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Energy Intensity Reduction of Ca-Looping CO₂ Capture by Applying Mixing Loop Seals and Cyclonic Systems

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Abstract: This work faces the challenge of cutting the specific energy demand in the CO₂ capture process based on Ca-looping technology. The use of high-temperature sorbents allows an efficient integration of the excess heat flows. Up to now, several investigations studied the Ca-looping integration with external systems such as a steam cycle. In this research, a further step is done by comparing technological solutions for the internal heat integration with the aim of reducing the energy needs. Particles preheating before entering the regeneration reactor appears as an opportunity for energy saving since solids have to be heated up around 250–300°C from one reactor to another. Two different internal heat integration possibilities making use of a particle separation device and a mixing valve are presented and compared. The former consists of the inclusion of a cyclonic preheater. This configuration presents the *a priori* advantage of a more developed technology since it is widely used in the cement industry but the drawback of a worse gas–solid heat exchange. Although there is a lack of practical experience regarding the use of a single seal valve to feed two reactors, this configuration presents a promising prospective related to the excellent heat exchange features of the solid flows. The aim is to obtain comparative results by means of implementing advanced thermochemical

models, in order to make progress on the development of less energy-intensive configurations of the calcium looping.

Keywords: mixing seal valve, cyclonic preheater, Ca looping, internal heat integration

1 Introduction

Despite the progress of renewable energies, estimations point out that fossil fuels will still account for 80% of the world's primary energy mix in 2030 (Metz et al. 2005). Thus, energy-related CO₂ will continue to dominate global greenhouse gases emissions. The most important international organizations have pointed the importance of carbon capture and storage as a feasible measure for short- and mid-term climate change mitigation (Metz et al. 2005, 2013; Committee on Stabilization Targets for Atmospheric Greenhouse Gas Concentrations; National Research Council 2011). Several developing post-combustion capture processes make use of high-temperature regenerable solids. Atmospheric carbonation of calcined natural limestone or calcium-based sorbents, known as calcium looping, is one of those promising new technologies. An important factor to develop and scaleup the process is the sorbent selection whose required properties include low cost, stable sorption capacity and mechanical strength to allow long operating periods under cyclic operation (IEA-GHG 2000).

Calcium looping exploits the reversible gas–solid carbonation reaction between CaO and CO₂ to remove it from a mixture of gases. Then, carbonate is calcined to generate a pure stream of CO₂ ready for sequestration. According to Figure 1, the sorbent and the flue gas enter the carbonator which operates at 650–670°C and atmospheric pressure. The partial pressure of CO₂ and the operation conditions will determine the removal efficiency of CO₂. Removal rates around 80–90% seem to be a reasonable target for this technology (Dean et al. 2011). Calcination is an endothermic reaction that takes place at 900–950°C, at atmospheric

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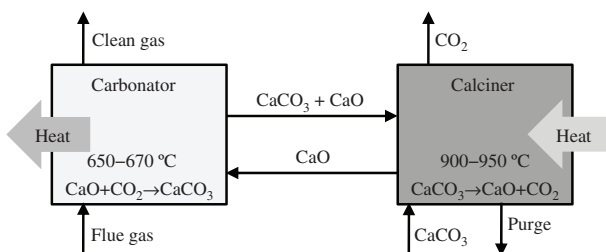


Figure 1: Calcium-looping basic diagram.

pressure and it is favored in the absence of CO₂. The required energy may be provided by oxy-fuel combustion to avoid the dilution of the resultant gas. CaCO₃ is calcined producing a concentrated stream of CO₂ suitable for capture and compression. Once regenerated, the sorbent is returned to the carbonator to begin a new sorption cycle.

The application of carbonation reaction to CO₂ capture requires that the sorbent is subjected to a significant number of repeated cycles of carbonation and calcination. One critical aspect deals with the cyclic sorbent degradation. The kinetics of the carbonation reaction suffers a transition from a fast reaction rate to a very slow rate controlled by diffusion through the newly formed product layer preventing the full carbonation of a particle (Bhatia and Perlmutter 1983; Alvarez and Abanades 2005). The partial conversion of sorbent at this transition point of the carbonation kinetics is known as the maximum carbonation conversion or carrying capacity, X_N (Silaban and Harrison 1995; Abanades, 2002). From a practical point of view, to allow a compact design of the carbonator reactor in Figure 1, only the fast reaction is of interest. The CO₂ carrying capacity of the sorbent and its decay with the increasing number of cycles directly affect the carbonation efficiency and cost of avoided CO₂. Two operating strategies are applied to compensate this degradation. One of them implies higher solid circulation between reactors to increase the CaO/CO₂ molar ratio in the carbonator. The other one implies higher amount of fresh limestone into the system to reduce the average age of the solid population.

The full CO₂ capture scheme of this application was first proposed by Shimizu et al. (1999) who developed a conceptual study on an atmospheric pressure system comprising two interconnected fluidized bed reactors. Circulating fluidized beds provide good gas–solid contact and a uniform temperature, making this technology adequate to build the carbonator and the calciner. The use of circulating fluidized beds, a mature technology, facilitates the scale-up of this technology.

The large energy demand is one of the main disadvantages of this capture technology (Fennell et al. 2007;

Lia et al. 2011). However, a significant fraction of this energy may be recovered due to the high temperatures at which this system operates. High-quality heat flows may be integrated to drive a steam cycle, reducing the energy penalty imposed to the power plant to values as low as 6–8 percentage points (Abanades et al. 2005). The substantial energy requirement entails intensive coal and oxygen consumptions as well as significant investment costs derived from the size of the CO₂ capture and steam cycle plants.

The main energy penalties in the calcium looping come from the heat requirement in the calciner, the oxygen separation process and the compression of captured CO₂. Oxygen needs are intimately related to the energy consumption in the regeneration reactor and a reduction of the coal consumption in the calciner means a reduction of the air separation unit requirements. The power consumption of the air separation unit nearly amounts a 60% of the total power consumption for carbon capture and storage (CCS) in oxy-fuel applications and reduces the overall efficiency of the power plant by about 7–9 percentage points (Andersson and Johnsson 2006; Toftegaard et al. 2010; Singh et al. 2003). For conditioning of CO₂ and compression to 100–120 bar, typical energy requirement reduces the overall efficiency of the power plant by about 3–4 percentage points (Romeo et al. 2009).

Calcium looping shows an important potential for external heat integration by retrofitting existing power plants or other stationary industrial CO₂ sources that reduce the energy penalty associated with the capture stage (Dean et al. 2011; Rodríguez et al. 2007). Up to now, research efforts have been mostly focused on minimizing energy penalties by external integration of the capture system with the associated plant which represents a large source of CO₂ (Romeo et al. 2009; Martínez et al. 2011; Lara et al. 2013). However, this retrofitting will imply complex and relatively expensive measures and the operation of a highly integrated system will always be more delicate. More attention should be paid to new options that account for self-integration of heat in the calcium looping to directly diminish the energy penalty of the process. Therefore, it is necessary to identify the possibilities of internal heat integration in the calcium looping itself by investigating new configurations.

Heat demand in the calciner is the most significant energy consumption and it may be divided into two terms. The main fraction corresponds to the endothermic reaction responsible for the regeneration of the sorbent. The remainder is required to heat up the solids that come from the carbonator, at around 650°C. Temperature difference between entering solids and calciner may be as

high as 300°C. Sorbent regeneration is an unavoidable energy intake if CO₂ capture efficiency and make-up flow are to be kept constant. However, the remaining energy consumption in the calciner may be reduced if solids are preheated diminishing the temperature difference.

The aim of this study is to compare from different points of view the reduction of the specific coal and oxygen consumptions in the calcium-looping cycle achieved by means of preheating the solids introduced in the calciner. Two different options of internal heat integration are analyzed to compare their potentiality of energy intensity reduction and their operating key points. Theoretical modeling and simulation were carried out to determine which configurations have a higher potential of energy demand reduction.

2 Technological Proposals for Internal Heat Integration

Solids preheating in the calciner will reduce the specific energy consumption, that is, the energy required per mass unit of captured CO₂. The capture system has surplus heat flows at high temperature that may be recovered to this aim. Solids from carbonator usually enter the calciner at around 650°C. Excess heat flows at higher temperatures are therefore required to preheat these particles. Solid and gaseous streams leaving the calciner may be suitable since their temperatures are as high as the calciner temperature, up to 950°C. Thus, there are two main possibilities of heat integration for solids preheating by exchanging heat with the highly concentrated CO₂ stream or with the flow of regenerated sorbent (Figure 2).

One possible configuration makes use of the gaseous stream leaving the calciner to preheat the solids entering this reactor. The installation of a third device was proposed to facilitate the heat transfer between gas and solids (Martínez et al. 2012). Carbonated sorbent was directed to this heat recovery equipment before entering the calciner together with the highly concentrated flow of CO₂. The use of a cyclonic heat exchanger, analogous to those used in the cement industry, to exchange heat between the gaseous and the solid streams was proposed and analyzed (Martínez et al. 2013).

Other interesting configuration makes use of the calcined particles to heat up the solids from the carbonator by means of a mixing seal valve (Martínez et al. 2012). In this system, particles from both reactors are collected in a single seal valve that also feeds both reactors. Solids can directly exchange heat, but the mixing of carbonated and

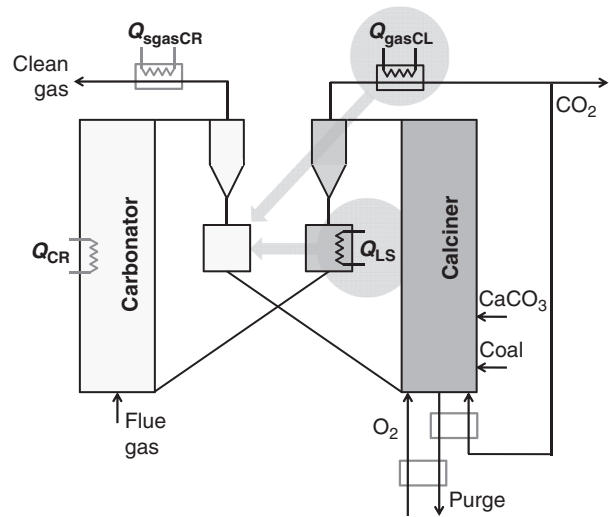


Figure 2: Heat integration possibilities for solids preheating in the calciner.

regenerated sorbent reduces the fraction of active calcium oxide entering the carbonator. Mixing seal valve configuration requires higher purge fractions or higher CaO to CO₂ ratios to achieve the same CO₂ capture efficiency (Martínez et al. 2014).

The ordinary calcium-looping configuration was also modeled and used for comparison as reference case. The systems are assumed to treat the flue gas from a 500 MWe coal power plant and surplus heat flows are assumed to be used to drive a steam cycle. Table 1 shows the hypothesis made in the power plant model.

Table 1: Power plant model hypotheses.

Electrical efficiency	40%
Oxygen excess	20%
Coal composition	72.04% _{db} C
	4.08% _{db} H
	1.67% _{db} N
	0.65% _{db} S
	7.36% _{db} ash
	8.1% H ₂ O
Coal low heating value	25,372 kJ/kg
Flue gas temperature	180°C

Regarding the CO₂ capture systems, the same assumptions are made in the three models to obtain conclusive results in the comparison process. Table 2 shows the carbonation model. These equations were developed by Alonso et al. (2009) and Charitos et al. (2011). Carbonation efficiency depends not only on the average capture capacity of the sorbent and the CaO to CO₂ ratio, but also on other parameters such as solid inventory in the reactor, temperature, CO₂ partial pressure, surface

Table 2: Carbonation model and hypotheses.

Carbonator temperature	650°C	
Carbonation efficiency	$\eta_{CR} = k_{CR} \cdot \varphi \cdot f_{a,CR} \cdot \tau_{CR} \cdot X_{ave} (\overline{v_{CO_2}} - v_{eq})$	(1)
Active sorbent	$f_{a,CR} = 1 - \exp\left(\frac{-t_{CR}^*}{n_{Ca}/\dot{n}_{Ca}}\right)$	(2)
Fast stage time	$t_{CR}^* = \frac{X_{ave} - X_{in}}{k_{CR} \cdot \varphi \cdot X_{ave} \cdot (\overline{v_{CO_2}} - v_{eq})}$	(3)
Carbonator space time	$\tau_{CR} = \frac{n_{Ca}}{\dot{n}_{CO_2}}$	(4)
Average capture capacity	$X_{ave} = \sum_{N=1}^{\infty} r_N X_N$	(5)

lime reaction rate constant and gas–solid contacting effectivity factor. Besides providing accuracy to the simulation, this fact increases the degrees of freedom in the system making easier to adapt its operation to process restrictions and requirements.

Advanced calcination model was developed by Martínez et al. (2013). Calciner is usually considered to operate at sufficiently high temperature to achieve instantaneous and complete calcination. However, the high CO₂ partial pressures and the need to operate at temperatures as low as possible to reduce the energy required to heat up the solids makes it necessary a model, shown in Table 3 , providing an accurate evaluation of the calcination efficiency under realistic operating features.

2.1 Two-Stage Cyclonic Preheater Configuration

A cyclonic preheater appears as an interesting option since it provides an excellent heat transfer between gas and solids due to the high swirl and turbulent motion of the flow inside (Mujumdaret al. 2007) and low investment costs. As temperature gradient in both gaseous and solid streams is important in the cement plants, around 700°C, cyclonic preheaters are usually composed of four or even five steps. Operating conditions in the calcium looping are less exigent, since the temperature gradient in each stream is lower, and the cyclonic preheater require a lower number of steps. Previous research work analyzed the behavior of three systems comprising one, two and three steps of cyclones and determined the two-stage cyclonic preheater as the most cost efficient for this application (Martínez et al. 2013) (Figure 3).

Table 3: Calcination model and hypotheses.

Calciner temperature	950°C	
Calcination efficiency	$\eta_{CL} = \frac{f_{a,CL}}{\ln\left(\frac{1}{1-f_{a,CL}}\right)}$	(6)
Active sorbent	$f_{a,CL} = 1 - \exp\left(\frac{-t_{CL}^*}{n_{Ca}/\dot{n}_{Ca}}\right)$	(7)
Full calcination time	$t_{CL}^* = \frac{3 \cdot X_{in}}{k_{CL} (C_{eq} - C_{CO_2})}$	(8)
Calciner coal composition	72.04% _{db} C 4.08% _{db} H 1.67% _{db} N 0.65% _{db} S 7.36% _{db} ash 8.1% H ₂ O	
Calciner coal low heating value	25,372 kJ/kg	
Calciner entrance oxygen fraction	60% _v	
Calciner purge temperature	200°C	
CO ₂ stream temperature	180°C	

The implemented model assesses the improvements this proposal entails in the calcium-looping technology for CO₂ capture. The two-stage cyclonic preheater configuration was modeled taking into account the most relevant phenomena (Martínez et al. 2013).

Carbonation and calcination may be partial and, thus, a fraction of the sorbent leaving the carbonator may still be carbonated. This fact makes it possible the carbonation reaction in the cyclonic preheater in which CO₂ partial pressures may be high enough to promote this reaction. Carbonation or calcination may take place in the cyclonic preheater, depending on the temperature

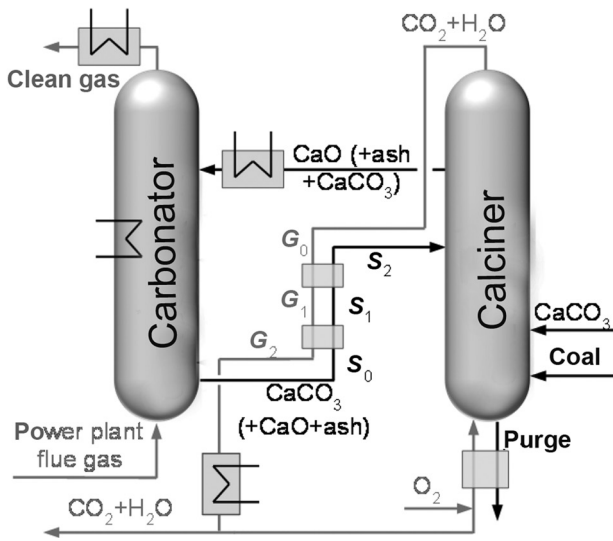
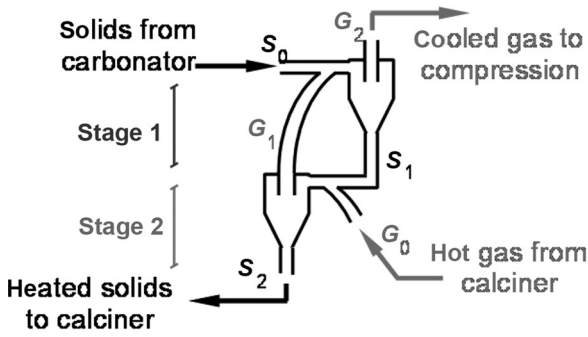


Figure 3: (a) Sketch of a two-stage cyclonic preheater. (b) Two-stage cyclonic preheater configuration.

and the CO₂ partial pressure. The effect of these reactions in the temperature and composition of the gaseous and solid streams leaving the cyclonic preheater are considered in the model.

Partial carbonation and calcination reactions and the fact that they may also take place in the cyclonic preheater affect the sorbent aging and, then, the average capture capacity of the solids entering the carbonator. The model used for the evaluation of the age distribution of the sorbent and its average capture capacity was derived by Martínez et al. (2013), eq. (9).

$$X_{ave} = \left(F_0 \eta_{CL,calc} + F_R \frac{F_0(1-f_{CL})}{F_0 + F_R f_{CL}} f_{CL} \right) \left[\frac{a_1 f_1^2}{F_0 + F_R f_{CR} f_{CL} (1-f_1)} + \frac{a_2 f_2^2}{F_0 + F_R f_{CR} f_{CL} (1-f_2)} + \frac{b}{F_0} \right] \quad (9)$$

where $a_1 = 0.1045$, $f_1 = 0.9822$, $a_2 = 0.7786$, $f_2 = 0.7905$ and $b = 0.07709$, are the coefficients fitted by Rodríguez,

Alonso, and Abanades (2010) in the deactivation curve of the limestone, X_N , proposed by Li, Cai, and Croiset (2008).

2.2 Mixing Seal Valve Configuration

Despite the significant requirements in terms of purge fractions and CaO/CO₂ molar ratios this configuration entails, its promising prospective related to the excellent heat exchange features of the solid flows motivated a thorough analysis of the mixing seal valve configuration (Martínez et al. 2014). Figure 4 (a) shows a sketch of the

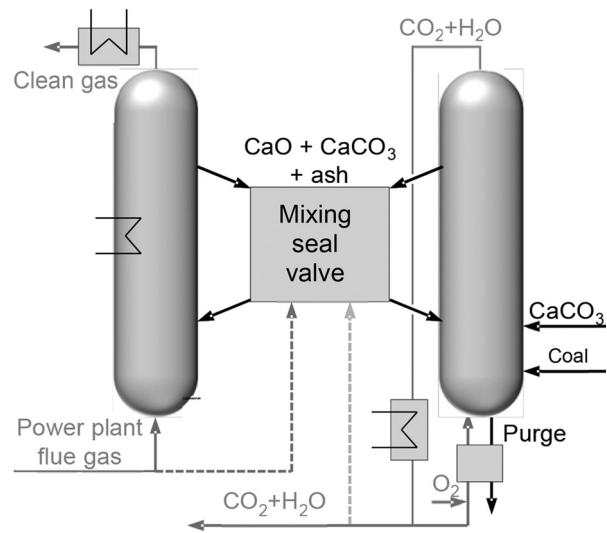
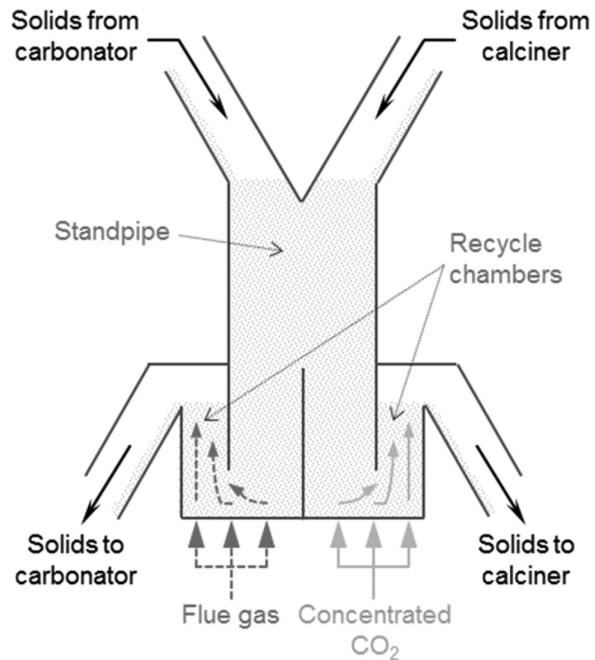


Figure 4: (a) Sketch of a mixing seal valve. (b) Mixing valve configuration (Martínez et al. 2014).

mixing seal valve with two entrances and two exits to collect the solids from both reactors and to distribute them back after mixing. The objective of this device is to provide the adequate pressure seal in both reactors while preheating the solids entering the calciner. The required fluidization in the seal valves is usually supplied by the same gas used in the corresponding bed that is fed with the solid stream from the seal valve avoiding gas mixing. In this case, a single seal valve feeds two beds fluidized by different gases (Figure 4).

The gas that fluidizes the mixing seal valve is directed to the reactor together with the flow of particles. Either a fraction of the flue gas from the power plant, or a fraction of the concentrated CO₂ stream or even a fraction of both streams at the same time might be used for the mixing seal valve fluidization. The changes in the composition of the reactors' gaseous phase may affect inter alia the capture efficiency in the carbonator and the CO₂ purity in the calciner. If a fraction of the flue gas is used, CO₂ is diluted in the calciner. On the other hand, if a fraction of the concentrated CO₂ stream from the calciner is used, coal savings are accompanied by considerable solid flow increments. Previous research work assessed which one is the optimal option to fluidize the mixing valve, and a compromise of both unmixed gases achieved the best results in terms of energy savings (Martínez et al. 2014). The final proposal

is to use the flue gas to recirculate the fraction of solids entering the carbonator, and the highly concentrated CO₂ for the particles entering the calciner with a solid distribution of 15% directed to the carbonator from the mixing seal valve.

The same advanced models for carbonation and calcination are applied, and the possibility of partial reactions is also assumed. Despite the assumptions related to the distinctive equipment, both models are accordant, which facilitates the comparison of the results. Solids in the mixing valve contain a mixture of carbonated and active sorbent; both possible fluidization agents contain a fraction of CO₂, which is more significant in the case of the gas stream leaving the calciner; and temperatures are in the range of 650–950°C. Therefore, carbonation or calcination may take place in the mixing seal valve. The effect of partial reactions in the seal valve on the temperature and composition of the leaving gaseous and solid streams are considered.

Analogously to the case of the cyclonic preheater, partial carbonation and calcination reaction and the fact that they may take place in the mixing seal valve also affects the sorbent aging and, thus, the average capture capacity. The specific model developed by Martínez et al. for the mixing of solids in the seal valve is used (Martínez et al. 2014) in eqs (10)–(15):

$$r_{0|carb} = \frac{F_{carb} \cdot r_{0|carb} \cdot (1 - \eta_{CL|SCR}) + F_{calc} \cdot r_{0|calc} \cdot (1 - \eta_{CL|SCR})}{F_{carb} + F_{calc}} \quad (10)$$

$$r_{1|carb} = \frac{F_{carb} \cdot [r_{0|carb} \cdot \eta_{CL|SCR} + r_{1|carb} \cdot (1 - f_{CR|carb} \cdot \eta_{CL|SCR})]}{F_{carb} + F_{calc}} + \frac{F_{calc} \cdot [r_{0|calc} \cdot \eta_{CL|SCR} + r_{1|calc} \cdot (1 - f_{CR|calc} \cdot \eta_{CL|SCR})]}{F_{carb} + F_{calc}} \quad (11)$$

$$r_{N|carb} = \frac{F_{carb} \cdot [r_{N-1|carb} \cdot f_{CR|carb} \cdot \eta_{CL|SCR} + r_{N|carb} \cdot (1 - f_{CR|carb} \cdot \eta_{CL|SCR})]}{F_{carb} + F_{calc}} + \frac{F_{calc} \cdot [r_{N-1|calc} \cdot f_{CR|calc} \cdot \eta_{CL|SCR} + r_{N|calc} \cdot (1 - f_{CR|calc} \cdot \eta_{CL|SCR})]}{F_{carb} + F_{calc}} \quad \forall N > 1 \quad (12)$$

$$r_{0|calc} = \frac{F_{carb} \cdot r_{0|carb} \cdot (1 - \eta_{CL|SCL}) + F_{calc} \cdot r_{0|calc} \cdot (1 - \eta_{CL|SCL})}{F_{carb} + F_{calc}} \quad (13)$$

$$r_{1|calc} = \frac{F_{carb} \cdot [r_{0|carb} \cdot \eta_{CL|SCL} + r_{1|carb} \cdot (1 - f_{CR|carb} \cdot \eta_{CL|SCL})]}{F_{carb} + F_{calc}} + \frac{F_{calc} \cdot [r_{0|calc} \cdot \eta_{CL|SCL} + r_{1|calc} \cdot (1 - f_{CR|calc} \cdot \eta_{CL|SCL})]}{F_{carb} + F_{calc}} \quad (14)$$

$$r_{N|_{\text{calc}}} = \frac{F_{\text{carb}} \cdot [r_{N-1|_{\text{carb}}} \cdot f_{\text{CR}|_{\text{carb}}} \cdot \eta_{\text{CL}|_{\text{SCL}}} + r_{N|_{\text{carb}}} \cdot (1 - f_{\text{CR}|_{\text{carb}}} \cdot \eta_{\text{CL}|_{\text{SCL}}})]}{F_{\text{carb}} + F_{\text{calc}}} + \frac{F_{\text{calc}} \cdot [r_{N-1|_{\text{calc}}} \cdot f_{\text{CR}|_{\text{calc}}} \cdot \eta_{\text{CL}|_{\text{SCL}}} + r_{N|_{\text{calc}}} \cdot (1 - f_{\text{CR}|_{\text{calc}}} \cdot \eta_{\text{CL}|_{\text{SCL}}})]}{F_{\text{carb}} + F_{\text{calc}}} \quad \forall N > 1 \quad (15)$$

3 Comparison of Results

The summary of the main energy saving results obtained for the three configurations is presented in Table 4. The purity achieved under each case for the concentrated CO₂ stream is comparable for every proposed system, around 92–93% in volume, which is an appropriate value for compression after dehydration. A significant increase of the reactors size will be required to implement the mixing seal valve configuration since the solid circulation rate must be duplicated to maintain adequate capture efficiency. Also solid inventories in the carbonator to achieve suitable CO₂ absorption efficiency are three times larger in this configuration.

Results show that solids in the *cyclonic preheater* are carbonated by the highly concentrated CO₂ stream. This fact contributes to the sorbent degradation, increasing the particles aging and reducing the average capture capacity. This effect may be nevertheless compensated by increasing either the make-up flow (6.6% higher) or the CaO to CO₂ ratio from 5 to 5.34; or having 5.5% more inventory in the carbonator. The equivalent temperature of the solids leaving the two-stage cyclonic preheater to the calciner that may be reached is 736°C which means a heat transfer from gas to solids of 127 MW.

The temperature increase of the particles entering the calciner produces a reduction of the energy requirements in this reactor. Consequently, the coal and oxygen needs to diminish in both cases. According to the model, the required mass ratio of coal consumed in the calciner to CO₂ captured in the carbonator in the ordinary configuration is 0.45 kg_{coal}/kgCO₂, while it is 13.3% lower (0.39 kg_{coal}/kgCO₂) with the system comprising a two-stage cyclonic heat exchanger. Also the oxygen

needs are reduced in a similar proportion, from 1.03 kgO₂/kgCO₂ for the ordinary configuration to 0.89 kgO₂/kgCO₂.

The coal burned in the calciner to carry out the regeneration of the sorbent implies an increase of the CO₂ produced in the system that adds to that generated in the power plant. Even if it is completely captured and the emission to the atmosphere is avoided, it has to be transported and stored. The coal savings related to the addition of a cyclonic preheater imply a 6.5% decrease of the CO₂ produced in the whole system and, thus, also a reduction of the transport and storage costs. Despite the increment of the sorbent degradation, it may be concluded that the cyclonic preheater configuration may reduce the coal and oxygen needs around 11–13%; and the CO₂ generation around 5.3–6.5%.

As expected, results obtained for the *mixing seal valve* configuration show that the sorbent mixing reduces the fraction of CaO entering the carbonator. It is therefore necessary an increase of the solid flows in the cycle, which becomes especially significant when particles are unequally distributed between carbonator and calciner. However, an increment of the sorbent inventory in the carbonator may moderate to some extent the required solid flows increase. CO₂ dilution is avoided and solid flows may be reduced in some measure, also obtaining good results in terms of coal and oxygen savings (up to 16%) and CO₂ generation reduction (up to 7.4%).

Although the design of the mixing seal valve presents some uncertainties, mainly related to the required fluidization flow and the possibility of keeping both gases completely unmixed, its significant potential of energy intensity reduction in the calcium-looping cycle has been revealed.

Table 4: Results comparison of three Ca-looping process configurations.

	CO ₂ concentration (db)	Solids flow (kg/s)	Specific coal consumption (kg _{coal} /kgCO ₂)	Specific O ₂ consumption (kgO ₂ /kgCO ₂)	Reduction of CO ₂ generation
Ordinary configuration	92%v	2,221	0.45	1.03	–
Two-stage cyclonic preheater	92%v	2,147	0.39	0.89	6.5%
Mixing seal valve	93%v	4,802	0.38	0.88	7.4%

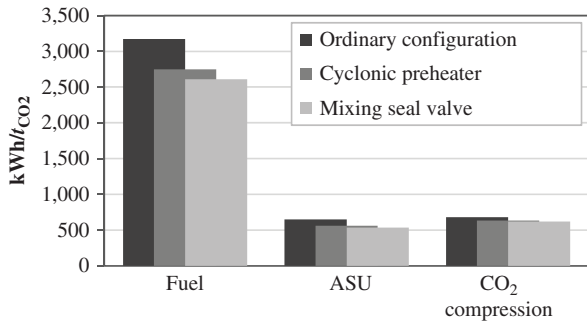


Figure 5: Primary energy consumption per ton of avoided CO₂.

The distribution of the primary energy consumptions per ton of avoided CO₂ in the calcium-looping configurations is illustrated in Figure 5. The main consumptions are related, as shown, to coal consumption in the calciner, oxygen production and CO₂ compression train. To derive these results, fuel and oxygen-specific consumptions and CO₂-specific generations are taken from Table 1 and an electrical efficiency of 35% is assumed in power generation.

As mentioned, surplus high-quality heat flows from Ca-looping process may be integrated to drive a new steam cycle that reduces the energy penalty imposed by the capture process implementation to the electricity generation (Romeo et al. 2009). The higher the amount of available heat at high temperature, the larger the extra power production. Figure 6 represents the GCC of the three compared Ca-looping configurations and illustrates the reduction of available heat after internal integration. The most significant loss deals with those gas and solid streams at 920°C whose energy content is used to preheat the solid stream at 650°C (43% less available energy in the cyclonic preheater and 79% less available energy at high temperatures in the mixing seal valve configuration). However, temperature levels still seem to be suitable to generate supercritical steam at around 600–620°C. The application of a systematic approach should be done to optimize the integration of this remaining surplus of energy into a new supercritical cycle (Lara et al. 2014).

4 Conclusions

The comparison of the potential reduction of the energy intensity in the calcium looping by means of different technological proposals is the principal objective of this work. Main efforts are focused on the calciner since it entails the most important energy consumption in the

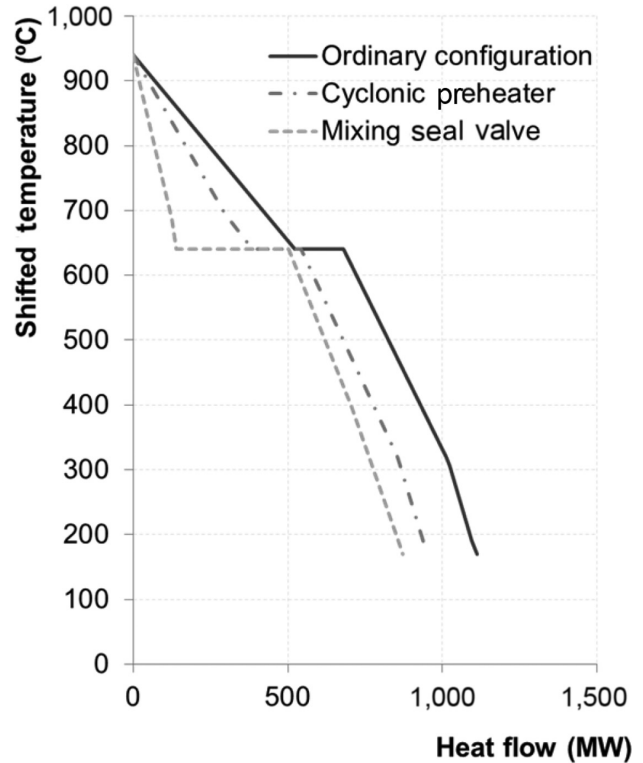


Figure 6: Grand composite curves of the three Ca-looping configurations.

system. The preheating of the solids entering the calciner appears as the most suitable way to achieve this saving. The use of a high-temperature sorbent allows efficient heat recovery. Internal integration of surplus heat flows to increase the temperature of the solids entering the calciner, consequently reducing the energy consumption in the cycle, was investigated.

There are two possible streams capable of transferring heat to the solids entering the calciner: the regenerated sorbent and the highly concentrated CO₂ stream. Both represent a significant heat flow at a temperature higher than that of the solids leaving the carbonator. The heat exchange is technically easier when using the gaseous stream leaving the calciner. However, the favorable features of the solids concerning heat transfer make the use of the particles leaving the calciner a promising option as well.

Two configurations that appear to be the most promising ones are investigated: the two-stage cyclonic preheater and the mixing seal valve configurations. The comparison between both is not straightforward since they are at a different level of development. The cyclonic preheater is widely used in the cement industry, whereas the mixing seal valve still needs to be experimentally analyzed. However, both systems present good results

in terms of fuel and oxygen savings (around 11–15%) and reduction of CO₂ generation (around 5.3–7.4%) that may entail a significant decrease of the energy needs in the calcium-looping technology.

This work explores innovative solutions to technical problems that Ca looping presents. In this case, the extremely high-specific energy consumption in the calcium-looping cycles is faced. The proposed configurations for the internal heat integration present an excellent potential that should enhance the competitiveness of the calcium looping enabling it to become a leading technology. Available energy for external integration is still high enough and deserves further study to optimize the use of this heat in a new supercritical cycle.

Abbreviations

ASU	air separation unit
CCS	carbon capture and storage
GCC	grand composite curve
GHG	greenhouse gases

Nomenclature

C_{CO_2}	Concentration of CO ₂ (kmol/m ³)
C_{eq}	Concentration of CO ₂ in equilibrium conditions (kmol/m ³)
F_0	Molar flow of fresh CaCO ₃ entering the calciner (kmol/s)
$f_{a,\text{CL}}$	Fraction of particles in the calciner with a residence time lower than t_{CL}^*
$f_{a,\text{CR}}$	Fraction of active sorbent reacting in the carbonation fast reaction regime
F_{calc}	Molar flow of CaO and CaCO ₃ circulating between mixing seal valve and calciner (kmol/s)
F_{carb}	Molar flow of CaO and CaCO ₃ circulating between mixing seal valve and carbonator (kmol/s)
f_{CL}	Maximum proportion of calcined sorbent in the cycle
f_{CR}	Maximum proportion of carbonated sorbent in the cycle
F_R	Molar flow of CaO and CaCO ₃ between the reactors (kmol/s)
k_{CL}	Kinetic constant of CaCO ₃ calcination (m ³ /kmol s)
k_{CR}	Surface carbonation rate constant (s ⁻¹)
N	Number of cycles accomplished by a volume of sorbent
n_{Ca}	Molar sorbent inventory in the carbonator, (kmol)
\dot{n}_{Ca}	Inlet molar flow of CaO and CaCO ₃ (kmol/s)
\dot{n}_{CO_2}	Inlet molar flow of CO ₂ (kmol/s)
Q_{CR}	Available heat in the carbonator
$Q_{\text{gas,CR}}$	Available heat in the clean gas stream
$Q_{\text{gas,CL}}$	Available heat in the highly concentrated CO ₂ stream
Q_{LS}	Available heat in the loop seal
r_N	Age distribution of particles, fraction of particles that has accomplished N carbonation/calcination cycles
t_{CL}^*	Time for full calcination under calciner operating conditions (s)
t_{CR}^*	Time for maximum fast kinetic-stage carbonation, X_{ave} (s)

v_{CO_2}	Average volume fraction of CO ₂
v_{eq}	Volume fraction of CO ₂ in equilibrium conditions
X_{ave}	Average maximum capture capacity of the sorbent
X_{in}	Inlet molar fraction of CaCO ₃ with respect to CaO and CaCO ₃
X_N	Capture capacity of a fraction of sorbent that has accomplished N carbonation–calcination cycles
η_{CL}	Calcination efficiency, fraction of CaCO ₃ calcined
η_{CR}	Carbonation efficiency, fraction of CO ₂ captured
τ_{CR}	Carbonator space time. Molar inventory of calcium compounds (CaO and CaCO ₃) per molar flow of CO ₂ (s)
φ	Gas–solid contacting effectivity factor

Subscripts

calc	Calciner
carb	Carbonator
SCL	Stream leaving the mixing seal valve to the calciner
SCR	Stream leaving the mixing seal valve to the carbonator

References

- Abanades, J.C., 2002. The maximum capture efficiency of CO₂ using a carbonation/calcination cycle of CaO/CaCO₃. *Chemical Engineering Journal* 90, 303–306.
- Abanades, J.C., Anthony, E.J., Wang, J., Oakey, J.E., 2005. Fluidized bed combustion systems integrating CO₂ capture with CaO. *Environmental Science and Technology* 39, 2861–2866.
- Alonso, M., Rodríguez, N., Grasa, G., Abanades, J.C., 2009. Modeling of a fluidized bed carbonator reactor to capture CO₂ from a combustion flue gas. *Chemical Engineering Science* 64, 883–891.
- Alvarez, D., Abanades, J.C., 2005. Determination of the critical product layer thickness in the reaction of CaO with CO₂. *Industrial & Engineering Chemistry Research* 44, 5608–5615.
- Andersson, K., Johnsson, F., 2006. Process evaluation of an 865 MWe lignite fired O₂/CO₂ power plant. *Energy Conversion and Management* 47, 3487–3498.
- Bhatia, S.K., Perlmutter, D.D., 1983. Effect of the product layer on the kinetics of the CO₂-lime reaction. *AIChE Journal* 29, 79–86.
- Charitos, A., Rodríguez, N., Hawthorne, C., Alonso, M., Zieba, M., Arias, B., Kopanakis, G., Scheffknecht, G., Abanades, J.C., 2011. Experimental validation of the calcium looping CO₂ capture process with two circulating fluidized bed carbonator reactors. *Industrial & Engineering Chemistry Research* 50, 9685–9695.
- Committee on Stabilization Targets for Atmospheric Greenhouse Gas Concentrations; National Research Council, 2011. *Climate Stabilization Targets: Emissions, Concentrations, and Impacts over Decades to Millennia*, Washington, D.C.: The National Academies Press.
- Dean, C.C., Blamey, J., Florin, N.H., Al-Jeboori, M.J., Fennell, P.S., 2011. The calcium looping cycle for CO₂ capture from power generation, cement manufacture and hydrogen production. *Chemical Engineering Research and Design* 89, 836–855.
- Fennell, P.S., Pacciani, R., Dennis, J.S., Davidson, J.F., Hayhurst, A.N., 2007. The effects of repeated cycles of calcination and

- carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand. *Energy and Fuels* 21, 2072–2081.
11. IEA, 2013. *World Energy Outlook – Factsheet*, Technical Report, International Energy Agency.
 12. IEA-GHG, 2000. *Leading Options for the Capture of CO₂ Emissions at Power Stations, Report PH3/14*, Technical Report, International Energy Agency.
 13. Lara, Y., Lisbona, P., Martínez, A., Romeo, L.M., 2013. Design and analysis of heat exchanger networks for integrated Ca-looping systems. *Applied Energy* 111, 690–700.
 14. Lara, Y., Lisbona, P., Martínez, A., Romeo, L.M., 2014. A systematic approach for high temperature looping cycles integration. *Fuel* 127, 4–12
 15. Li, Z.S., Cai, N.S., Croiset, E., 2008. Process analysis of CO₂ capture from flue gas using carbonation/calcination cycles. *AIChE Journal* 54, 1912–1925.
 16. Lia, Y., Zhao, C., Chen, H., Ren, Q., Duan, L., 2011. CO₂ capture efficiency and energy requirement analysis of power plant using modified calcium-based sorbent looping cycle. *Energy* 36, 1590–1598
 17. Martínez, I., Grasa, G., Murillo, R., Arias, B., Abanades, J.C., 2013. Modelling the continuous calcination of CaCO₃ in a Ca-looping system. *Chemical Engineering Journal* 215–216, 174–181.
 18. Martínez, A., Lara, Y., Lisbona, P., Romeo, L.M., 2012. Energy penalty reduction in the calcium looping cycle. *International Journal of Greenhouse Gas Control* 7, 74–81.
 19. Martínez, A., Lara, Y., Lisbona, P., Romeo, L.M., 2013. Operation of a cyclonic preheater in the Ca-looping for CO₂ capture. *Environmental Science & Technology* 47, 11335–11341.
 20. Martínez, A., Lara, Y., Lisbona, P., Romeo, L.M., 2014. Operation of a mixing seal valve in the Ca-looping for CO₂ capture. *Energy & Fuels* 28, 2059–2068.
 21. Martínez, I., Murillo, R., Grasa, G., Abanades, J.C., 2011. Integration of a Ca-looping system for CO₂ capture in an existing power plant. *Energy Procedia* 4, 1699–1706.
 22. Metz, B., Davidson, O., de Connick, H., Loos, M., Meyer, L. (Eds), 2005. *IPCC Special Report on Carbon Dioxide Capture and Storage*, Cambridge University Press for the Intergovernmental Panel on Climate Change, Cambridge.
 23. Mujumdar, K.S., Ganesh, K.V., Kulkarni, S.B., Ranade, V.V., 2007. Rotary cement kiln simulator (RoCKS): Integrated modeling of preheater, calciner, kiln and clinker cooler. *Chemical Engineering Science* 62, 2590–2607.
 24. Rodríguez, N., Alonso, M., Abanades, J.C., 2010. Average activity of CaO particles in a calcium looping system. *Chemical Engineering Journal* 156, 388–394.
 25. Rodríguez, N., Alonso, M., Grasa, G., Abanades, J.C., 2007. Heat requirements in a calciner of CaCO₃ integrated in a CO₂ capture system using CaO. *Chemical Engineering Journal* 138, 148–154.
 26. Romeo, L.M., Bolea, I., Lara, Y., Escosa, J.M., 2009. Optimization of intercooling compression in CO₂ capture systems. *Applied Thermal Engineering* 29, 1744–1751.
 27. Romeo, L.M., Lara, Y., Lisbona, P., Escosa, J.M., 2009. Optimizing make-up flow in a CO₂ capture system using CaO. *Chemical Engineering Journal* 147, 252–258.
 28. Shimizu, T., Hiramata, T., Hosoda, H., Kitano, K., Inahaki, M., Tejima, K., 1999. A twin fluid bed reactor for removal of CO₂ from combustion processes. *Chemical Engineering Research and Design* 77, 62–68.
 29. Silaban, A., Harrison, D.P., 1995. High temperature capture of carbon dioxide characteristics of the reversible CaO (s) and CO₂ (g). *Chemical Engineering Communications* 137, 177–190.
 30. Singh, D., Croiset, E., Douglas, P.L., Douglas, M.A., 2003. Techno-economic study of CO₂ capture from an existing coal-fired power plant: MEA scrubbing vs. O₂/CO₂ recycle combustion. *Energy Conversion and Management* 44, 3073–3091.
 31. Toftegaard, M.B., Brix, J., Jensen, P.A., Glarborg, P., Jensen, A. D., 2010. Oxy-fuel combustion of solid fuels. *Progress in Energy and Combustion Science* 36, 581–625.