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Process integration of a Ca-looping carbon capture process in a cement plant

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An analysis of the integration of a Ca-looping process into a cement plant is presented. The capture process, based on selective absorption of CO2 by calcium oxide, has two interconnected reactors where the carbonator captures CO2 from the preheater flue gases and the calciner regenerates the CaCO3 into CaO by oxy-combustion. The study also considers the purge rate of part of the circulating CaO, given the tendency of the material to sinter and reduce its capture capacity. Fresh CaCO3 is added to maintain reactivity in the carbonator, while the purged sorbents are utilised as a cement kiln feed. The detailed carbonator model has been implemented using Matlab and incorporated into Unisim to provide a full flowsheet simulation for an exemplary dry-feed cement plant as a user-defined operation. The effect of molar flowrate ratio of lime make-up to feed CO2 (F0/FCO2) between two operational limits has been investigated. This process configuration is capable of achieving over 90% CO2 capture with additional fuel consumption of 2.5–3.0 GJ/t from CO2 avoided which depends on the F0/FCO2 ratio. It is found that a proper heat recovery system supplementary to the Ca-looping process makes the Ca-looping process more competitive than the traditional low temperature absorption process based on amine solvents.

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1. Introduction

The cement industry accounts for more than 5% of global CO2 emission from stationary sources amounting to 1.88 Gt CO2/year in 2006 (IEA, 2009). It is foreseen that the emissions for the cement sector will continue to grow in parallel with increasing demand of cement (CW Group, 2012) and reach 4.3 Gt CO2/year until 2050 (WWF, 2008) which is regarded as one of the major industrial carbon emission sources for which it is worth implementing carbon capture and storage solutions. The CO2 emissions from cement plants originates from different sources; over 50% of the emissions result from the calcination of limestone in the raw material while the rest is generated by fuel combustion (40%) and indirect emissions relating to use of electricity (IEA, 2011). The fuel consumption is significant due to the highly endothermic calcination reaction and high temperature operation in a kiln (around 1450 °C). It has been reported that, with modern technology, the average energy consumption in a cement plant has been reduced to around 2.9 GJ/ton clinker (WBCSD, 2009) and CO2 emission by calcination can be increased to almost 70% by a more efficient use of the fuel (Rodriguez et al., 2009).

CO2 emissions in a cement process can be partially reduced by modifications: improving the process for more efficient use of the fuel, replacing fossil fuels with alternative renewables including waste residues, and mixing clinkers with mineral additives (Hasanbeigi et al., 2012). Even though these measures can reduce CO2 emissions resulting from fuel combustion significantly, they cannot tackle the CO2 emission originating from the calcination reaction. Therefore, it is essential to deploy a carbon capture technology on cement processes in order to reduce CO2 emissions by more than 90%.

Several carbon capture technologies including amine scrubbing (IEA, 2008; Hassan, 2005), ammonia scrubbing (Dong et al., 2012), oxy-combustion (IEA, 2008; ECRA, 2009), anti-sublimation (Pan et al., 2013), calcium looping (Bosoag et al., 2009; Vera, 2009; Rodriguez et al., 2012; Stallmann, 2013) and indirect calcination (Rodriguez et al., 2011a) have received great interest to capture CO2 from cement industry. The most conventional technology available for carbon capture in a cement plant is a post-combustion amine process. The amine scrubbing (MEA) based post-combustion method has been proposed to reduce CO2 emissions from a cement plant and shows the possibility to capture the released CO2 by up to 85% (IEA, 2008; Hassan, 2005). As there is no source of steam available in situ for the regeneration of the amine, unlike in a power plant, there is the need to install a new external steam generator to supply the stripper reboiler of the amine process with low pressure steam while part of the steam requirement can be fulfilled by
Nomenclature

\[ a \] decay constant of solid concentration in the lean region (m\(^{-1}\))

\[ A_t \] cross sectional area of the reactor (m\(^2\))

\[ b \] decay constant of contacting efficiency in the lean region (m\(^{-1}\))

\[ C_{CO_2,eq} \] equivalent CO\(_2\) concentration in the CFB riser (mol/m\(^3\))

\[ C_{CO_2,d} \] CO\(_2\) concentration in the dense region exit (mol/m\(^3\))

\[ C_{CO_2,eq} \] CO\(_2\) concentration allowed by chemical equilibrium (mol/m\(^3\))

\[ C_{CO_2,in} \] CO\(_2\) concentration in the reactor inlet (mol/m\(^3\))

\[ d_p \] particle diameter (m)

\[ E_{CO_2} \] fraction of CO\(_2\) captured to total CO\(_2\) entering the carbonator

\[ f_t \] fraction of sorbent particles with a residence time \( t \)

\[ F_{ash} \] molar flow rate of ash entering the Ca-looping system (kmol/s)

\[ F_0 \] make-up flow rate (kmol/s)

\[ F_{CO_2} \] molar flow rate of CO\(_2\) in a flue gas stream entering the carbonator (kmol/s)

\[ F_R \] circulated sorbent flow rate (kmol/s)

\[ F_S \] molar flow rate of sulfur entering the Ca-looping system (kmol/s)

\[ H_d \] height of the dense region (m)

\[ H_f \] height of the lean region (m)

\[ H_t \] total height of the carbonator (m)

\[ k_{1,ave} \] average kinetic constant of the population of potentially active Ca-based solids (s\(^{-1}\))

\[ k_5 \] rate constant for the carbonation reaction at the surface of CaO (m\(^2\)/mol/s)

\[ k_{cw} \] core-wall mass transfer coefficient (s\(^{-1}\))

\[ M_s \] molar mass of total solids (kg/kmol)

\[ M_{Ca,p} \] molar mass of potentially active Ca-based solids (kg/kmol)

\[ n_{Ca,p} \] moles of potentially active Ca-based solids (kmol)

\[ N \] number of carbonation/calcination cycles

\[ p \] pressure (Pa)

\[ P_{CO_2,eq} \] equilibrium CO\(_2\) partial pressure (Pa)

\[ r_N \] mass fraction of particles after N cycles of carbonation–calcination

\[ S_N \] specific surface area available after N cycles of carbonation–calcination (m\(^2\)/m\(^3\))

\[ t \] time (s)

\[ t_{lim} \] time required for a particle to reach its maximum carbonation (s)

\[ T \] temperature (K)

\[ T_C \] condenser temperature (C)

\[ T_{HF} \] superheated steam temperature (C)

\[ u_0 \] superficial velocity of a gas (m/s)

\[ V_{gi,m} \] volumetric flow rate of inlet gas stream (m\(^3\)/s)

\[ V_{go,m} \] volumetric flow rate of outlet gas stream (m\(^3\)/s)

\[ W_s \] solid inventory in the carbonator (kg)

\[ x_{ash} \] molar fraction of ash

\[ x_{CaSO_4} \] molar fraction of CaSO\(_4\)

\[ X \] conversion of CaO to CaCO\(_3\)

\[ x_{ave} \] average carbonation level

\[ X_{max,ave} \] maximum average carbonation degree of the sorbent after N cycles of carbonation–calcination

\[ X_{max,N} \] maximum carbonation conversion rate after N cycles of carbonation–calcination

Greek letters

\[ \varepsilon \] asymptotic solid volumetric fraction

\[ \varepsilon_{x,c} \] volume fraction of solids in the lower dense region

\[ \varepsilon_{x,d} \] volume fraction of solids in the lower dense region

\[ \varepsilon_{x,e} \] volume fraction of solids at the carbonator exit

\[ \varepsilon_{x,w} \] volume fraction of solids in the lower dense region

\[ \rho_s \] density of total solids (kg/m\(^3\))

\[ \rho_{Ca,p} \] density of potentially active Ca-based solids (kg/m\(^3\))

\[ \mu \] viscosity (kg/m/s)

\[ \eta_{ad} \] the contact efficiency of the dense region

\[ \eta_t \] steam turbine efficiency

\[ \delta \] the core volumetric fraction of the dense region

\[ \xi \] volume ratio between the potentially active solids and the total solids

\[ \tau \] average residence time of solids particles (s)

\[ \Delta X_{CaSO_4} \] average fraction of sorbent sulfated at each cycle

Chemical compounds

\[ \text{AS}_4 \text{H} \] pyrophyllite

\[ \text{AS}_5 \text{H}_2 \] kaolinite

\[ \text{C}_3 \text{S} \] alite

\[ \text{C}_2 \text{S} \] belite

\[ \text{C}_3 \text{A} \] tricalcium aluminate

\[ \text{C}_4 \text{AF} \] tetracalcium aluminate

the use of hot gases generated in the kiln (Handagama et al., 2013). The steam generator to be deployed could generate some electricity with one back pressure turbine as well as steam (IEA, 2008) but such a steam cycle would have a very low power plant efficiency since it would not be designed with the same complexity as a steam cycle in a purposely designed power plant. Oxy-combustion processes can also be an alternative to the amine capture process. In this case pure oxygen is supplied to the reactor instead of air, so that it is in principle possible to capture CO\(_2\) from the pre-calciner, but there is technical uncertainty in operating a cement kiln under oxy-combustion conditions (IEA, 2008). For that reason, in the IEA (2008), oxy-combustion has not been applied to the cement kiln but only the pre-calciner. Therefore, the overall carbon capture rate is limited since only part of the CO\(_2\) emitted can be captured.

One of the promising technologies for carbon capture from industrial sources is an absorption process based on the reversible reaction of CO\(_2\) on specific metal oxides at high temperature. CaO-based sorbents have attracted the most attention owing to their high absorption capacity, wide availability, and low cost. The post-combustion calcium looping (Ca-looping) process, first proposed by Shimizu et al. (1999), uses a state-of-the-art circulating fluidized bed (CFB) system and offers relatively small energy penalty (Martínez et al., 2011; Zhao et al., 2013). In addition to significant efforts on laboratory scale investigations (Alonso et al., 2010; Charitos et al., 2010; Rodríguez et al., 2011b), several different projects around the world have been initiated to scale up the Ca-looping technology, including a 1.7 MW\(_{th}\) pilot plant which has been in operation to demonstrate the concept in La Prada, Spain, funded under the “CaOling” project (Arias et al., 2013). Furthermore, promising results have also been reported from 1 MW\(_{th}\) pilot plant in Darmstadt (Plötz et al., 2012) and 200 kW\(_{th}\) pilot plant in Stuttgart University (Dieter et al., 2012). The Ca-looping process has been proposed as a proper way to reduce CO\(_2\) emissions from power plants (Strohle et al., 2009). One of the greatest challenges related to this method is the deterioration of the CO\(_2\) capture capacity when these materials are used over countless cycles of carbonation.
and calcination reactions (Curran et al., 1967). Hence, while some spent sorbents are removed as purge from the system, fresh make-up sorbents are introduced. The purge stream from the calciner is mainly composed of CaO with small amounts of CaSO4 and ash. It has already been suggested that the spent CaO from a Ca-looping unit integrated with a power plant can be utilised as feedstock in a cement plant in place of limestone (Dean et al., 2011a). In a later work, it was shown experimentally that cement can be successfully produced from the purge of the Ca-looping process (Dean et al., 2011b). Therefore, it can be envisaged that a significant cut in carbon emission from power and cement plants can be made by process integration between both industries, but colocation is seldom possible. However, it should be noted that the use of purge for clinker production cannot inhibit all CO2 emission relating to calcination unless colocation is possible (Romeo et al., 2011). Thus, the potential use of the purge stream in a cement plant leads to an interest in the direct integration of the Ca-looping process with a cement plant. Rodríguez et al. (2012) investigated two alternative process configurations for carbon capture from cement plants. They reported that a retrofit replacing the existing pre-calciner with an oxy-calciner can achieve 85% capture and in addition the capture rate can be improved to up to 95% by capturing CO2 from the kiln gas using the carbonator. In their study, the carbonator is fed with the mixture of limestone and clay which is preheated by CO2-rich gas stream leaving the calciner: therefore, there is a need of an air-leakage-free preheater for the production of high purity CO2.

A novel process configuration having an external combustor to generate heat for the pre-calciner instead of oxy-combustion has been suggested as a way of recovering CO2 in cement plants (Rodríguez et al., 2011a). This process is capable of producing an enriched-CO2 stream from the pre-calciner by supplying the heat required for calcination using hot CaO circulating between the combustor and the pre-calciner instead of using the heat of combustion inside the pre-calciner. While this process can capture the CO2 involved in calcination, it cannot recover the CO2 generated by fuel combustion. Therefore, this process is a worthwhile option only when a moderate level of CO2 recovery is required.

In this study, we present a detailed analysis of a typical cement manufacturing process and study the reasonable selection of location of the capture process with respect to process conditions when a Ca-looping process is integrated in a cement plant. Process simulation includes the implementation of a detailed carbonator model and its incorporation into a full cement process simulation.

2. Process simulation of a cement plant (base case)

Fig. 1 shows the block flow diagram of a dry cement process, hereinafter named the base case configuration. The base case includes all the major units in the cement plant: raw mill; preheaters; pre-calculator; kiln and cooler. The base case simulation takes into account key reactions taking place in the process of cement production. Several auxiliary units, such as crushing and milling of the raw materials, cement mixing and milling with fly ash and gypsum are not included in this study since their contribution to the energy balance is not as important as the major units included. In addition, their operations are not affected by retrofitting the carbon capture units into the cement plant. It should be highlighted that the base configuration has a separate pre-calciner upstream of a kiln instead of having a single reactor for calcination and clinkerization since it is well-known that it can provide a lower energy consumption and shorter kiln length (IEA, 2008). The ratio of heat supply into pre-calciner and kiln is maintained at 6 to 4 in this study.

It is crucial to identify the chemical reactions occurring in each unit and determine their conversion rate in order to have accurate mass and energy balances. Table 1 shows the reactions being considered which can be classified into the decomposition of the raw

### Table 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH (kJ/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO3 (calcite) → CaO + CO2</td>
<td>+1782</td>
<td>CaCO3</td>
</tr>
<tr>
<td>AS1H (pyrophyllite) → α-Al2O3 + 4SiO2 (quartz) + H2O(g)</td>
<td>+224</td>
<td>AS1H</td>
</tr>
<tr>
<td>A3H (kaolinite) → α-Al2O3 + 2SiO2 (quartz) + 2H2O(g)</td>
<td>+538</td>
<td>A3H</td>
</tr>
<tr>
<td>2FeO OH (goethite) → α-Fe2O3 + H2O(g)</td>
<td>+254</td>
<td>FeO OH</td>
</tr>
<tr>
<td>2CaO + SiO2 (quartz) → β-C2S</td>
<td>−734</td>
<td>C2S</td>
</tr>
<tr>
<td>3CaO + SiO2 (quartz) → C3S</td>
<td>−495</td>
<td>C3S</td>
</tr>
<tr>
<td>3CaO + α-Al2O3 → C3A</td>
<td>−27</td>
<td>C3A</td>
</tr>
<tr>
<td>4CaO + α-Al2O3 + α-Fe2O3 → C4A</td>
<td>−105</td>
<td>C4A</td>
</tr>
<tr>
<td>S + O2 → SO2</td>
<td>−17,813</td>
<td>S</td>
</tr>
<tr>
<td>CaO + SO2 + 0.5SO2 → CaSO3</td>
<td>−7656</td>
<td>SO2</td>
</tr>
</tbody>
</table>
Table 2
Composition of the raw meal fed to the raw mill (Taylor, 1990).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>72.5</td>
</tr>
<tr>
<td>Quartz</td>
<td>6.0</td>
</tr>
<tr>
<td>Pyrophylite</td>
<td>9.0</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.4</td>
</tr>
<tr>
<td>Goethite</td>
<td>1.8</td>
</tr>
<tr>
<td>Moisture</td>
<td>8.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

Table 3
Comparison of Bogue equation approximation and the simulation results.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Bogue calculation [wt%]</th>
<th>Simulation [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite (C₃S)</td>
<td>60.6</td>
<td>60.4</td>
</tr>
<tr>
<td>Belite (C₂S)</td>
<td>17.5</td>
<td>17.2</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)</td>
<td>11.0</td>
<td>10.9</td>
</tr>
<tr>
<td>Tetracalcium aluminite (C₄AF)</td>
<td>8.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Free CaO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CaO SO₃</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Ash</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

materials and the clinkerization stages (Taylor, 1990). Given the raw meal composition in Table 2, the approximate chemical composition of the four main clinker phases, C₃S, C₂S, C₃A, and C₄AF, can be estimated by Bogue equation (Bogue, 1929).

\[
C₃S = 4.0710CaO - 7.6024SiO₂ - 6.7187Al₂O₃ - 1.4297Fe₂O₃ \tag{1}
\]

\[
C₂S = -3.0710CaO + 8.6024SiO₂ + 5.06383Al₂O₃ + 1.0785Fe₂O₃ \tag{2}
\]

\[
C₃A = 2.6504Al₂O₃ - 1.6920Fe₂O₃ \tag{3}
\]

\[
C₄AF = 3.0432Fe₂O₃ \tag{4}
\]

The simulated clinker compositions are in good agreement with those estimated by the Bogue equation as shown in Table 3. It is assumed that 30% of sulphur in the raw material reacts with oxygen to become SO₂ in the first preheater and then leave the plant via the raw mill. The remaining sulphur is converted into SO₂ in the pre-calciner and subsequently all the SO₂ formed reacts with CaO and oxygen to form CaO-SO₃ in the pre-calciner which is included in the clinker product (IEA, 2008).

The raw meal having 8% moisture is dried passing the raw mill where it is heated by contacting the flue gas leaving the preheaters directly. The flue gas flowrate to be fed to the raw mill is determined such that both gas and solid streams leave the raw mill at around 110°C. The gas stream leaving the pre-calciner at 915°C is cleaned of the entrained fine particles passing the four cyclones in series comprising the preheater where it heats up the raw meal up to 760°C as shown in Fig. 2(a). The solid removal efficiency is assumed to be 94%, 90%, 85% and 80%, respectively from the preheater stage 1–4 (Alsop et al., 2007). It should be noted that calcination and clay decomposition start to take place at the 4th preheater with the 10% for calcination and 30% for clay decomposition set in this study referring to the clinker phase diagram in Taylor (1990).

The preheated raw meal enters the pre-calciner where 90% of the remaining calcites are calcined and all clays are decomposed into their constituents, such as alumina, silica, and ferrite, at the operating temperature of 915°C. As the calcination and clay decomposition reactions are all endothermic, the pre-calciner is supplied with the heat generated from coal combustion with the tertiary air heated up to 908°C by the clinker cooler. The flue gas leaving the kiln at 1025°C flows into the pre-calciner in order to lower the CO₂ partial pressure and supply an additional heat source for the endothermic reaction.

The rotary kiln, where cement clinker is produced by counter-current contact of the gas and solid streams, has been simulated in three separate units so that the temperature change along the length can be simulated. The first unit, corresponding to the solid feed end of the kiln, is simulated as a heat-exchanger to heat the solid stream from 915°C to 1250°C by its direct contact with the kiln gas flowing in the opposite direction. Subsequently, the temperature of the solid stream increases up to 1450°C by fuel combustion with primary and secondary airs in the reactor (second unit) in order to calcine the remaining calcite and make all clinkerization reactions completed. Finally, the kiln product formed in the second unit is cooled to 1370°C with the incoming secondary air at the solid product end (third unit) (see Supporting information – S1).

The kiln product is sent to the clinker cooler in which it is cooled to 60°C by ambient air. Even though there is a potential to burn alternative fuels such as tyres and biomass fuels in
the pre-calciner, coal is selected as a heat provider following the reference (IEA, 2008). The high temperature requirement in the kiln restricts the fuel flexibility; therefore, pet coke with low ash content is generally combusted in this reactor. Both fuel streams are dried completely by the hot flue gases from preheater. The excess air ratio is set as 10% to guarantee complete combustion in both reactors. The compositions of the fuels used in this study has been constructed from IEA (2008) report and presented in Table 4.

Tables 5 and 6 show the mass and heat balance around the cement plant obtained by the base case simulation. Given the raw meal composition, 1.66 kg/s of raw meal are required to produce 1 kg/s of clinker. The CO₂ generation intensity is around 0.8 ton CO₂/ton clinker that is within the range of 0.65–0.92 ton CO₂/ton cement given as the average CO₂ intensity for cement manufacture (IEA, 2007). Based on the heat balance, the required thermal energy for unit clinker production is estimated to be 3.13 MJₖₑₜ/kg clinker. The overall heat of chemical reactions involved in conversion of raw meal to clinker is estimated at about 178.4 GJₖₑₜ/h (1.57 MJₖₑₜ/kg clinker) by the difference between enthalpy in and out. The overall heat of reaction is lower in this simulation than in the reference (Taylor, 1990) (1.76 MJₖₑₜ/kg clinker) since it also takes into account the heat of the two highly exothermic reactions of sulphur conversion to SO₂ and its reaction with CaO.

### Table 4
Composition of the fuels fed to the pre-calciner, kiln and calciner.

<table>
<thead>
<tr>
<th></th>
<th>Precalcer (coal¹), wt%</th>
<th>Kiln (pet coke¹), wt%</th>
<th>Calciner (pet coke), wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>64.4</td>
<td>85.6</td>
<td>87.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.5</td>
<td>3.5</td>
<td>3.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.4</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.9</td>
<td>5.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Ash</td>
<td>12.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>7.2</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Moisture</td>
<td>9.5</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Total</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

¹ Data from IEA (2008).

### Table 5
Mass balance of the base case simulation [kg/s].

<table>
<thead>
<tr>
<th>Mass in</th>
<th>Mass out</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw meal</td>
<td>52.41</td>
</tr>
<tr>
<td>Air</td>
<td>99.55</td>
</tr>
<tr>
<td>Fuel</td>
<td>2.26</td>
</tr>
<tr>
<td>Wet coal to pre-calciner</td>
<td>1.18</td>
</tr>
<tr>
<td>Wet pet-coke to kiln</td>
<td>1.18</td>
</tr>
<tr>
<td>Total in</td>
<td>155.40</td>
</tr>
<tr>
<td>Clinker</td>
<td>31.61</td>
</tr>
<tr>
<td>Excess Air</td>
<td>75.49</td>
</tr>
<tr>
<td>Total out</td>
<td>155.40</td>
</tr>
</tbody>
</table>

3. Process simulation of a Ca-looping process

In all simulations, the operating condition of the carbonator is carefully chosen to capture 90% CO₂ from the feed gas and the CaCO₃ fed to the calciner is regenerated to CaO at complete conversion. The calciner temperature is selected to be 930 °C, which is higher than the pre-calciner temperature (915 °C), to guarantee complete calcination due to the CO₂ partial pressure in the calciner close to 1 atm. The temperature of the carbonator, which should be kept as close to the calciner temperature as possible in order to save the energy consumption for reheating the circulating solid, is fixed at 650 °C in this study.

The operating conditions inside the carbonator and the calciner are also favourable to the capture of SO₂ (Anthony et al., 1987). It is assumed that all SO₂ generated by combustion in the calciner is captured by CaO and the negative effects of sulphation on the maximum carbonation degree is taken into account in the carbonator model (Romano, 2012). As a result of the deterioration of the CO₂ absorption capacity through the carbonation/calcination cycles, fresh CaCO₃ needs to be added into the calciner while some amount of spent sorbents (CaO) on a molar basis are removed from the calciner. The CaCO₃ make-up, fuel, and oxygen streams fed to the calciner are neither preheated nor dried but directly fed to the calciner due to the lack of flue gas availability for preheating.

All the mathematical models for the carbonator have been solved in Matlab and then the carbonator unit was incorporated into the UniSim process simulation for a cement plant as a user defined operation. The Visual Basic code in a user defined operation transfers the input values from UniSim into the Matlab environment where the design calculations are implemented via a component object model (COM) interface. The calculated values are then sent back to Unisim and used for the mass and energy balance calculations in the complete process flowsheet. A detailed explanation of the mathematical models used for the carbonator unit can be found in Appendix A.

4. Process integration of a Ca-looping unit with a cement plant

One of the important issues while integrating a Ca-looping unit with a cement plant is the selection of a feed gas stream for the Ca-looping process. As the flue gas from pre-calciner flows through the process in the opposite direction to the solid flow for heat recovery, its temperature and CO₂ mole fraction varies over the process as shown in Fig. 2. Therefore, the optimal flue gas stream for the capture process should be selected taking into account the operating condition of a selected capture unit, ease of heat integration, and CO₂ partial pressure.

For the ease of retrofit, it can be envisaged that the flue gas stream after the raw mill and fuel drying would be an optimal feed for the capture unit. However, the flue gas at this location has
around 22 vol% CO₂ as shown in Fig. 2(b), which is the lowest value over the entire process. On the contrary, its volumetric flowrate is its highest at this point so a larger equipment size of the capture unit would be required. Furthermore, the flue gas may need to be reheated prior to being fed to the carbonator in order to initiate the carbonation reaction as the temperatures of the flue gases are around 110 °C. In addition, the heat of the CO₂-depleted gas from the carbonator needs to be recovered to improve the energy efficiency but an additional facility for heat recovery should be deployed for this purpose. In conclusion, the applications of Ca-looping processes to the end-of-the-pipe gas streams of the cement plants would require a complexity similar to those of power plants.

However, the flue gas at the exit of the 3rd preheater has a temperature of around 650 °C, as shown in Fig. 2(a), which is similar to the operating temperature of the carbonator. It indicates that the flue gas from the 3rd preheater would not require any pre-heating of the feed gas and would be preferable for the start-up of the carbonator. Moreover, there is no need to recover the heat from the CO₂-depleted flue gas stream for power generation and instead it is possible to return it back to the cement plant in order to heat up the raw materials in a similar way to the operation in the conventional cement plant. The flue gas at the 3rd preheater exit has a higher CO₂ concentration (~35 vol%) compared to the end-of-pipe stream (~22 vol%) as shown in Fig. 2(b) and, in proportion, such a lower gas flow rate would require a smaller carbonator size leading to lower capital expenditure. Therefore, a decision was made that the flue gas from the 3rd preheater stage is diverted to a Ca-looping unit for CO₂ capture as shown in Fig. 3. The CO₂-depleted flue gas from the carbonator is routed to the 2nd preheater stage for preheating the raw material further. It should be noted that it is still possible to capture CO₂ from all sources including calcination and fuel combustion with this configuration, which was initially proposed by ECRA (2007).

On the other hand, the CO₂ depleted flue gas flowing from the carbonator to the 2nd preheater would have a lower flow rate than that in the base case as a result of carbon capture and its heat duty is not large enough to heat the raw material up to a temperature that would be reached in the base case. Thus, part of the excess air from the clinker cooler as well as CO₂-depleted flue gas should be utilised for heating the raw material as shown in Fig. 3. In all cases of this study, the flowrate of excess air being sent to the raw mill was determined to heat the raw material entering the 1st preheater up to 110 °C. It should be noted that the clay components are not fed into the capture unit in this study as distinct from the reference (Rodriguez et al., 2012) since the sorbent performance has not been proven for this mixture yet and there would be a need of additional efforts for the circulation of inert. As the purge stream of the Ca-looping unit is mixed with pre-calcined raw materials and then the mixture is sent to the kiln for clinker production, the mass and heat balance in the cement plant is significantly affected by changing the CaCO₃ make-up flow rate of the Ca-looping process. Firstly, since the CaO for clinkerization can be produced in the calciner as well as the pre-calciner, the ratio of calcite to clay in the raw meal should be decreased with an increasing F₀/F₀CO₂ in order to maintain the same clinker composition as that in the base case. Subsequently, the decreasing ratio of calcite to clay in the raw meal results in reduction in heat demand in the pre-calciner and, to a lesser extent, in the kiln.

In order to save the energy consumption for a Ca-looping process further, it is possible to recover the heat of reaction in the carbonator and the heat from the CO₂-rich stream and excess air. The heat of these hot streams can be recovered by way of generating steam for a steam cycle. The power generated can be utilised for the cement plant operation, the CO₂ compression unit, the air separation unit (ASU), etc. Since the solid removal efficiency is not 100% on the 3rd preheater stage, a new cyclone with higher efficiency has been included to prevent the solid transfer from the cement plant to the capture unit for the precise prediction of the carbonation efficiency in this unit. It is estimated that the additional pressure increment of the gaseous feed flowing to the carbonator would be approximately 0.16 bar. This would be sum of the pressure loss in operating the carbonator (pressure drop along the carbonator bed, 0.10 bar + gas injection through the nozzle, 0.03 bar) and the pressure drop relating to the additional cyclone (0.03 bar) (Alsop et al., 2007). 0.20 bar of a total pressure loss including a 25% safety margin is estimated. The boost of the gas stream pressure has been achieved
by increasing the cooling air pressure flowing to the cement kiln. The ASU power consumption is set as 231 kWh per ton O₂ product at 99.5% oxygen purity (Marion et al., 2003). The CO₂ compression unit consists of a four-stage turbo compressor with intermediate cooling, followed by a pump once the CO₂ becomes a dense phase. The inlet temperature of each stage is fixed at 45 °C and the adiabatic efficiency of each compressor is assumed to be 75%. The power requirement for CO₂ compression up to 150 bar is estimated at 1.08 MJ/kg CO₂ using a 0.4 conversion factor of power to equivalent thermal energy. An example mass and energy balance calculations for the capture cases can be seen in Supporting Information – S2.

5. Results and discussion

Two mathematical models for the carbonator have been compared in this study as shown in Appendix A. While it is assumed that all the active fraction of CaO reacts with CO₂ in the feed gas in the ‘simple model’, the ‘rigorous model’ includes the effects of both hydrodynamics and reaction kinetics in the fluidised bed reactor. Moreover, the effects of sulphation on the maximum carbonation degree were taken into account in the rigorous model based on the experimental data of Plasek for limestone sulphation up to 1% in each carbonation/calcinations cycle (Grasa et al., 2008a). Given a F₀/F₂O₂, the corresponding F₀/F₂O₂ to achieve 90% CO₂ capture has been evaluated using the simple and rigorous models with results shown in Fig. 4. The minimum value of the F₀/F₂O₂ being examined is set as 0.20 since the heat demand at the raw mill cannot be met even by employing the entire excess air in addition to the flue gas at a F₀/F₂O₂ less than 0.20. The heat requirement in the raw mill keeps decreasing with increasing F₀/F₂O₂ since the flowrate of raw meal into the raw mill decreases with an increase of the ratio. The upper limit of the F₀/F₂O₂ ratio is determined as 5.10 since there is no calcite in the raw meal at this condition, that is to say, all the calcites in the feed are fed to the calciner. Therefore, the carbonator captures CO₂ generated only from the fuel combustion at this ratio. As shown in Fig. 4, it is clear that as the F₀/F₂O₂ ratios estimated by the rigorous model using sulphur-free fuel are definitely higher than those by the simple model in range of the F₀/F₂O₂ investigated. The extent of the difference between the two models is affected by the residence time of sorbents in the carbonator which is determined by the amount of sorbent inventory in the reactor. However, when utilising the fuel having sulphur in the calciner, the required F₀/F₂O₂ ratios need to be increased way above those with sulphur-free fuel since the CaO is significantly deactivated by sulphation. In this study the sulphur content in the fuel used in the calciner was adjusted so that the maximum sulphation, obtained at the 5.10 F₀/F₂O₂ case can be 1%. It implies that the use of sulphur-free fuel would alleviate the severity of its operation condition due to the lower amount of solid circulation required given a F₀/F₂O₂ ratio.

Fig. 5(a) shows the variation of the thermal energy requirement per unit clinker in terms of fuel combustion (pre-calciner, kiln, and calciner) and power consumption (ASU and blower) with the F₀/F₂O₂. The thermal requirement for the pre-calciner decreases with increasing F₀/F₂O₂ as the heat requirement for the pre-calciner decreases in proportion to the reduction in calcite fed to the raw mill. The thermal requirement for the kiln has decreasing trends with the F₀/F₂O₂ too since it is assumed that the calcite is completely calcined in the calciner while its conversion is only 90% in the pre-calciner. However, the reduction of energy demand in the kiln is not as significant as that in the pre-calciner because the solid flowrate to the kiln is almost constant regardless of the F₀/F₂O₂ due to nearly constant clinker production rate in all cases. The heat requirement for the calciner shows a minimum over the F₀/F₂O₂ range investigated. Before the minimum, it is decreasing due to decreasing
circulating amount of solid, that is to say, the \( F_0/F_{CO_2} \) as shown in Fig. 4. However, after the minimum, the effect of the increase in the heat duty at the calciner caused by the \( F_0/F_{CO_2} \) increase dominates. The total fuel requirement shows a steady overall decrease with the increase of the \( F_0/F_{CO_2} \) ratio. The energy requirement for the ASU is proportional to the fuel consumption in the calciner and that for the cold air blower is constant with the \( F_0/F_{CO_2} \) ratio. The electric power consumptions in the ASU and blower are converted to their corresponding thermal energy consumption using a power plant efficiency of 0.4. This allows an overall comparison of different options in terms of the equivalent total thermal energy required. At least in terms of total thermal energy consumption for the fuel, the ASU and the blower it is preferable to operate a Ca-looping process at as high \( F_0/F_{CO_2} \) ratio as possible.

On the other hand, it is intuitively conceivable that a Ca-looping process can be made more efficient in terms of energy consumption if it is combined with a steam cycle for heat recovery. There are three different sources from which the heat can be recovered by generating steam and subsequently running a steam turbine. It is possible to generate steam by evaporating the water inside the carbonator in order to keep the reactor temperature constant at 650 °C and also recovering the heat from a \( CO_2 \)-rich stream and the excess air as shown in Fig. 3. In case of heat recovery from the two gaseous streams, it is assumed that the hot gas can supply the steam cycle with thermal energy which is estimated as an enthalpy to be generated when cooled down to 150 °C. At 0.2 \( F_0/F_{CO_2} \), as shown in Fig. 5(b), the heat that can be recovered in the carbonator is a maximum over the range due to the greatest heat of reaction generated in the carbonator and the largest amount of hot solids conveyed from calciner to carbonator (see Fig. 4). There is no heat to be recovered from the excess air since all the excess air should be diverted to the raw mill in order to compensate the deficiency of heat duty of the flue gas. Considering the energy consumption inclusive of \( CO_2 \) compression, the net energy consumption per unit clinker production is in the range of 5.2–5.5 GJ/ton clinker. This is equivalent to around 66% increase in energy consumption of a cement plant producing the same amount of clinker.

A simplified steam cycle design has been used to evaluate the power generation from the recovered heat. The turbine adiabatic efficiencies have been fixed at 86%, 86% and 95% for HP, IP and LP turbines, respectively (Ahn et al., 2013). With the proposed configuration (see Supporting information – S3) it is possible to estimate a lumped conversion factor of 0.44 which can be used to evaluate the electrical power generation from the total heat to be recovered from the cement plant integrated with the Ca-looping process. The total electricity generation ranges from 30 to 70 MWe and is shown in Fig. 6. It is predicted that the power generated in the steam cycle can exceed the power demand in the cement plant integrated with a Ca-looping process up to ~1.5 \( F_0/F_{CO_2} \). The power use for the cement plant operation is assumed as 120 kW/ton clinker (IEA, 2008; Taylor, 1990) regardless of the \( F_0/F_{CO_2} \).

It should be noted that what is fixed in this study is not a \( CO_2 \) recovery in the overall cement process but a \( CO_2 \) recovery in the calciner. As shown in Fig. 7 the percentage of \( CO_2 \) avoided is as low as 92% at 0.2 \( F_0/F_{CO_2} \) since most \( CO_2 \) is captured in the carbonator with 90% capture rate. It increases up to 99% at 5.10 \( F_0/F_{CO_2} \) because most \( CO_2 \) is captured with 100% \( CO_2 \) recovery in the calciner. In this study, the limiting case named ‘oxy-calciner only’ has been simulated without a carbonator. All calcites are calcined in the calciner separate from the pre-calciner in a similar way to the 5.10 \( F_0/F_{CO_2} \) case, but there is no carbon capture applied to the kiln gas. In this case, the percentage of \( CO_2 \) avoided is 90% since this process can capture \( CO_2 \) relating to calcinations and fuel combustion in the calciner, but cannot capture \( CO_2 \) generated by fuel combustion in the kiln with a loss of 9% in overall capture efficiency.

The incremental energy consumption per \( CO_2 \) avoided without heat recovery also shows decreasing trends with \( F_0/F_{CO_2} \) similarly to the total energy input per unit clinker in Fig. 5(a). It implies that it would be better to generate CaO by oxy-combustion rather than by the pre-calciner in the existing plant if no heat recovery system is added. The incremental energy consumption per \( CO_2 \) avoided at the ‘oxy-calciner only’ and 5.10 cases are 5.1 and 5.5 GJ/ton \( CO_2 \) avoided respectively without heat recovery. It is thought that the difference between the two cases (0.4 GJ/ton \( CO_2 \)) can be explained by additional energy consumption resulting from circulating solids between the carbonator and the calciner. It was indicated that the thermal energy consumption in the MEA process when it is used for carbon capture from a cement plant (IEA, 2008) requires around 9.2 GJ/ton \( CO_2 \) avoided including its compression work. In this respect, even without heat recovery, the energy consumption at the 5.10 \( F_0/F_{CO_2} \) case is significantly lower than that for MEA process (IEA, 2008). With heat recovery put in place, the resulting energy consumption decreases further to 2.5 GJ/ton \( CO_2 \) avoided for the 5.10 case and 2.3 GJ/ton \( CO_2 \) avoided for the ‘oxy-calciner’ case. Table 7 shows the quantitative difference of fuel and power consumptions between the cement plant without capture and those integrated with Ca-looping units and heat recovery steam cycle at various \( F_0/F_{CO_2} \) conditions. Table 7 also includes the change of mass flow rates of limestones entering the plant through the raw mill and calciner with the value of \( F_0/F_{CO_2} \). The proposed cement plants
integrated with Ca-looping units are designed with a steam cycle that can recover heat contained in the hot excess air which would be lost in the conventional cement plant. As a result the net thermal energy consumption in the cement plants with Ca-looping units is always lower than that in the conventional cement plant as shown in Table 7. It is clear that it would be extremely inefficient to operate a Ca-looping unit at low F0/FCO2 ratio without heat recovery but CO2 can be recovered with almost constant energy consumption regardless of the F0/FCO2 ratio if a proper heat recovery is deployed. Moreover, the electricity required to operate a cement plant integrated with a Ca-looping process can be generated in situ by a steam cycle attached to the capture unit without any external source of electricity which would be associated with carbon emissions.

6. Conclusions

A way of capturing CO2 from cement plants by integrating it with a Ca-looping process has been investigated. The cement process simulation implemented in this study was proven to be reliable in that the total energy consumption estimated by the simulation lies within the range of those reported in the literature and the clinker compositions estimated in the simulation are in good agreement with those calculated by the Bogue equation. Among the flue gas streams, the gas stream leaving the 3rd preheater was selected to be the optimal feed suitable for the Ca-looping capture unit since (1) it does not have to be preheated, (2) it has a higher CO2 partial pressure and a lower total volumetric flowrate, and (3) a simpler design of the steam cycle for heat recovery is possible.

The upper and lower limits of the F0/FCO2 ratio have been set in this study in order to see the effect of F0/FCO2 on the energy consumption. Given 90% carbon capture in the carbonator, the CO2 avoided in the overall integrated process ranges from 92% to 99% depending on the F0/FCO2 ratio. The incremental energy consumption by carbon capture decreases with the F0/FCO2 ratio but, with heat recovery from the capture unit, the energy consumption can be almost constant regardless of the ratio.

It should be noted that there may be a constraint in the minimum fuel supply to the kiln to ensure a stable operation in the kiln as pointed out in the IEA study (2008). Therefore, the actual upper limit of the F0/FCO2 ratio needs to be defined considering plant operability. Moreover, the estimation of the amount of heat that can be recovered from three high temperature sources can be made more accurate by inclusion of a detailed steam cycle in the integrated process flowsheet.

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### Appendix A. Carbonator design

In the simple model, the maximum average carbonation degree of sorbent in the solid population is defined as Eq. (A1) (Abanades, 2002) where \( X_{\text{max},N} \) is maximum carbonation degree after \( N \) cycles of carbonation/calcination in Eq. (A2) (Grasa and Abanades, 2006) and \( r_N \) is mass fraction of particles calculated from mass balance in Eq. (A3) (Abanades, 2002). The CO2 capture efficiency in the carbonator (\( E_{\text{CO2}} \)) is defined as Eq. (A4).

\[
X_{\text{max},N} = \frac{1}{1 - (1 - X_r) + k_N N} + X_r
\]

\[
r_N = \frac{F_0 F_r^{N-1}}{(F_0 + F_r)^N}
\]

\[
E_{\text{CO2}} = \frac{F_0 X_{\text{max},\text{ave}}}{F_{\text{CO2}}}
\]

Fig. 8. Graphical explanation of Eq. (A5) at 650 °C (\( k = 0.66 \) and \( X_r = 0.0969 \)).
\( X_\text{c} \) and \( k \) are constants specific to the type of limestone. For nonsulfated Piaseck limestone the values of the constants are \( k = 0.66 \) and \( X_\text{c} = 0.0969 \) (Romano, 2012; Grasa et al., 2008a). The capture efficiency calculated from this model is shown in Fig. 8. The maximum carbonation efficiency is also limited by the equilibrium of CO\(_2\) over CaO as shown in Eq. (A5) (Garcia-Labiano et al., 2002). The equilibrium at 850 °C is shown as a horizontal dotted line in Fig. 8.

\[
P_{\text{CO}_2,\text{eq}} = 4.137 \times 10^{12} \exp \left( - \frac{20474}{T} \right) \tag{A5}\]

The target is to achieve 90% carbon capture in the carbonator. As it can be noticed from Fig. 8, various sets of \( F_\text{in}/F_{\text{CO}_2} \) and \( F_\text{g}/F_{\text{CO}_2} \) can provide capture efficiency of 90% according to Eqs. (A1)–(A4). However, an advanced carbonator model is necessary in order to deal with the hydrodynamics of a fluidized bed system. Detailed carbonator design has been investigated including the design of a bubbling fluidized bed (Abanades et al., 2004) and a fast fluidized bed (Romano, 2012; Lasheras et al., 2011). Therefore, in this study, the detailed circulating fluidized bed (CFB) model for fast fluidization has been employed based on the approach proposed in the literature (Romano, 2012; Rampinelli, 2010) and named rigorous model in this study. This model is briefly described here but further details can be found in the literature (Romano, 2012).

The particle distribution part of the rigorous model has been based on the Kunii–Levenspiel model for CFBs (Kunii and Levenspiel, 1991), and the reactor is divided into two sections, a lower dense region and an upper lean region. To calculate the values of \( H_l \) (height of the upper lean region) and \( \varepsilon \text{se} \) (existing solid fraction), the particle distribution equations (Eqs. (A6) and (A7)) need to be solved simultaneously.

\[
\varepsilon \text{se} = \varepsilon \text{se}^* + (\varepsilon \text{se,d} - \varepsilon \text{se}^*)e^{-\alpha H_l} \tag{A6}
\]

\[
\frac{W_{se}}{\alpha H_l} = \frac{(\varepsilon \text{se,d} - \varepsilon \text{se})}{a} + H_l(\varepsilon \text{se,d} - \varepsilon \text{se}^*) \tag{A7}
\]

The solution of the gas phase material balance in the CFB which can be rearranged with the first order kinetic law for the carbonation reaction (Grasa et al., 2008b) leads to two final equations, (A8) and (A9) which give CO\(_2\) concentrations at the top of the dense region \( C_{\text{CO}_2,d} \) and at the reactor exit \( C_{\text{CO}_2,\text{out}} \), respectively.

\[
C_{\text{CO}_2,d} = C_{\text{CO}_2,\text{eq}} + (C_{\text{CO}_2,\text{in}} - C_{\text{CO}_2,\text{eq}}) \times e^{-[\varepsilon \text{se}^* + (\varepsilon \text{se,d} - \varepsilon \text{se}^*)e^{-\alpha H_l}](X_1 + 1)} \tag{A8}
\]

\[
C_{\text{CO}_2,\text{out}} = C_{\text{CO}_2,\text{eq}} + (C_{\text{CO}_2,d} - C_{\text{CO}_2,\text{eq}})e^{-(\varepsilon \text{se} - \varepsilon \text{se}^*)/a} \tag{A9}
\]

The average kinetic constant \( k_{\text{.react}} \) and volume fraction of potentially active solids \( \xi \) should be known initially to solve Eqs. (A8) and (A9). Therefore, as another approach, the considerations of solid composition in the carbonator, probability density function \( f_i \), i.e. the fraction of particles with certain residence times, in Eqs. (A12)–(A14) and the distribution of the particle based on the number of carbonation–calcination cycles as given in Eq. (A3) allows the calculation of the average carbonation level, \( X_{\text{ave}} \) (Eq. (A15)) as well as \( k_{\text{react}} \) (Eq. (A16)) and \( \xi \).

\[
f_i = \frac{1}{\tau} e^{-(t/\tau)} \tag{A12}
\]

\[
\tau = \frac{M_h}{F_g} \tag{A13}
\]
Appendix B. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:10.1016/j.jgcgc.2013.10.009.

References