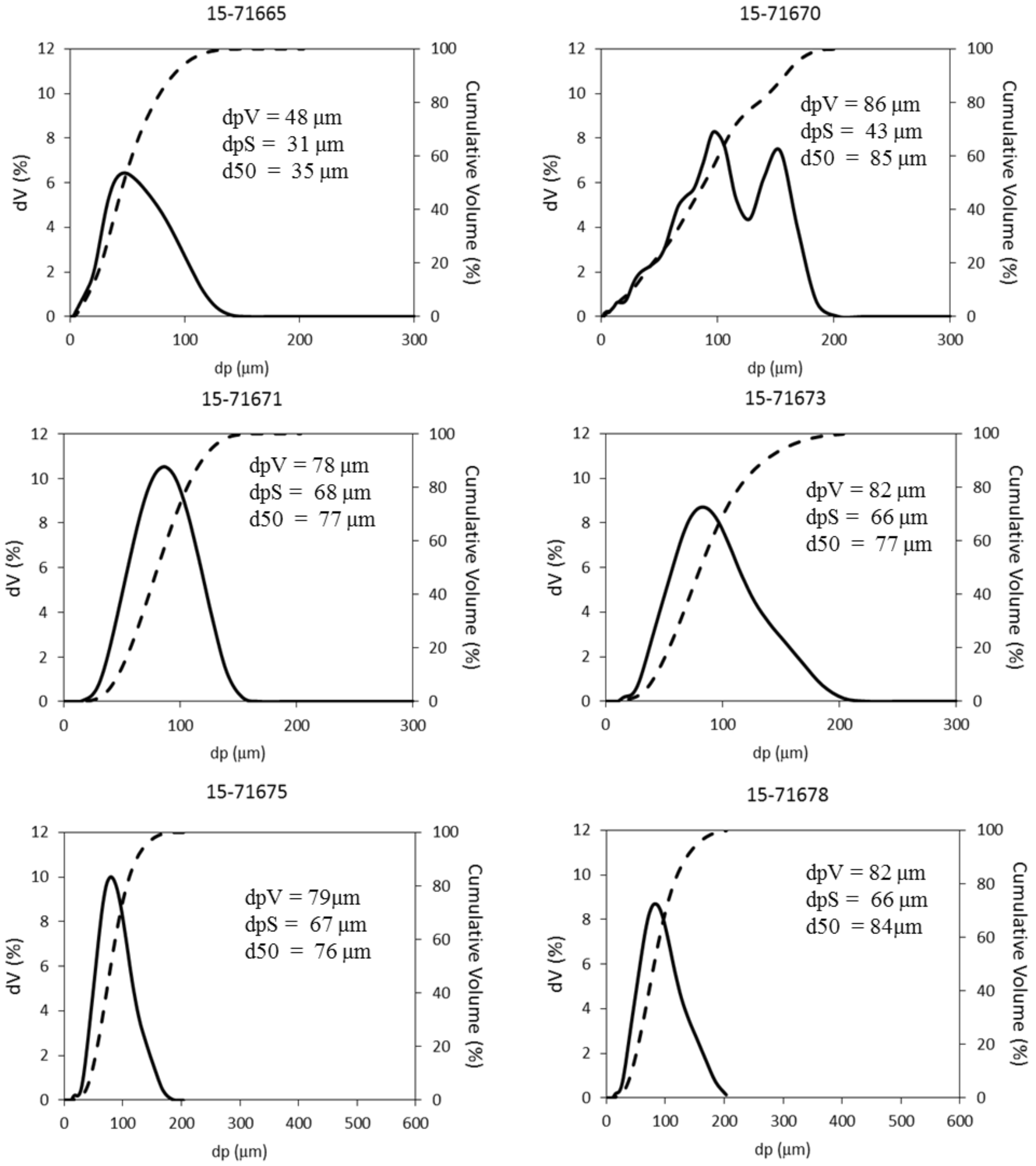


Figure 8.20. (cont.). Particle size distributions of samples extracted during test 12.

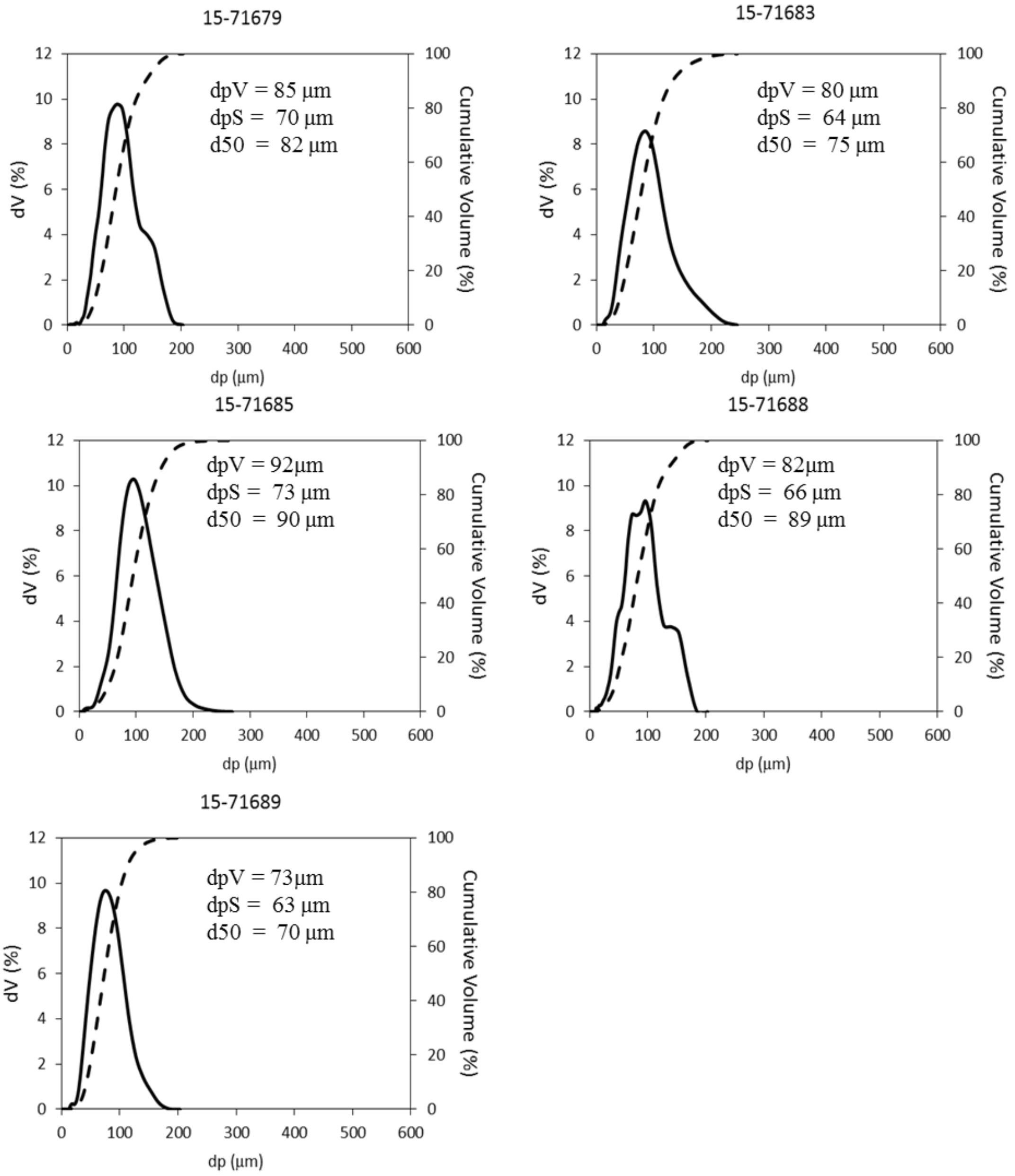


Figure 8.20. (cont.). Particle size distributions of samples extracted during test 12.