Investigation of the dynamic evolution of the CO₂ carrying capacity of solids with time in La Pereda 1.7 MW_{th} calcium looping pilot plant

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Abstract

Calcium Looping (CaL) is a technology that makes use of CaO to capture CO₂ from industrial flue gas sources in a carbonator, after which the CO₂ is released in a concentrated form in an oxyfired calciner. The CO₂ carrying capacity of the particles circulating between the carbonator and calciner is a key variable, as it is intimately linked to CO₂ capture efficiency in the carbonator reactor. Therefore, the ability to predict dynamic changes in the CO₂ carrying capacity of the sorbent is required to understand the dynamic performance of CaL systems. This work investigates the dynamic evolution of the average CO₂ carrying capacity of the sorbent (X_{ave}) during transient scenarios in a large CaL pilot plant. Several experimental campaigns with extensive solids sampling and analyses were carried out to analyse the evolution of X_{ave} with time when the make-up flow fed into the calciner is modified (between 0 and 2.7 kmol CaCO₃/h). Variations in X_{ave} were tracked and the observed trends were interpreted using two residence time distribution models of different complexity. The main characteristics and limitations of each model are discussed in this study. The choice between the two modelling approaches developed in this work depends on the input information available and the degree of accuracy required for each specific application.

Keywords: CO₂ capture; calcium looping; dynamic; CO₂ carrying capacity; flexibility

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1. Introduction

Deep cuts in CO₂ emissions are required to limit the global temperature rise to 1.5-2°C to avoid undesirable climate effects (IPCC, 2018; UNFCCC). Despite the increase in the use of renewables (REN21, 2017), flexible power generation from fossil fuels can still play a key role in future low-carbon electricity systems in association with flexible CO₂ capture and storage (CCS) (IEA, 2012, 2017). Indeed, flexible CCS power systems can guarantee a secure supply of low-carbon electricity in scenarios where the production of electricity from renewable sources is intermittent and/or below the demand curve (e.g., peak periods) (IEA, 2017).

Among the CO₂ capture technologies currently available, post-combustion calcium looping (CaL) is a promising option that employs CaO particles as CO₂ sorbent (Shimizu et al., 1999). The most advanced reactor configuration for CaL is a dual interconnected circulating fluidized bed system to allow solids to flow between the carbonator and the calciner reactors (Abanades et al., 2015; Blamey et al., 2010; Dean et al., 2011; Fan et al., 2012; Hanak et al., 2015a; Hanak et al., 2018; Martínez et al., 2016; Perejón et al., 2016), as schematically represented in Figure 1. The flue gas enters through the bottom of the carbonator, where the CO₂ reacts with CaO particles present in the bed to form CaCO₃ at ~650°C. High CO₂ capture efficiencies (≥90%) can be achieved in this reactor (Arias et al., 2013; Chang et al., 2014; Dieter et al., 2014; Kremer et al., 2013). The resulting stream of partially carbonated solids is then sent to the calciner, where the CaCO₃ particles decompose to produce a continuous stream of CaO, which is transported back to the carbonator, and a highly concentrated CO₂ gas, which can be then purified and compressed. If this CO₂ is permanently stored underground, the original CO₂ emissions at the source are largely avoided, whereas they are only reduced by a maximum of 50% if the CO₂ is used to manufacture short-lived products (Abanades et al., 2017). In the most developed CaL process, the thermal power required for the endothermic calcination (at temperatures of around 920°C) can be supplied by the oxy-combustion of a fuel.

Figure 1. Schematics of a post-combustion CaL system showing the main gas/solids streams and the calcium inventory of the reactors ($W_{Ca,CB}$ and $W_{Ca,CC}$) and loop seals ($W_{Ca,CB\ LS}$ and $W_{Ca,CC\ LS}$).

The system illustrated in Figure 1 requires a continuous supply of fresh CaCO_3 material to counteract the progressive loss of sorbent activity towards CO_2 with the number of calcination-carbonation cycles (Barker, 1973; Curran et al., 1967). A purge stream also needs to be extracted continuously in order to remove deactivated solids from the system and to avoid the undesired accumulation of inerts (Diego et al., 2013).

Post-combustion CaL systems offer a reduced energy penalty (usually around 6 to 9 net percentage points (Hanak et al., 2015b; Hawthorne et al., 2009; Lisbona et al., 2010; Martínez et al., 2011; Ortiz et al., 2017; Perejón et al., 2016; Romano, 2009; Romeo et al., 2008; Ströhle et al., 2009; Yang et al., 2010)), since a large fraction of the calciner energy input can be efficiently recovered from high-temperature sources to produce power. CaL technology has experienced a rapid development in the last 10-15 years, from laboratory scale experiments at thermogravimetric scale to tests in several large pilot plants at TRLs 4-6 (up to the MW_{th} scale) (Alonso et al., 2014; Arias et al., 2013; Chang et al., 2014; Diego and Alonso, 2016; Dieter et al., 2014; Dieter et al., 2013; Kremer et al., 2013). Several aspects of CaL have been analysed in these pilot plants, including demonstration of the technology and the study of alternatives for characterising and optimising the performance of the system (Alonso et al., 2014; Arias et al., 2013; Arias

et al., 2018; Chang et al., 2014; Diego and Alonso, 2016; Diego et al., 2017; Diego et al., 2016; Dieter et al., 2014; Dieter et al., 2013; Hilz et al., 2017; Kremer et al., 2013; Ströhle et al., 2014).

Experimental studies at large pilot plants have been carried out mainly for steady-state operation, and to date hardly any attention has been paid to the dynamic behaviour of CaL systems (only a few works report dynamic CaL aspects, such as variations in solids composition with changes in the system variables (e.g., the make-up flow) (see for example Arias et al., 2013; Hilz et al., 2017)). A better understanding of the behaviour of CaL systems during transient scenarios is important for being able to predict their performance after modifications to the operating conditions, either deliberate (i.e., to adapt the CaL conditions to the flue gas load) or unexpected (due to malfunctions in auxiliary equipment). This is also important for designing and optimising flexible operating and control strategies to enable CaL systems to adapt rapidly to changes, and at the same time maintain an appropriate level of performance. For example, this is the case of CaL systems coupled to back-up power plants (Astolfi et al., 2019; Criado et al., 2017; Hanak et al., 2016), which will need to operate flexibly and quickly to accommodate changes in load in future energy scenarios involving a large share of renewables.

There are only a limited number of modelling and simulation studies which deal with the performance of CaL systems operating under off-design conditions or which focus on the dynamic aspects of these systems (Astolfi et al., 2019; Cormos and Simon, 2015; Diego et al., 2015; Lara and Romeo, 2017). A first evaluation of the residence time distribution of particles was carried out by Diego et al. (Diego et al., 2015) to gain a better understanding of the different timescales involved in the dynamic behaviour of CaL systems. Moreover, a 1-D CaL dynamic model has also been presented by Ylätaalo et al. (Ylätaalo et al., 2012), and a comprehensive model has been developed by Cormos et al. (Cormos and Simon, 2015), who performed an analysis of the dynamic behaviour of CaL systems and evaluated the changes in CO₂ capture efficiency as a result of load modifications.

A key variable in CaL systems is the average CO₂ carrying capacity of the particles (X_{ave}), which determines the CO₂ capture efficiency that is to be achieved for a set of operating conditions (solids circulation rate, carbonator bed inventory and calciner performance). Several works have been dedicated to analysing the average CO₂ carrying capacity at steady state as a function of the CaL operating

conditions (Abanades, 2002; Arab et al., 2015; Li et al., 2008; Rodríguez et al., 2010). There are works that have also measured X_{ave} in CaL pilot plants (Arias et al., 2013; Charitos et al., 2011; Duelli et al., 2015), including a recent interpretation of the experimental results (Diego et al., 2017) based on the model developed by Rodríguez et al. (Rodríguez et al., 2010). However, these X_{ave} values were obtained in steady state scenarios in rigs over different operating times.

Despite the importance of the average CO_2 carrying capacity of the sorbent for the performance of CaL systems, none of the studies so far published analyse dynamic changes in X_{ave} . Accordingly, the present work investigates the evolution of the average CO_2 carrying capacity of CaO particles with time in La Pereda 1.7 MW_{th} CaL pilot plant during several dynamic tests in order to obtain useful experimental information that can contribute to a better understanding of the performance of CaL systems during transient scenarios. A model for predicting the evolution of X_{ave} during transient states with only a limited amount of experimental information as input is presented and applied here to interpret the results. Furthermore, an alternative approach based on particle population balances is also developed. Both methodologies are tested in several scenarios, evidencing the main benefits and limitations of each approach.

2. Experimental

La Pereda 1.7 MW_{th} CaL facility is only briefly described here, whilst a more detailed description is available elsewhere (Arias et al., 2013). The pilot plant is integrated in a 50 MW_e coal-fired CFB power plant. It consists of two interconnected refractory-lined circulating fluidized bed reactors, namely the carbonator and the calciner, with a height equal to 15 m and internal diameters of 0.65 and 0.75 m, respectively. Both reactors are interconnected via two loop seals to allow a continuous flow of solids between the reactors. Coal is continuously fed into the calciner to supply the energy required in this reactor. The fuel can be burnt under air or oxy-firing conditions, in the latter case using an O_2/CO_2 mixture delivered from cryogenic tanks. Fresh limestone can be continuously supplied to the calciner to compensate for the decrease in the sorbent activity experienced as a result of successive calcination-carbonation cycles. A purge can also be extracted from this reactor through a water-cooled screw conveyor in order to maintain a constant inventory of solids in the facility and to remove deactivated

121 solids and inerts. Three gas analysers continuously measure the composition of the gas entering the
122 carbonator and leaving the carbonator and calciner reactors. Solid samples are taken periodically from
123 both reactors using isokinetic probes. The extracted solid samples are subjected to chemical analysis in
124 order to measure the calcium carbonate, calcium sulphate, calcium oxide and ash contents. In addition,
125 thermogravimetric (TG) tests are carried out to determine the average CO₂ carrying capacity of the
126 particles.

Table 1. Average values of the main key operating parameters and variables in the pilot plant.

	Test 1	Test 2	Test 3	Test 4
Total calcium inventory, W_{Ca} (kmol)	7.7	9.8	6.6	13.0
Calcium molar flow circulating between reactors, F_{Ca} (kmol/h)	80.2	104	73.2	62.7
Make-up flow rate, F_0 (kmol/h)	0.9	2.7	0	0-1.4
Molar CO_2 flow rate, F_{CO_2} (kmol/h)	6.7	6.3	3.7	5.8
Fractional carbonation conversion, f_{carb}	0.75	0.40	0.55	0.66
Fractional calcination conversion, f_{calc}	0.48	0.42	0.42	0.86
Average CO_2 carrying capacity of the particles at $t=0$, $X_{ave,ini}$	0.096*	0.096*	0.21	0.25

*Particles in Tests 1 and 2 have been deliberately deactivated in the pilot plant prior to beginning the tests (the residual activity of the sorbent is $X_r=0.096$).

Several dynamic tests have been selected to investigate the evolution of the average CO_2 carrying capacity of the particles with time in La Pereda pilot plant. The main experimental conditions during the tests are summarized in Table 1, which shows the average values of the key input parameters that are used in the models, as described in the following sections. These include the total calcium inventory in the system (W_{Ca}), the molar circulation rate of calcium between reactors (F_{Ca}), the make-up flow rate of fresh limestone (F_0), the initial activity ($X_{ave,ini}$) and the fractional carbonation and calcination conversions (f_{carb} and f_{calc} , respectively), which can be obtained using the average CO_2 carrying capacity and the $CaCO_3$ content of the solids at the exit of the carbonator and calciner reactors (X_{carb} and X_{calc} , respectively) (Rodríguez et al., 2010):

$$f_{carb} = \frac{X_{carb} - X_{calc}}{X_{ave} - X_{calc}} \quad (1)$$

$$f_{calc} = \frac{X_{carb} - X_{calc}}{X_{carb}} \quad (2)$$

It is important to note that the calciner was operated under air conditions during these tests to avoid undesired effects that might deactivate the sorbent, which could result in misleading the X_{ave} experimental measurements (as occurs if particles experience additional carbonation-calcination cycles in the calciner (Charitos et al., 2011; Diego et al., 2017)). In the case of large-scale systems, this can be avoided by ensuring that appropriate operating conditions are maintained in this reactor, as explained elsewhere (Diego et al., 2017).

The total inventory of solids in the facility (including that of the loop seals) was determined by carrying out a sulfur mass balance, as described in (Diego et al., 2017). During the experiments, the calcium inventory was kept constant by removing solids from the calciner when limestone was fed into system. In addition, the molar circulation rate was calculated continuously by means of energy balances and was also measured periodically using isokinetic probes, as detailed elsewhere (Arias et al., 2013; Diego et al., 2016). The values of f_{carb} and f_{calc} were calculated from the carbonate content of the solids taken from the carbonator and calciner reactors, together with the experimental measurements of the CO_2 carrying capacity in TG. It should be noted that the experimental measurements of the CO_2 carrying capacities of the samples taken from the pilot plant are affected by the presence of $CaSO_4$, which forms as a result of the presence of sulphur in the coal supplied to the calciner and the SO_2 contained in the flue gases fed into the carbonator. However, the modelling approach described in the following section and used to estimate the evolution of X_{ave} with time does not take into account the effect of sulphur and its irreversible reaction with CaO . In order to compare the experimental average CO_2 carrying capacities and the calculated model values, the X_{ave} data reported in Table 1 have been estimated as the sum of the experimental X_{ave} resulting from the TG analysis, plus the increase in the calcium sulphate content of the solids due to the SO_2 captured during the period analysed, on the conservative assumption that SO_2 reacts with the CaO particles that are active for CO_2 capture.

Four experiments have been selected to investigate the dynamic evolution of X_{ave} over time in a CaL system (see Table 1). The first test corresponds to a case where the calcium inventory in the pilot plant was initially composed of highly-deactivated particles with residual activity (the CO_2 carrying capacity measured experimentally is 0.09). From the beginning of this experiment, a continuous fresh limestone flow is supplied to the system, thus increasing the average CO_2 carrying capacity of the solids. A second test similar to the previous one has also been included (i.e., in which the calcium inventory in the system is composed of particles with residual activity at time $t=0$), but with a substantially higher make-up flow rate of limestone. The third case corresponds to a test in which the make-up flow of limestone is stopped and the X_{ave} of the sorbent is allowed to decrease over time towards the residual value. Finally, Test 4 is a combination of the previous experiments, as it alternates periods of no limestone make-up flow feeding

(where the activity of the sorbent decreases) with short periodic additions of fresh limestone, which lead to gains in the average CO₂ carrying capacity of the particles.

3. Modelling the dynamic evolution of X_{ave} with time

In CaL systems using fluidized beds, the inventory of solids is well mixed and is composed of particles that have undergone a different number of calcination-carbonation cycles and, therefore, have different CO₂ carrying capacities. Therefore, the average CO₂ carrying capacity of the solids is a function of the fractions of particles with N_{age} cycles ($r_{N_{age}}$) in the total calcium bed inventory at any given time, and the carrying capacity associated with each N_{age} fraction ($X_{N_{age}}$) (Abanades, 2002; Rodríguez et al., 2010):

$$X_{ave} = \sum_{N_{age}=1}^{\infty} r_{N_{age}} X_{N_{age}} \quad (3)$$

Rodríguez et al. (Rodríguez et al., 2010) proposed a methodology based on mass balances to estimate the $r_{N_{age}}$ fractions of particles in the total calcium bed inventory (and hence, the value of X_{ave}) as a function of the main operating variables. Nevertheless, this approach is only valid when the system is at steady state, and a new model is required to predict the dynamic evolution of X_{ave} with time.

The main assumption of the model presented in this work is that the activity of the whole inventory of particles within the system can be characterized at any one time by an average number of calcination-carbonation cycles ($N_{age,ave}$), which is linked to the average CO₂ carrying capacity of the solids (X_{ave}) according to the CaO deactivation curve (X_N vs N) (Grasa and Abanades, 2006):

$$X_{ave} = \frac{1}{\frac{1}{1 - X_r} + k N_{age,ave}} + X_r \quad (4)$$

where X_r is the residual conversion and k is the deactivation constant of the CaO particles (equal to 0.61 and 0.096, respectively, for the high purity limestone used as sorbent precursor in this work).

Hence, the initial inventory of solids is characterized by $X_{ave,ini}$ ($t=0$) and therefore, all the particles are assumed to have initially experienced the same average number of cycles ($N_{age,ave,ini}$, calculated according to equation 4). The model also assumes that the total inventory in the calcium looping system behaves as

in a perfectly and instantly mixed reactor (CSTR) with regards to X_{ave} (see Figure 1). It also considers that the total inventory of solids remains constant with time, i.e., when a make-up flow (F_0) is fed into the calciner, an equivalent purge is taken out of the system.

In order to explain the procedure used to calculate the evolution of the average CO_2 carrying capacity with time using the model developed in this work (see Figure 2), a particular scenario is first discussed. This corresponds to a case where no fresh make-up flow of limestone is fed in.

As the particles are cycled between reactors, the change in the average CO_2 carrying capacity with time is the result of the average increment in the number of calcination-carbonation cycles experienced by the solids ($\Delta N_{capture,ave}$), which can be estimated using the following expression (Charitos et al., 2011):

$$\Delta N_{capture,ave} = \int_0^t \frac{F_{CO_2 \text{ captured}}}{W_{Ca} X_{ave}} dt \quad (5)$$

The molar flow of CO_2 captured ($F_{CO_2 \text{ captured}}$) can be calculated using the molar circulation rate of calcium between the carbonator and calciner and the increase in the carbonate content of the particles:

$$F_{CO_2 \text{ captured}} = F_{Ca}(X_{carb} - X_{calc}) = F_{Ca} \frac{X_{ave} f_{carb} f_{calc}}{f_{calc} + f_{carb}(1 - f_{calc})} \quad (6)$$

Considering that F_{Ca} , W_{Ca} , f_{carb} and f_{calc} are constant in the time period analysed, equation 5 can be integrated to obtain the following expression:

$$\Delta N_{capture,ave} = \frac{F_{Ca} f_{carb} f_{calc}}{W_{Ca} [f_{calc} + f_{carb}(1 - f_{calc})]} t \quad (7)$$

Therefore, the average number of cycles experienced by the particles in the CaL system at any one time during the period considered can be calculated as follows:

$$N_{age,ave} = N_{age,ave,ini} + \Delta N_{capture,ave} \quad (8)$$

And the evolution of the CO_2 carrying capacity of the sorbent with time can be estimated using the resulting value of $N_{age,ave}$ together with equation 4, as summarized in Figure 2.

Figure 2. Calculation procedure of the model to evaluate the evolution of X_{ave} with time.

A more general scenario is that of a CaL system with a continuous feed of a make-up stream of fresh limestone with possible modifications to this F_0 flow, which leads to changes in X_{ave} . In this case, it is assumed that the total inventory is composed of two different fractions of solids, as represented in Figure 3. One fraction corresponds to the “old” particles initially present in the system at time $t=0$ (r_{old}), which are characterized by an initial average CO_2 carrying capacity ($X_{ave,old,ini}$), whereas the second fraction (r_{new}) corresponds to the “new” particles entering the system with the fresh limestone make-up flow ($N_{age,ave,new,ini}=0$).

Figure 3. Schematics of the two families of solids considered in the model (old and new particles) of the CaL system of Figure 1 at time t for a scenario with a make-up flow.

The new inventory gradually replaces the old particles with time as the make-up flow is fed into the system ($r_{old,ini}=1$ and $r_{new,ini}=0$ at $t=0$, whereas $r_{old}=0$ and $r_{new}=1$ at $t \rightarrow \infty$). A molar balance for the new particles allows both fractions of solids to be calculated over time by means of the following expressions:

$$r_{old} = e^{-\frac{F_0}{W_{Ca}}t} \quad (9)$$

$$r_{new} = 1 - e^{-\frac{F_0}{W_{Ca}}t} \quad (10)$$

The average CO_2 carrying capacity of the solids in the system is calculated as the contribution of both the r_{old} and r_{new} fractions, as indicated in equation 11. For this purpose, it is important to note that if the conversion of the CaCO_3 in the calciner is only partial (i.e. $f_{calc}<1$), then there will be a fraction of solids in the new inventory that has never been calcined and, therefore, without any activity towards CO_2 . Hence, only new particles entering the system and calcined at least once ($N_{age,ave,new} \geq 1$) contribute to the X_{ave} of the solids in the CaL system, which can be expressed as follows:

$$X_{ave} = r_{old}X_{ave,old} + r_{new}(1 - r_{0,new})X_{ave,new_{N \geq 1}} \quad (11)$$

where $X_{ave,old}$ is the average CO_2 carrying capacity of the old particles, $r_{0,new}$ is the fraction of uncalcined solids ($N_{age}=0$) in the new inventory and $X_{ave,new_{N \geq 1}}$ represents the average CO_2 carrying capacity of the new particles that have experienced at least one calcination ($N_{age,ave,new} \geq 1$).

235 In equation 11, the evolution of the $X_{ave,old}$ value with time can be calculated using the procedure described
 236 above for the scenario with no make-up flow, whereas r_{old} and r_{new} are calculated using equations 9 and 10,
 237 respectively (see Figure 2). Moreover, the fraction $r_{0,new}$ of solids in the new inventory that have never
 238 been calcined can be estimated by means of a population balance:

$$W_{Ca} \frac{d(r_{new}r_{0,new})}{dt} = -(F_0 + F_{Ca}f_{calc})r_{new}r_{0,new} + F_0(1 - f_{calc}) \quad (12)$$

239 By integrating equation 12, the evolution of the $r_{0,new}$ fraction with time can be calculated as follows:

$$r_{0,new} = \frac{F_0(1 - f_{calc}) \left(1 - e^{-\frac{F_0 + F_{Ca}f_{calc}}{W_{Ca}}t} \right)}{(F_0 + F_{Ca}f_{calc}) \left(1 - e^{-\frac{F_0}{W_{Ca}}t} \right)} \quad (13)$$

240 It should be noted that when the system reaches steady state ($t \rightarrow \infty$), equation 13 leads to the expression
 241 obtained by Rodríguez et al. (Rodríguez et al., 2010) for estimating the fraction of particles in a CaL plant
 242 that have not experienced any calcination cycle.

243 As in the approach described above for the case of no make-up flow, $X_{ave, new_{N \geq 1}}$ is calculated on the basis
 244 of the average number of cycles undergone by these particles ($N_{age\ ave, new_{N \geq 1}}$). This can be expressed as the
 245 sum of the first calcination step (first cycle) plus the number of subsequent carbonation-calcination cycles
 246 ($\Delta N_{capture\ ave, new_{N \geq 1}}$):

$$N_{age\ ave, new_{N \geq 1}} = 1 + \Delta N_{capture\ ave, new_{N \geq 1}} \quad (14)$$

247 As indicated above, the total calcium inventory in the system is initially composed of old particles that are
 248 progressively replaced by new particles over time. This system achieves steady state when it is composed
 249 solely of new particles, i.e., when they have entirely displaced the old solids (which occurs at $t \rightarrow \infty$). The
 250 average CO_2 carrying capacity of the new particles once steady state has been reached ($X_{ave\ new, SS}$) can be
 251 calculated by means of the expression developed by Rodríguez et al. (Rodríguez et al., 2010):

$$X_{ave\ new,SS} = (F_0 + F_{Ca}r_{0,new\ SS})f_{calc} \left[\frac{a_1 f_1^2}{F_0 + F_{Ca}f_{carb}f_{calc}(1 - f_1)} + \frac{a_2 f_2^2}{F_0 + F_{Ca}f_{carb}f_{calc}(1 - f_2)} + \frac{b}{F_0} \right] \quad (15)$$

where a_1 , a_2 , f_1 , f_2 and b are the limestone deactivation parameters as in the expression proposed by Li et al. (Li et al., 2008), and $r_{0,new\ SS}$ is the fraction of particles that have never been calcined in the new inventory at steady state. However, the $X_{ave\ new,SS}$ obtained from equation 15 includes the contribution of all the fractions of new particles within the system (including those with $N_{age}=0$). Thus, in order to use the methodology proposed in the present work, it is necessary to discount the fraction of particles that have never been calcined:

$$X_{ave\ new,SS_{N \geq 1}} = \frac{X_{ave\ new,SS}}{1 - r_{0,new\ SS}} \quad (16)$$

The value of $X_{ave\ new,SS_{N \geq 1}}$ is linked to the average number of calcination-carbonation cycles experienced by the sorbent that has been calcined at least once at steady state ($N_{age\ ave\ new,SS_{N \geq 1}}$). It includes the first calcination and the additional average number of carbonation-calcination cycles ($\Delta N_{capture\ ave\ new,SS_{N \geq 1}}$), which can be estimated as follows:

$$\Delta N_{capture\ ave\ new,SS_{N \geq 1}} = N_{age\ ave\ new,SS_{N \geq 1}} - 1 \quad (17)$$

To define how $\Delta N_{capture\ ave\ new,SS_{N \geq 1}}$ evolves during a transient period before reaching the new steady state, the residence time of the particles in the system has been used. At steady state, the average residence time of the new particles in the CaL plant can be defined as:

$$\tau = \frac{W_{Ca}}{F_0} \quad (18)$$

Similarly, the average residence time of the new particles at any time in the system can be estimated from the expression:

$$\tau_{new} = \frac{W_{Ca} r_{new}}{F_0} \quad (19)$$

It is assumed in this work that the increase in the average number of carbonation-calcination cycles $\Delta N_{capture\ ave, new_{N \geq 1}}$ is proportional to the average residence time of the new solids in the system (τ_{new}). Hence:

$$\Delta N_{capture\ ave, new_{N \geq 1}} = \frac{\Delta N_{capture\ ave\ new, SS_{N \geq 1}}}{\tau} \tau_{new} \quad (20)$$

This simplification makes it possible to estimate the value of $\Delta N_{capture\ ave, new_{N \geq 1}}$ and $X_{ave, new_{N \geq 1}}$ and therefore, the average CO₂ carrying capacity of the particles in the system at any time using equation 11 (see Figure 2).

The implementation of the equations shown above into higher-level dynamic models is straightforward due to the simplicity of these expressions and the need for only a limited number of inputs (this approach relies on the initial average CO₂ carrying capacity of the particles as input), which is a great advantage of the model.

4. Results and discussion

The evolution of the average CO₂ carrying capacity of the samples taken during Test 1 is shown in Figure 4. As mentioned above, the initial inventory is composed of particles with residual activity ($X_{ave}=0.09$) and a make-up flow of 0.9 kmol/h is fed into the system from time $t=0$ onwards. This results in a progressive increase in the average CO₂ carrying capacity, especially at the beginning of the experimental period, to a point where a value of 0.17 is achieved after 2.8 hours (the dispersion in the experimental data is mainly due to unavoidable experimental errors during the extraction of the samples and X_{ave} determination, which lead to a maximum uncertainty of 0.02 points in the value of the average CO₂ carrying capacity of the solids). The figure also shows the X_{ave} values predicted by the model described above (blue line) using the data in Table 1 as input. As can be seen, the model line agrees with the experimental trend observed and predicts a similar evolution for X_{ave} with time over the period of time shown in the figure.

Figure 4. Increase in the X_{ave} of the particles over time in Test 1. The empty dots represent the experimental X_{ave} values, and the blue line shows the values predicted by the model. The black dotted line corresponds to the predictions of the particle population model.

The results of Test 2 are shown in Figure 5. In this experiment, the average CO_2 carrying capacity of the particles increases rapidly, gaining 0.09 points in only 1.5 hours. This rise is significantly higher than that of Test 1 for the same period of time, mainly due to the higher make-up flow fed into the calciner (2.7 vs 0.9 kmol/h as indicated in Table 1). For these experimental conditions, the model (blue line) also shows a good agreement with the experimental data, following the same trend and providing similar sorbent X_{ave} values over time.

Figure 5. Increase in the X_{ave} of the particles over time in Test 2. The empty dots represent the experimental X_{ave} values, and the blue line shows the values predicted by the model. The black dotted line corresponds to the predictions of the particle population model.

The evolution of X_{ave} with time in Test 3 where no make-up flow is added is shown in Figure 6. As can be seen, the experimental CO_2 carrying capacity of the solids samples extracted from the system decays from 0.21 to 0.11 in 8 hours, approaching residual sorbent activity. The values calculated using the model are represented by the blue line in Figure 6. With this approach, the average number of cycles experienced by the sorbent evolves from 12.5 at $t=0$ to 40.4 at $t=8$ h during the test, resulting in a progressive reduction of X_{ave} from 0.21 to 0.13.

Figure 6. Decay in the X_{ave} of the particles with time in Test 3. The empty dots represent the experimental X_{ave} values, and the blue line shows the predictions of the model.

As can be seen in the figure, the model predicts reasonably well the evolution of the average CO_2 carrying capacity of the particles over time, with maximum X_{ave} deviations of only ~ 0.02 after 8 hours. Apart from the unavoidable dispersion of the X_{ave} experimental data (as shown in Figures 4-5), some of the differences observed between the experimental and calculated values during this test may be due to the limitations of the model. As explained in Section 3, this approach assumes that the system inventory is composed of particles with the same average number of calcination-carbonation cycles, instead of a mixture of particles with different numbers of cycles. Particles with a lower cycle number make a large

contribution towards the average CO₂ carrying capacity of the solids (due to the higher $X_{N_{age}}$), and they also experience a greater decay in their activity every time they experience a calcination-carbonation cycle (Grasa and Abanades, 2006). In contrast, particles with high cycle numbers will evolve slowly towards residual activity. Therefore, if the initial calcium inventory in this test were composed of a mixture of solids with very different cycle numbers, the most active particles would experience a larger decay in their activity than that predicted by the model, resulting in a sharper decrease in X_{ave} .

A final experiment (Test 4) was carried out to evaluate the performance of the model when the solids inventory is deliberately composed of particles with very different cycle numbers. Starting with an inventory of deactivated solids (with residual activity), a fresh batch of limestone was fed into the system to generate a fraction of particles with a high $X_{N_{age}}$. These particles were first calcined, whilst keeping the carbonator fluidized with air (i.e. without CO₂ capture). The fluidizing gas in this reactor was then switched over to flue gas in the last part of the first calcination stage, allowing the particles to cycle for a short period of time until the desired initial operating conditions for Test 4 were established. As a result, an inventory with a $X_{ave,ini}=0.25$ was obtained, which is the result of the contribution of a fraction of largely deactivated particles (~56% of the total inventory, corresponding to those initially present in the system with residual activity) and another fraction of solids with a low cycle number (estimated to be $N_{age}=3$), obtained after the calcination and initial cycling of fresh limestone (representing ~44% of the total inventory).

During this test, the X_{ave} of the particles was allowed to decay towards residual activity with periods of no limestone make-up flow feeding (periods P1, P3, P5 and P7), which were alternated with short additions of fresh limestone to the calciner (periods P2, P4 and P6, lasting 0.5, 0.4 and 0.1 hours at a limestone feeding rate of 1.4, 1.2 and 1.4 kmol CaCO₃/h, respectively). The results obtained are shown in Figure 7.

Figure 7. Evolution of the average CO₂ carrying capacity of the particles in La Pereda pilot plant for Test 4 (divided into periods P1, P3, P5 and P7 where $F_0=0$, and periods P2, P4 and P6 where a make-up flow of 1.4, 1.2 and 1.4 kmol Ca/h, respectively, is supplied to the system). The empty dots represent the experimental data, and the blue line shows the values predicted by the model. The black dotted line corresponds to the predictions of the particle population model.

The figure shows that the experimental average CO₂ carrying capacity of the solids decreases progressively from 0.25 to ~0.13-0.14 after 10 hours as it heads towards residual activity. Moreover, the model described in Section 3 was applied to predict the changes in X_{ave} with time (see the blue line in Figure 7), using the final values of each period as the inputs for the next stage. As can be seen, the predicted values deviate from the experimental data (differences of up to 0.05 points are observed), especially at the beginning of the test. As mentioned above, the initial calcium inventory is composed of a fraction of highly active solids and a fraction of largely deactivated particles. The activity of the deactivated fraction remains almost unchanged with the increase in the number of cycles, as all these particles have already reached their residual value. However, the CO₂ carrying capacity of the highly active fraction of solids experiences a sharp decay with each calcination-carbonation cycle, as indicated by equation 4. Accordingly, a pronounced decrease in the X_{ave} of the total calcium inventory is to be expected during the first period of this test (P1, where no make-up flow is supplied), especially when it is considered that the particles experiencing a larger decay in activity (i.e., the highly active solids at $t=0$) make a larger contribution towards the average CO₂ carrying capacity.

Using the initial $X_{ave,ini}$ value of 0.25, the model assigns an average number of calcination-carbonation cycles to these particles of 9.2 at $t=0$. However, this $N_{age,ave,ini}$ value does not satisfactorily represent the actual number of calcination-carbonation cycles undergone by each particle in the initial inventory (which is composed of a mixture of highly active and largely deactivated particles as shown in Figure 8 for $t=0$). As a result, the calculated evolution for X_{ave} with time shows a much lower decrease than the experimental decay in the sorbent activity experienced by the particles. This is due mainly due to the presence of a large fraction of particles with a low cycle number ($N_{age}=3$, as mentioned above) that leads to a sharper X_{ave} decay than that predicted by the model in P1 (see blue line in Figure 7). Since the inputs for the subsequent periods depend on the predictions of the previous stages, differences between the model results and the experimental data occur throughout the test.

Test 4 highlights the main limitation of the model presented in section 3, which results from assigning the same number of cycles (and hence, the same activity) to all the particles in the system. This assumption leads to inaccuracies when the calcium inventory is mainly formed by two (or more) fractions of particles with very different numbers of cycles, since the average CO_2 carrying capacity assigned to the total inventory of solids is not representative of the particles in the system but is just a mean value of the activity of the individual solids. This can also occur in unusual scenarios where there is a large fraction of uncalcined particles ($N_{age}=0$ and therefore, $X_N=0$) at $t=0$, since the calculated initial “age” of the sorbent based on $X_{ave,ini}$ and used as an input for the model is misleading.

In these cases, a more accurate prediction of the evolution of X_{ave} with time can be obtained by accounting for all the fractions of solids with different cycle number (r_{Nage} fractions, associated with N_{age} cycles) individually. This can be achieved by performing a particle population balance for each fraction of particles with a different number of cycles (see the procedure described in the Appendix for developing an alternative model for predicting the dynamic evolution of X_{ave} based on particle population balances). In this way, the average CO_2 carrying capacity of the solids inventory can be calculated at any one time by estimating the dynamic evolution of the different fractions (r_{Nage}), together with equation 1. For the sake of comparison, the particle population model has been applied to Tests 1, 2 and 4 (it should be noted that it has not been used in Test 3 as the “history” of the sorbent is unknown in this experiment and therefore, it

is not possible to assume a realistic $r_{N_{age,ini}}$ distribution.) The results obtained using this approach are represented as grey dotted lines in Figures 4, 5 and 7, respectively. The values of the initial fractions of particles with different cycle number ($r_{N_{age,ini}}$) required as input have been assumed for these cases in accordance with the explanation given in the Appendix, where the procedure for applying this approach is described in detail.

In the case of Test 1, the values calculated using this second approach overlap those of the model presented in Section 3 (see Figure 4). Likewise, both approaches also follow the same trend and provide similar values for the sorbent X_{ave} over time in Test 2 (see Figure 5). There is only a small deviation of around 0.01 after 1.5 hours, which is attributed to the accumulation of particles with low cycle numbers in the system (faster in Test 2 than in Test 1 due to the larger amount of F_0 used). This is satisfactorily predicted when taking into account the evolution of the individual $r_{N_{age}}$ fractions, and leads to a rapid increase in X_{ave} over time since these solids make a large contribution towards X_{ave} because of their higher CO_2 carrying capacity. Nevertheless, the assumption of representing the total solids inventory as a mixture of particles all with the same average number of cycles disguises the contribution of the more active particles to X_{ave} , and results in a slower increase of this variable with time as the fraction of solids with low cycle numbers increases.

Larger differences between the two models are found in Test 4, as shown in Figure 7. In this case, the deactivation of the particles can be successfully predicted by considering the different fractions of solids at any one time in accordance with the particle population approach. Thus, a sharp decrease in X_{ave} is predicted in period P1, which is related to the deactivation of the highly active particles present in the system inventory as their cycle numbers increase, as explained above. This effect is illustrated in Figure 8, which shows the evolution of the different fractions of particles with different cycle number in the system. As can be seen, the fractions of particles with a low cycle number (e.g., $r_{N<5}$) rapidly disappear from the system during the first test period (P1). Subsequent additions of limestone in periods P2, P4 and P6 lead to the appearance of particles with low cycle numbers (see Figure 8). However, these represent a small fraction of the total calcium inventory and therefore have only a limited influence on the X_{ave} value. As the

particles advance in their cycle number in the subsequent periods of Test 4, the differences in X_{ave} between the model and the experimental data become less prominent.

Figure 8. Evolution of the r_{Nage} fractions of particles with different cycle number in Test 4 as calculated by the particle population model in periods P1 to P7. The values of the r_3 and $r_{Nage>150}$ red lines should be read using the left red vertical axis, whereas those of the black and purple lines should be read using the black right vertical axis.

The results obtained during these tests reveal some limitations in the model presented in Section 3, which assigns the same number of cycles to all the particles in the system. This assumption leads to accurate results in most of the scenarios analysed in this work. However, assigning an average number of cycles to the sorbent in cases where the system contains particles with very different cycle numbers can lead to inaccuracies that can be solved by using the particle population model. In any case, the differences in X_{ave} between both approaches and the experimental data are limited in the cases considered here (maximum deviations of 0.05), with both models converging towards the same X_{ave} steady state value (although different times may be needed to achieve this value). Therefore, the choice between the modelling approaches elaborated in this work must be the result of a trade-off between the accuracy needed for each specific application, the input information available (the particle population model requires knowledge of the $r_{Nage,ini}$ distribution, which is often unknown) and the complexity of the model (which is greater in the case of the particle population approach).

5. Conclusions

433 The evolution of the CO₂ carrying capacity, X_{ave} , of the sorbent has been studied in a series of dynamic
 434 experiments in La Pereda 1.7 MW_{th} pilot plant. Limestone make-up flow rates from 0 to 2.7 kmol/h were
 435 tested in the pilot plant, resulting in changes in the CO₂ carrying capacity of the sorbent of up to 0.12
 436 points for the cases analysed. The experimental results confirmed that the X_{ave} of the particles changes
 437 rapidly after modification to the CaCO₃ make-up flow. Moreover, it has been demonstrated that the
 438 evolution of the CO₂ carrying capacity of the particles with time was successfully predicted during most of
 439 the dynamic experiments by assuming that the activity of the total inventory of solids can be characterized
 440 by an average number of calcination-carbonation cycles. However, there may be some scenarios where the
 441 fractions of particles with different cycle number need to be accounted for individually using a particle
 442 population balance in order to adequately estimate the evolution of X_{ave} with time. This second approach
 443 provides a higher level of accuracy, although it comes at the expense of the need to provide the initial
 444 distribution of the fractions of particles with different cycle number (r_{Nage} fractions, which are usually
 445 unknown) and of greater complexity, which might complicate its integration with high-level CaL reactor
 446 models. In contrast, the implementation of the first model based on averaging the number of calcination-
 447 carbonation cycles of the solids inventory is more straightforward and can be used in cases where there is
 448 no information on the initial distribution of the r_{Nage} fractions. Deviations of 0.02-0.03 were found between
 449 the models and the experimental values under most of the conditions investigated, confirming the view
 450 that they can be employed as useful tools for predicting changes in X_{ave} over time. These can be integrated
 451 into higher-level dynamic models to help simulate and scale up the flexible operation conditions of CaL
 452 systems.

453 Nomenclature

a_1	Characteristic lime deactivation parameter ($a_1=0.1277$ in this work)
a_2	Characteristic lime deactivation parameter ($a_2=0.6827$ in this work)
b	Characteristic lime deactivation parameter ($b=0.1082$ in this work)
CPU	Compression and purification unit
f_{calc}	Fractional calcination conversion
f_{carb}	Fractional carbonation conversion
f_1	Characteristic lime deactivation parameter ($f_1=0.9643$ in this work)
f_2	Characteristic lime deactivation parameter ($f_2=0.7629$ in this work)
F_{Ca}	Calcium molar flow circulating between reactors
$F_{CO_2 \text{ captured}}$	Molar flow of CO ₂ captured in the carbonator
F_0	Make-up flow of limestone
k	Decay constant

$N_{age\ ave}$	Average number of full carbonation and calcination cycles experienced by the particles
$N_{age\ ave, ini}$	Average number of full carbonation and calcination cycles experienced by the particles at $t=0$
$N_{age\ ave, newN \geq 1}$	Average number of cycles undergone by the fraction of new particles which have experienced at least one calcination
$N_{age\ ave\ new, SS\ N \geq 1}$	Average number of cycles undergone by the fraction of new particles which have experienced at least one calcination at steady state conditions
$\Delta N_{capture\ ave}$	Increase in the average number of cycles experienced by the solids due to successive carbonation-calcination stages
$\Delta N_{capture\ ave, newN \geq 1}$	Increase in the average number of capture cycles undergone by the fraction of new particles which have experienced at least one calcination
p	Group of variables ($p=F_0+F_{Ca} \cdot f_{calc}$)
q	Group of variables ($q=F_0 \cdot (1-f_{calc})$)
s	Group of variables ($s=F_0+F_{Ca} \cdot f_{carb} \cdot f_{calc}$)
t	Time
r_{Nage}	Fractions of particles that experienced N_{age} calcination-carbonation cycles
$r_{Nage, ini}$	Initial distribution of the r_{Nage} fractions of particles at time $t=0$
r_{new}	Fraction of new particles in the total system inventory
r_{old}	Fraction of old particles in the total system inventory
$r_{0, new}$	Fraction of particles with $N_{age}=0$ (uncalcined solids) in the new inventory
$r_{0, new\ SS}$	Fraction of particles with $N_{age}=0$ (uncalcined solids) in the new inventory at steady state conditions
W_{Ca}	Molar bed inventory of calcium in the carbonator
x	Group of variables ($x=f_{calc}/s \cdot (F_0+F_{Ca} \cdot q/p)$)
X_{ave}	Average maximum CO_2 carrying capacity of the particles
$X_{ave, ini}$	Initial activity of the particles at time $t=0$
$X_{ave, newN \geq 1}$	Average CO_2 carrying capacity of the new particles that have experienced at least one calcination
$X_{ave\ new, SS}$	Average CO_2 carrying capacity of the new particles when steady state has been achieved
$X_{ave\ new, SSN \geq 1}$	Average CO_2 carrying capacity of the new particles at steady state that have been calcined at least once
$X_{ave, old}$	Average CO_2 carrying capacity of the old particles
X_{calc}	Molar carbonate content of the solids in the calciner
X_{carb}	Molar carbonate content of the solids in the carbonator
X_r	Residual activity of the sorbent
y	Group of variables ($y=-(r_{0, ini}-q/p)/(1-f_{carb})$)
z	Group of variables ($z=F_{Ca} \cdot f_{carb} \cdot f_{calc}$)
τ	Average residence time of the particles in the system
τ_{new}	Average residence time of the new particles in the system

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