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Recent progress of the Ca-Cu technology for decarbonisation of power plants and carbon intensive industries

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\section*{ABSTRACT}

Highly efficient pre-combustion systems are sustainable alternatives for producing hydrogen with reduced carbon footprint. The Ca-Cu looping process is a novel CO\textsubscript{2} capture process that combines Sorption Enhanced Reforming (SER) for the production of (almost) pure H\textsubscript{2} with a Cu/CuO redox cycle to regenerate the CO\textsubscript{2} sorbent with a low energy penalty and potential reduction in capture cost. Over the last few years, the Ca-Cu looping process has seen noticeable progresses in its development and has recently been demonstrated up to TRL4/5 within the Ascent EU project, under conditions that are relevant for a range of industrial applications. This work reviews the most recent achievements and open gaps of knowledge in the development of this emerging process, focusing on experimental validation performed in lab-scale fixed bed reactors and on techno-economic assessment of the application in industrial plants for hydrogen, ammonia and steel production.

\section*{1. Introduction}

Hydrogen has gained importance as an alternative to fossil fuels due to its flexibility, fuel density and low carbon footprint at the end user. However, around 96% of the hydrogen production worldwide still uses fossil fuels as feedstock (Voldsund et al., 2016). On the other hand, CO\textsubscript{2} capture and storage (CCS) remains as the best option for achieving drastic carbon dioxide emission cuts in large stationary sources (Edenhofer et al., 2014). For this reason, the deployment of large-scale hydrogen production technologies including CO\textsubscript{2} capture (pre-combustion), with the aim of reducing the H\textsubscript{2} production cost and improving the efficiency, may be crucial for the mitigation of climate change (Boo-Handford et al., 2014; Jansen et al., 2015; Voldsund et al., 2016).

Steam methane reforming (SMR) with simultaneous separation of CO\textsubscript{2} has gained importance as a method for producing almost pure hydrogen with reduced carbon content in a single step (Di Giuliano and Gallucci, 2018; Harrison, 2008). In this process, referred to as sorption enhanced reforming (SER), the reforming of methane is carried out in the presence of a CO\textsubscript{2} sorbent that separates in situ the CO\textsubscript{2} from the gas phase, thereby pushing the reaction equilibrium towards hydrogen production. CaO-based materials have been commonly recommended as CO\textsubscript{2} sorbents for the SER process due to their good performance, wide availability and favourable kinetics (Di Giuliano and Gallucci, 2018; Erans et al., 2016; Kierzkowska et al., 2013). Based on the equilibrium of the three main reactions taking place in the SER process (Eqs. 1–3), H\textsubscript{2} contents of up to 96 vol.% and about 1 vol.% of CO and CO\textsubscript{2} (on a dry basis) can be reached at 650–700 °C in one single step (Balasubramanian et al., 1999; Johnsen et al., 2006; Lopez Ortiz and Harrison, 2001; Yi and Harrison, 2005). Moreover, the energy released by the water gas shift (WGS) and carbonation reactions compensates for the endothermic steam reforming enthalpy, resulting in an almost neutral system where the need for external energy supply is avoided (unlike the energy-intensive SMR).

\begin{equation}
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \Delta H_{298K} = 206.2 \text{kJ/mol}
\end{equation}

\begin{equation}
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \Delta H_{298K} = -41.0 \text{kJ/mol}
\end{equation}

\begin{equation}
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \Delta H_{298K} = -178.8 \text{kJ/mol}
\end{equation}

The main issue that has hindered so far the deployment of the SER process is the need to reduce the energy penalty associated to the regeneration of the CO\textsubscript{2} sorbent (i.e. by CaCO\textsubscript{3} calcination to generate...
pure CO₂ and CaO). The most widely proposed method to supply the energy required for CaCO₃ calcination in both pre-combustion SER processes and in post-combustion Ca-Looping processes is the combustion of a fuel using a pure O₂ stream as oxidant (Martínez et al., 2013b; Ochoa-Fernandez et al., 2007; Romano et al., 2011; Shimizu et al., 1999), which facilitates the purification of the CO₂-rich stream generated for being subsequently stored. However, the energy consuming air separation unit (ASU) needed in this configuration affects noticeably both the efficiency and the capital cost of the technology. For this reason, alternative methods have been explored in the literature. Generally, the methods studied propose fulfilling the calxiner heat demand by means of a solids stream at a high temperature coming from a third reactor (Fernández and Abanades, 2016; Martínez et al., 2011), transferring the heat needed indirectly to the regeneration chamber from a high temperature combustor by means of heat pipes (Reitz et al., 2015) or through a metallic wall separating both reactors (Abanades et al., 2005; Hodgson et al., 2018). However, the challenges associated to the design of the heat exchange surfaces or the operation of multiple interconnected fluidized beds limit the application of these methods at a sufficient scale (Martínez et al., 2016).

The decomposition of the CaCO₃ formed during the hydrogen production step by means of an additional redox loop of Cu/CuO was proposed (Abanades and Murillo, 2009) in order to boost the efficiency and reduce the cost of such calcination process in SER systems. The Ca-Cu looping concept proposes the coupling in the same bed of solids the CaCO₃ calcination together with the reduction of CuO (highly exothermic) using a gaseous fuel containing H₂, CO and CH₄. The thermal power supplied by the reduction of CuO avoids the need of energy consuming equipment like the ASU in oxy-fired calcination systems or costly heat exchange devices in indirect fired calciners referred above. This process has undergone a noticeable progress in terms of materials development, reactor design, experimental validation and process modelling analysis. The objective of this work is to review the most recent achievements for this emerging process, with a particular focus on the experimental validation (up to TRL4-5) of the most developed reactor concepts that involve packed-bed reactors operating in different reaction stages. This work also reviews techno-economic studies of the application as pre-combustion CO₂ capture systems in hydrogen, ammonia and iron & steel industries using a wider variety of reactor options.

2. The Ca-Cu looping concept

A simple arrangement of the main reaction steps of the Ca-Cu looping process is shown in Fig. 1. Three functional materials are required to operate the process, namely a Cu-based material, a CaO-based CO₂ sorbent and a reforming catalyst, all packed and mixed in the same bed at certain proportions (see below). Many studies have been done in the development of Cu-based materials and CO₂ sorbents with the requirements for this process, as recently reviewed by Fernández and Abanades (2017a, 2017b). A highly stable material with high proportion of CuO (i.e., over 60 wt.%) is desired to reduce the amount of inert in the solid bed, which would absorb part of the energy released by CuO reduction (acting as a thermal ballast). Moreover, synthetic Cu-based materials with a highly steady CO₂ carrying capacity along calcination/calcination cycles are the preferred option for the Ca-Cu process, leaving the naturally derived CaO-based sorbents, which decrease their maximum CO₂ carrying capacity with the cycles, ruled out for this process (Fernández et al., 2012c). Finally, conventional reforming Ni-based catalysts have been proposed for the SER stage. They have shown good performance under relevant conditions for the system (Díez-Martín et al., 2018b; Grasa et al., 2017).

The Ca-Cu process has been typically proposed to be operated in parallel pressurized fixed-bed reactors (Fernández et al., 2012c). This configuration allows the functional materials to remain steady whereas the reacting gases are repetitively switched between SER and redox conditions. A H₂-rich gas is first obtained through the SER of natural gas. Steam methane reforming (SMR), WGS and CaO carbonation take place simultaneously in the reactor, which is operated between 600 and 700 °C and between 10 and 25 bar, depending on the main output of the process (i.e., hydrogen or power production) (Fernández and Abanades, 2017c; Martínez et al., 2014, 2013a). The active CaO reacts with the CO₂ to form CaCO₃, whereas the reforming catalyst and the Cu-based solid continue unreacted. This operation finishes when the CO₂ sorbent has been fully carbonated.

In the next reaction stage, diluted air is fed into the reactor to oxidise the Cu-based solids under controlled pressure and temperature to limit the maximum bed temperature and avoid both the prompt CaCO₃ calcination and operational issues related to the Cu-based material (i.e., agglomeration, secondary reactions and/or reactivity loss). Low temperature and O₂ concentration in inlet air (i.e., around 300 °C and 3 vol.% O₂) allow the maximum temperature to be maintained under the safety margin of 830–850 °C that minimises the aforementioned issues (Alarcón et al., 2017; Díez-Martín et al., 2018b; Fernández et al., 2014, 2012c). This stage is also operated at high pressure to reduce the driving force towards CaCO₃ decomposition. The dilution of inlet air is obtained by recirculating a large amount of the O₂-depleted gas leaving this reactor.

The Ca-Cu loop is closed with the key step of the process that is the calcination of the CaCO₃ by means of the exothermic reduction of CuO with CH₄, H₂ or CO (Fig. 1). This step is carried out at atmospheric pressure to reduce the calcination temperature to 850–870 °C (Baker, 1962). The proportion of CaO and CuO in the solid bed mainly depends on the fuel gas composition, since the energy released by CuO reduction should be enough for bringing the solids and gas up to 850–870 °C and then driving the endothermic CaCO₃ calcination. According to the enthalpies of the reactions (4–6), a maximum CuO/ CaCO₃ molar ratio of 3.1 is required when using pure CH₄ as fuel gas whereas only a CuO/ CaCO₃ molar ratio of 1.3 is needed if pure CO is used (Alarcón and Fernández, 2015). Typically, mixtures of H₂, CO and CH₄ are proposed for the reduction/calcination operation, which come from the off-gas of a hydrogen purification unit or from a separate reforming stage (Fernández and Abanades, 2017c; Martínez et al., 2014).

\[ 4\text{CuO} + \text{CH}_4 \rightarrow 4\text{Cu} + \text{CO}_2 + 2\text{H}_2\text{O} \Delta H_{298K} = -39.6\text{kJ/mol}_{\text{CuO}} \] (4)

\[ \text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O} \Delta H_{298K} = -86\text{kJ/mol}_{\text{CuO}} \] (5)

\[ \text{CuO} + \text{CO} \rightarrow \text{Cu} + \text{CO}_2 \Delta H_{298K} = -127\text{kJ/mol}_{\text{CuO}} \] (6)

Fig. 1. Schematic of the Ca-Cu looping process.
3. Ca-Cu reactors design

3.1. Kinetics for the main reactions involved in the process

Several dynamic reactor models have been elaborated to describe in detail each reaction step of the Ca-Cu process. These are basically one-dimensional models, in which well-known kinetic equations reported in the literature were implemented to represent the reaction rates. For the SER stage, Fernández et al. (2012a) and Fernández and Abanades (2017b) developed a reactor model in which the kinetics reported by Xu and Froment (1989) were incorporated to represent both the steam methane reforming (SMR) and the WGS reactions using a Ni-based catalyst. In other study, Martini et al. (2016) used the kinetics from Numaguchi and Kikuchi (1988) for the SMR and WGS reactions in an attempt to avoid possible overestimation of the reaction rates when the stage is performed at high temperature and pressure with high content of H₂O and no H₂ in the inlet gas. Fernández et al. (2012a) and Fernández and Abanades (2017b) used the experimental equation proposed by Rodríguez et al. (2011) to estimate the carbonation of CaO during the SER operation, in which the reaction rate constant is assumed to be independent of the temperature when the carbonation takes place below 600 and 700 °C. Martini et al. (2016) also used the shrinking core model (SCM) proposed by Lee (2004) to represent the carbonation of CaO during the SER. In a more recent work, Perreault and Patience (2016) reported a carbonation model at a particle scale for a combined CuO/CaO material, which relies on the experimental results acquired in a packed bed. This model takes into account the progressive loss of reactivity observed in the solids after several cycles caused by increasing solid crystallinity.

The typical mechanism reported to represent the oxidation kinetics of Cu-based materials in chemical looping systems is the SCM. García-Labiano et al. (2004) and Hamers et al. (2014) obtained the kinetic parameters using TGA for Cu-based solids containing around 10 wt.% of active phase. More recent works are focused on investigating the oxidation and reduction kinetics of Cu-based materials with high CuO loadings (i.e., higher than 50 wt.% CuO), which makes them especially suitable for compact Ca-Cu looping systems. Díez-Martín et al. (2018a, 2018c) evaluated the oxidation kinetics of two Cu-based solids containing about 65 wt.% Cu at atmospheric and pressurized conditions (up to 20 bar) in a thermogravimetric analyser (TGA). A SCM was used to describe the results obtained in the tests. It was also demonstrated that the operating pressure had no noticeable effect on oxidation kinetics. Then, the kinetic parameters calculated at atmospheric pressure described accurately the oxidation conversion at high pressure. To model the CuO reduction/CaCO₃ calcination stage, the dynamic reactor models developed by Fernández and Abanades (2017b) and Martini et al. (2016) assumed the calcination kinetics obtained by Martínez et al. (2012), which considers an homogeneous reaction model to represent the calcination of two limestones with particle size below 300 μm at temperatures of up to 920 °C and CO₂ partial pressures between 0 and 100 kPa. García-Lario et al. (2013) studied in a TGA the reduction kinetics of CuO-based material pellets containing 60 wt.% of Cu, which showed reasonably fast reduction rates with CH₄, H₂ and CO at temperatures higher than 700 °C, even after 100 reduction/oxidation cycles. The reduction rate was also modelled by means of a SCM. Qin et al. (2015) evaluated both reduction and calcination reaction rates using synthetic CaCO₃ (99 wt.% purity) and CuO-based (75 wt.% CuO/Al₂O₃) powders. TGA tests at temperatures up to 900 °C with inlet gases containing of up to 40 vol.% of CH₄ (for the reduction) and 60 vol.% of CO₂ (for the calcination) showed that a random nucleation model for the reduction reaction and an experimental equation for the CaCO₃ calcination, based on that reported by Fang et al. (2009), described reasonably well the experimental data. In a more recent study, Díez-Martín et al. (2018b) studied the reduction of a Cu-based solid in powder and pellet form (65 wt.% Cu) with H₂, CO and CH₄ at 850 °C and evaluated its chemical stability throughout 100 redox cycles in a TGA. The experimental data showed that a SCM controlled by the chemical reaction described well the reduction conversion of the solid. San Pío et al. (2018) investigated the reaction rates for both the oxygen uncoupling and reduction of CuO-based solids with active contents between 13 and 70 wt.%. It was found that a grain model was suitable to fit both reactions using H₂ as reducing agent at temperatures below 1000 °C. Regarding combined functional Ca-Cu materials, Qin et al. (2016a, 2016b) developed a changing grain size model to represent the decomposition of CaCO₃ in homogeneously distributed CaO-CuO solids. Moreover, the reduction of CuO was found to be faster when the solids presented large porosity and small grain size. In the case of core-in-shell Ca-Cu composites (i.e., CuO grains located in the core and covered by a layer of CaCO₃), the calcination reaction was described by means of an analogous particle model, in which the simultaneous CuO reduction/CaCO₃ calcination were only feasible at temperatures above 900 °C (Qin et al., 2016a).

3.2. Reactor modelling

As indicated above, an arrangement of packed-bed reactors performing at different pressure and temperature is the preferable process scheme to operate the Ca-Cu looping process. Diverse reactor models of different complexity are reported in the literature to describe each reaction step of the Ca-Cu looping process. Fernández et al. (2012b) defined a preliminary design of the Ca-Cu process using a quite simple reactor model based on plug flow mode operation, in which steep reaction and heat exchange fronts were assumed, following an early approach by Noorman et al. (2007) and Eigenberger (2012) for packed bed chemical looping combustion reactors. This model approach served to define the operating conditions for every stage of the process (i.e., temperature, pressure, steam-to-carbon (S/C) ratio, etc). In later works, Fernández et al. (2012b, 2012a) developed a more elaborated pseudo-homogeneous model (PHM) to represent the SER stage of the process. The reactor model was designed for adiabatic conditions and assumed an ideal plug flow with negligible axial dispersion, taking into account the high velocities expected in large-scale reactors. Moreover, ideal gas behaviour, unvarying void fraction in the packed bed, uniform particle size and mixing for the functional solids, negligible catalyst deactivation and no dependence of physical properties with temperature and composition were also assumed for this model. These modelling works showed that during the SER operation, H₂ concentrations of up to 95 vol.% (on a dry basis) are feasible by operating at temperatures around 650 °C, low pressures (below 20 bar), high S/C molar ratios (3–5) and catalyst/sorbent weight ratios of about 0.3.

A similar model was also used by Fernández et al. (2013) to theoretically describe the oxidation step of the process. In this study, it was theoretically demonstrated that recirculating around 80–85% of the N₂ rich stream produced during the oxidation to achieve about 3–4 vol.% of O₂ in the feed is enough for keeping the maximum temperature in the oxidation front below 850 °C, which limits the CaCO₃ calcination when working under pressure. Alarcón and Fernández (2015) developed a similar PHM to predict the performance of the CO₂ sorbent regeneration step. In this case, axial mass and heat dispersion were assumed in the model. The effective bed conductivity λeff was determined using the equation obtained by Vortmeyer and Berninger (2018). The convective heat transfer were described by the correlations reported by (Gunn, 1978) and Gunn and Misbah (1993). Axial mass dispersion was described using the equation proposed by Edwards and Richardson (1968). An analogous model was recently used by Fernández and Abanades (2017c) to simulate the continuous operation of a complete cycle of the Ca-Cu looping process, considering that every reaction step started under the conditions of temperature and solids conversion left in the previous step.

To describe the Ca-Cu process, Martini et al. (2016) developed a simplified reactor model assuming sharp fronts, which was based on the
previous investigation carried out by Noorman et al. (2007) for chemical looping combustion (CLC) in fixed beds. This model considered the development of reaction fronts and heat exchange fronts that moves ahead in the bed at velocities calculated assuming complete conversion at the reaction front and very fast heat exchange between gas and solids. Moreover, the Ca-Cu process was also simulated using a 1-D pseudo-homogeneous reactor model previously validated with experimental results for CLC (Hamers et al., 2014; Noorman et al., 2010) and chemical looping reforming (Spallina et al. (2017). This model considered both gas and solids components, accounted for axial mass and heat dispersion and ignored mass and heat transfer resistances between the gas and solid phases. Axial heat and mass transfer dispersion were estimated with the same equations used by Alarcón and Fernández (2015). The outcomes of both simple and advanced models were finally compared finding a good agreement between them concerning the temperature and concentration profiles.

In a more recent work, the same PHM model was used by Martini et al. (2017) to simulate the different stages of the Ca-Cu process, in which the final condition of each step was assumed to be the starting point to initiate the following reaction step.

4. Experimental validation at lab-scale of the Ca-Cu process

The feasibility of the reaction steps of the Ca-Cu looping process was experimentally confirmed in packed-bed reactors up to TRL4-5 during the recently concluded EU-FP7 Project ASCENT (“ASCENT project, 2019”). Three different lab-scale facilities were used to validate individually each reaction stage of the process. The effect of the most important operating variables (i.e., CH₄ spatial velocity needed for the SER stage, S/C ratio, Ca/Cu molar ratio, etc) was assessed through specific experimentation for each individual stage accompanied by model validations. Once the operating conditions were defined, the feasibility of the full Ca-Cu process was demonstrated through consecutive SER-oxidation-calcination/reduction cycles in two different lab-scale facilities using both commercial and synthetic materials specifically prepared during the ASCENT project.

4.1. Lab-scale packed bed facilities description

Three lab-scale packed bed facilities of different characteristics (located at ICB-CSIC, INCAR-CSIC and TU/e) have been used for the validation of the Ca-Cu process. The fixed bed located at ICB-CSIC (Spain) is made of stainless steel with an internal diameter (ID) of 0.018 m. It is externally heated by a 5-m-long electric wire of 1.25 kW. Solids bed height is around 0.2 m and it is located in the mid part of the reactor, as shown in Fig. 2. An external insulation of quartz wool surrounds the reactor and the electric wire to minimise the heat losses to the ambient. The axial temperature profile along the reactor length is measured through 15 thermocouples placed throughout the reactor. Bed temperature is controlled by a thermocouple located at the bottom of the fixed bed. The feed gas is introduced through the upper part after being preheated up to 400 °C in an electric oven, which also serves as evaporator when steam is needed. Water contained in a pressurised vessel is mixed with other inlet gases before being fed into the evaporator, as indicated in Fig. 2. Inlet gas flow rate and composition are regulated through the corresponding mass flow controllers. A condenser is placed downstream the reactor to separate the steam from the product gas. The operating pressure can be raised up to 10 bar by means of an end-valve. The concentration of permanent gases (e.g. H₂, CH₄, CO and CO₂) is measured online using a SICK GMS810 analyser and a flow rate of N₂ is used as internal standard for calculating the dry gas flow rate produced. In this facility, the feasibility of every reaction stage of the process, as well as their performance under cyclic tests, was demonstrated. Three functional materials were used for the experiments (with particle diameter between 0.6–2 mm). A total mass of around 90 g was loaded in the reactor. Commercial Cu- and Ni-based catalysts (72 wt.% CuO/Al₂O₃ and 16–20 wt.% Ni/CaAl₂O₄, respectively) were used together with a synthetic CaO-based sorbent synthesized by mechanical mixing using calcined limestone as CaO precursor and calcium aluminate cement as support. Specific information about the preparation route followed for this material as well as its textural properties and CO₂ carrying capacity can be found elsewhere (Grasa et al., 2017). CO₂ carrying capacity for this synthetic CaO-based sorbent resulted in 0.2 gCO₂/g calcined sorbent in the long term.

The core of the experimental set-up built at INCAR-CSIC (Spain) consists of an Inconel tube (1 m long, ID of 0.038 m), whose scheme is presented in Fig. 3. The axial temperature profile is registered in 15 points by a multipoint K-type thermocouple introduced from the upper part of the reactor. The tubular reactor is surrounded by an insulating layer (0.15 m wide) of quartz wool that highly reduces the heat loss. A ceramic furnace of 14 kW surrounds the tubular reactor and the thermal insulation in order to preheat fixed bed and compensate the heat loss during the experiments. Moreover, two heating-tapes of 800 W preheat the inlet gas, as depicted in Fig. 3. The flow rate and inlet gas composition are regulated by Bronkhorst mass-flow controllers. A bed with silica gel situated downstream of the reactor exit is used to eliminate the steam contained in the product gas. Finally, a SICK GMS810 analyser equipped with infrared (for CO, CH₄ and CO₂), paramagnetic (for O₂) and thermal conductivity (for H₂) detectors measures the composition of the product gas. The experiments were carried out at

![Fig. 2. Schematic (left) and picture (right) of the lab-scale fixed bed reactor rig at ICB-CSIC.](Image)
atmospheric pressure. In this facility, the feasibility of the oxidation and the CaCO3 calcination/CuO reduction stages was assessed, using commercial Cu-based material (i.e., 65 wt.% CuO over SiO2) and CO2 sorbent (i.e., 98 wt.% of CaO) as functional materials for the experiments. A homogeneous solid mixture of about 1000 g was loaded in this reactor, varying the proportion between the Cu-based material and the CO2 sorbent to analyse the effect of the solid composition on the performance. Both solids were crushed and sieved until an average particle diameter of around 3 mm was achieved.

Finally, the packed-bed setup located at the Eindhoven University of Technology (TU/e, The Netherlands) was used for demonstrating the feasibility of the overall process at TRL5. A schematic overview of this experimental device is illustrated in Fig. 4. The tubular packed bed reactor (1.6 m long, outer and inner diameters 0.4 and 0.063 m, respectively) was designed and built by Array Industries BV to operate at temperatures of up to 1200 °C and pressures of up to 10 bar without external heat supply. The solids are loaded in an Inconel tube with a wall thickness of 6 mm, which is surrounded by insulation material to reduce the heat losses. An outer carbon steel reactor wall allows the operation at high pressures. The reactor wall is heated with tracers at 300 °C to minimize the heat losses. A scheme of the reactor cross-section is represented in Fig. 5. As appreciated in this scheme, there is a tube (0.7 m long, and outer diameter of 0.014 m) inside the reactor with 20 K-type thermocouples to measure the axial temperature inside the bed. The thermocouples are protected by an Inconel layer of 2 mm.

Functional solids are placed in the zone where the axial temperature is monitored (up to 80 cm), whereas in the rest of the reactor an inert material (clay granules) has been used. Feed gas flow rate and
composition are regulated by the corresponding mass flow controllers. The feed gas is heated up to the desired feed temperature by two electric ovens of 2.2 kW installed in series (see Fig. 4). To produce steam, demineralized water is pressurized by a HPLC pump and mixed with the other gases in the oven. High-temperature tracers surrounding the pipe between the oven and the reactor maintain the temperature before the gas stream is fed into the reactor.

The product gas is cooled through an air cooler, where steam is removed from the gas phase. The operating pressure in the reactor is controlled by a digital back pressure regulator. Finally, the dried gas is sent to an infrared SICK analyser and an O₂ paramagnetic analyser (Siemens Ultramat 23) connected in parallel. The residence time of the gas circulating along the lines, ovens and coolers is about 1 min, which is subtracted from the experimental data. All the setup is automated and can be run 24 h per day for more than 500 cycles. In this setup, complete Ca-Cu looping cycles have been performed under different operation conditions. The three functional materials required for the process were therefore introduced in the reactor. The bed was loaded with a combination of commercial Ni-based catalyst (HiFUEL) supplied by Johnson Matthey, a CaO-based solid from Carmeuse (99% of CaO) and the same commercial Cu-based material used at the ICB-CSIC rig (i.e., 72%wt. CuO on Al₂O₃). Solid bed composition was calculated to have 4 wt.% of Ni inside the bed and a Cu/CaO molar ratio of 2.1. The particle size of all the solids was around 0.003 m.

Table 1 summarises the operating conditions used in the described facilities for the validation of each stage of the Ca-Cu process, which is described in the following paragraphs.

4.2. Validation of sorption enhanced reforming (SER) stage

The feasibility of the SER stage was first demonstrated at the ICB-CSIC facility using commercial Ni-based catalyst and synthetic CaO/\text{Ca}_{12}\text{Al}_{17}\text{O}_{33} sorbent (Grasa et al., 2017). The operation was carried out at 650 °C, at pressures between 3 and 9 bar, CH₄ spatial velocities between 0.75 and 2.5 kg CH₄ h⁻¹ kg cat⁻¹ (i.e., up to 0.045 m/s), S/C molar ratios up to 4 and sorbent/catalyst ratios between 4 and 15. Under these experimental conditions, a gas stream with H₂ concentrations between 90 and 94 vol.% (on a dry basis), less than 6 vol.% of CH₄ and the same CH₄ space velocity of 2.5 kg CH₄ h⁻¹ kg cat⁻¹ and varying the steam flow rate for keeping a S/C ratio between 3 and 5. Operating pressure was modified between 2 and 7 bar for these tests. The results obtained in this facility corroborated those obtained at smaller scale. SER equilibrium was reached during the operation of this hydrogen production stage, and H₂ contents of 97.5vol.% (in dry basis) were reached when operating with S/C = 5 at 2 bar. When the operating pressure increased up to 7 bar, the H₂ content in the product gas decreased to 93.5vol.% due to the negative impact of this operating variable on the SER equilibrium (Fernández et al., 2012a). Gas composition stabilised at 93.6vol.% H₂, 5.9vol.% CH₄, 0.17vol.% CO and 0.33vol.% CO₂ (in dry basis) when operating with S/C = 3 at 7 bar, which practically matches the composition obtained at ICB-CSIC for similar conditions (i.e. S/C = 3 and 10 bar) as depicted in Fig. 6. Differences observed in the duration of the pre-breakthrough are due (mainly) to the different CO₂ carrying capacities of the CaO-based synthetic sorbents used in each facility.

4.3. Validation of Cu oxidation stage

The viability of this stage has been experimentally validated at the ICB-CSIC lab-scale rig (Díez-Martin et al., 2018b) and at TRL4 in the INCAR-CSIC facility (Alarcón et al., 2017). Additional tests at TRL5 have been performed at the TU/e facility, which have not been yet published in the literature. As widely reported, the oxidation of Cu to CuO is a very exothermic reaction and, therefore, restricted conditions of initial temperatures and O₂ concentration in the feed (below 5 vol.% CO) are required to avoid overheating during the operation at temperatures beyond 830–850 °C (Fernández et al., 2014).

During the oxidation tests performed at the INCAR-CSIC rig, a flow rate of 30 Nl/min containing 3 vol.% of O₂ in N₂ was fed into the packed bed, which initially contained around 20–25 wt.% of Cu (Alarcón et al., 2017). Oxidation experiments were carried out at atmospheric pressure. Both the inlet gas and the solids bed were pre-heated up to 400 °C. Even at this low initial temperature and low O₂ content in the gas, the Cu oxidation was observed to be significantly faster taking place in narrow reaction fronts throughout the reactor. The low O₂ content made the oxidation front advance at lower velocity than the heat exchange front. At these circumstances, the O₂ reached the reaction zone at relatively low temperature (i.e., at about 400 °C), while the heat generated during the oxidation was absorbed downstream by the solids located between the oxidation and heat exchange fronts. The maximum temperature measured during the operation was around 800 °C, which should prevent the agglomeration or sintering of the Cu-based material and diminish the loss of CO₂ by partial decomposition of the CaO-based sorbent. Full O₂ conversion was achieved despite the very low O₂ concentration in the feed and the high gas velocity (around 1.6 m/s at 800 °C) and virtually pure N₂ was obtain as product gas.

Díez-Martin et al. (2018b) carried out the Cu oxidation stage by feeding 114 Nl/h of gas containing 5vol.% O₂ (in N₂). The operation was accomplished at 10 bar, preheating the solid bed and the feed gas to 725 °C. The combination of high pressure operation and reduced gas flow rate fed into the packed bed at the ICB-CSIC facility resulted in a limited gas velocity during the oxidation tests (i.e. 0.04 m/s). This reduced gas velocity is far from the value of around 1.6 m/s achieved in the INCAR-CSIC facility, which makes the oxidation results obtained in both facilities be non-comparable. Due to the relatively high heat loss inherent to the ICB-CSIC experimental setup, significantly lower increases in temperature in the solids bed were observed (of only around
70 °C) with absence of a heat plateau during the advance of both oxidation and heat exchange fronts.

In the experimental campaign carried out in the packed-bed reactor at TU/e, a total flowrate of 100 NL/min was used for the Cu oxidation tests varying the O2 concentration in the feed gas between 3, 5 and 10 vol.% O2 in N2. Total pressure was also modified between 2 and 7 bar using a temperature of around 650 °C for the inlet feed gas. At both pressures, when increasing the O2 concentration in the feed gas, the maximum temperature reached within the solid bed increased due to the increase in the reaction front velocity, which approaches the heat front velocity. Operating with an O2 concentration in the feed of 10 vol. %, a maximum value of 840 °C was reached at an operating pressure of 2 bar and a maximum value of 810 °C at 7 bar. With concentrations of 5 vol.% of O2, maximum temperatures of around 800 °C and 780 °C at 2 bar and 7 bar, respectively, were obtained. The decrease in the maximum temperature reached within the solid bed as the operating pressure is raised is due to the reduction of the total gas velocity, and so of the reaction and heat front velocities. Experiments performed at the TU/e reactor at 2 bar allowed working with a gas velocity of around 1 m/s (calculated at an average temperature of 800 °C), which is in the order of the gas velocity reached at the INCAR-CSIC reactor. Fig. 7 shows the gas concentration profile obtained at TU/e reactor outlet at 2 bar and with 3 vol.% O2 in the feed gas. As noticed, full O2 conversion was reached at this stage despite of the very low O2 content in the feed gas since only CO2 and N2 were measured at the outlet. These results confirmed the behaviour observed at the INCAR-CSIC facility for similar conditions of gas velocity and O2 content in the feed gas, despite of the lower maximum temperature reached within the solid bed in this case (i.e., around 750 °C). Based on the calculation of the O2 consumed during this stage, it could be concluded that full oxidation of the Cu present in the solid bed into CuO occurred during the oxidation tests.

4.4. Validation of CaCO3 calcination/CuO reduction stage

In the facility located at ICB-CSIC, the reduction/calcination stage was studied using a fuel gas with 58 vol.% H2, 29 vol.% CH4 and 13 vol. % CO (without accounting for N2) (Díez-Martín et al., 2018b). This fuel gas composition corresponds to that calculated by Fernández and Abanades (2017c) for a gas stream resulting from the mixing of a gas produced in a separate SMR stage and the off-gas obtained from a hydrogen purification unit (PSA). A gas flow of 0.9 NL/min was fed to the reactor, which was previously heated up to a sufficiently high temperature 825 °C to compensate the heat losses to the ambient and for carrying out the tests without operating the electric resistance. Under these conditions, the reaction and heat exchange fronts evolved together through the reactor, resulting in a maximum temperature of 852 °C, which was sufficiently high to fulfil complete decomposition of the CaCO3 present in the solid bed. During the breakthrough period, the evolution of both H2 and CO curves at the reactor exit were similar, showing a maximum value when the CuO-based particles approach total conversion, followed by a progressive reduction of the concentration until relatively low values for H2 and CO were achieved. In contrast, the concentration of CH4 during the breakthrough gradually increased but at a slower velocity than CO and H2. This phenomenon may occur due to the partial decomposition of CH4 into H2 and carbon and the reverse WGS reaction catalysed by the Ni- and Cu-based materials, respectively (Borghi et al., 2010; Snoeck et al., 2002; Zhou et al., 2013).

Reduction/calcination experiments were also performed at INCAR-CSIC, in which different gas mixtures were used as fuel gas, such as H2 diluted in N2, H2/CO mixtures and pure CH4. Before each reduction/calcination test, a stream of pure CO2 at 600 °C was passed through the solids bed to partially carbonate the CaO-based CO2 sorbent, thus ensuring the appropriate ratio of CuO and CaCO3 depending on the fuel gas composition. The CuO/CO2 molar ratio present in the bed was between 1.6 and 3.2, which should be sufficiently high to carry out the reduction/calcination avoiding additional energy supply (Alarcón and Fernández, 2015) (i.e., the oven was used exclusively for compensating the reactor heat losses). In a first work, a flowrate of 15 NL/min (50 vol. % of H2 in N2) at 400 °C was used as reducing gas (Fernández et al., 2016). It was observed a rapid increase in the temperature profile as the CuO reduction progressed due to the great reactivity of the CuO-based
material with H₂ even at moderate temperatures. While the maximum temperatures achieved in the bed were below 800 °C, CaCO₃ calcination was impeded and very low CO₂ concentrations were measured at the reactor exit (i.e., below 1 vol.%). Only when temperatures of around 900 °C were reached, an increasing CO₂ concentration at the reactor outlet of up to 40 vol.% (dry basis) was observed, as a result of a fast CaCO₃ calcination. During the pre-breakthrough period, the H₂ fed to the reactor achieved almost complete conversion (only CO₂ was detected in the dry product gas) and during the breakthrough (3–4 min) the H₂ concentration rapidly increased until it reached the inlet value due to the high reactivity of CuO with H₂.

In other experiments, mixtures of up to 20 vol.% of CO in H₂ were used as feed gas for the reduction/calcination process (Alarcón et al., 2017), which also served to demonstrate the good reactivity of CuO with these gases. Fig. 8 shows the outlet gas concentration and temperature profile obtained for the test with 20 vol.% CO and 30 vol.% H₂ in the feed gas for the INCAR-CSIC facility. As shown in this figure, temperature profiles of about 880 °C were achieved that allowed the complete conversion of the fuel gas. An increasing amount of CO was observed at reactor outlet during the breakthrough period, indicating the presence of the reverse WGS reaction that was enhanced by the high temperature and the high concentration of CO₂ in the reactor. Finally, the reduction/calcination stage using pure CH₄ as fuel gas has been recently tested (Fernández et al., 2018; Fernández and Abanades, 2019). Poor reactivity of the CuO with CH₄ was observed by feeding the H₂ concentration rapidly increased until it reached the inlet value (i.e., below 1 vol.%). Only when temperatures of around 900 °C were reached, an increasing CO₂ concentration at the reactor outlet of up to 40 vol.% (dry basis) was observed, as a result of a fast CaCO₃ calcination. During the pre-breakthrough period, the H₂ fed to the reactor achieved almost complete conversion (only CO₂ was detected in the dry product gas) and during the breakthrough (3–4 min) the H₂ concentration rapidly increased until it reached the inlet value due to the high reactivity of CuO with H₂.

The feasibility of consecutive Ca-Cu looping cycles was first experimentally demonstrated in the packed-bed reactor located at ICB-CSIC under relevant conditions for the process at large scale (Díez-Martín et al., 2018b). During the successive SER stages (carried out with S/C molar ratio of 3, at 650 °C and 10 bar), the CO₂ sorbent maintained a relatively constant CO₂ carrying capacity of 0.35 gCO₂/g calcined sorbent. Due to the heat losses, the maximum temperature achieved in the carbonation front (about 720 °C) was slightly lower than the theoretical value predicted by the PHM reactor models in the literature (Fernández and Abanades, 2017c; Martín et al., 2017). Almost pure H₂ was produced during the pre-breakthrough period and once the CO₂ sorbent was fully carbonated (post-breakthrough), it was observed that CO and H₂ concentrations stabilized above the corresponding SMR equilibrium values whereas CH₄ concentration stabilized below SMR equilibrium. These results are due to the presence of reduced Cu-based solids, which favour the thermal cracking of a fraction of the CH₄ fed into the reactor into C and H₂ and then the gasification of the C formed takes place to form CO (Díez-Martín, et al., 2018b).

During the subsequent reaction stage, the operating pressure was maintained at 10 bar and diluted air (5 vol.% O₂) preheated at 725 °C allowed the fast and complete oxidation of both Cu- and Ni-based solids. A maximum temperature of around 770 °C was registered, which minimized the loss of CO₂ by partial calcination of the CaCO₃ formed during the SER step. Nevertheless, higher concentration of CO₂ than expected was measured in the product gas (i.e., up to 0.85 vol.% CO₂ instead of 0.013 vol.% given by the CaO/CaCO₃ equilibrium at 770 °C and 10 bar), due to the oxidation of carbon deposited in the bed during the SER operation. The CuO-based material presented high reactivity during the reduction/calcination stages carried out with a mixture of H₂, CH₄ and CO₂ simulating the composition of a PSA off-gas. A CuO/ CaCO₃ molar ratio of 2 allowed about 95% of the CaCO₃ present in the bed to be calcined, while obtaining almost pure CO₂ (and steam) as product gas. The results obtained during three consecutive cycles were very reproducible demonstrating the stability of the materials.

More recently, the continuous operation of the Ca-Cu process was proven at the TU/e packed-bed reactor over 285 SER-oxidation-reduction/calcination cycles. The results of few selected cycles can be seen in Fig. 9 and Table 2. For these cycles, the SER stage was studied at 650 °C and 2 bar with the S/C ratio equal to 3, whereas for the Cu oxidation stage the same operating pressure of the SER stage was used for a feed gas containing 5 vol.% O₂. For the reduction/calcination stage, a H₂/N₂ fuel gas mixture was used at 2 bar and 650 °C with a H₂ content of 40 vol.%. As appreciated from the results shown in Fig. 9 (a), there is a loss in the CO₂ carrying capacity of the Ca-based material from 14 gCO₂/ g calcined sorbent in cycle 100 to 10 gCO₂/g calcined sorbent in cycle 185 that makes the pre-breakthrough period to be shortened by 3 min. However, despite of this CO₂ carrying capacity loss, the H₂ content of the gas produced in this stage remains practically unaltered at around 97.5 vol.% (dry basis) (Table 2). Regarding the temperature profiles during the SER and reduction stages (Fig. 9), lower maximum temperatures than those predicted by the PHM models in the literature were measured, due to the heat losses to the ambient. Despite all these
The performance of a large scale hydrogen production plant based on a Ca-Cu process was evaluated for the first time by Martínez et al. (2014) who proposed the reactors system depicted in Fig. 10. These authors considered as a starting point for the Ca-Cu looping scheme that described by Fernández et al. (2012c), where the three main reaction stages indicated in Fig. 1 were completed with two additional ones: (1) an intermediate heating stage right after completing the Cu oxidation and before the calcination/reduction stage, using as heating source the \( \text{O}_2 \)-depleted gas recirculated from Cu oxidation outlet, and (2) a cooling step by means of the endothermic reforming of additional \( \text{CH}_4 \) or natural gas right after the calcination/reduction process. All the reaction steps in the Ca-Cu looping process were calculated using the simplified approach described by Fernández et al. (2012c). As shown in Fig. 10, intermediate stages of rinsing, pressurization and depressurization were also included in the analysis by Martínez et al. (2014). Moreover, the desulphurisation of the natural gas considered as a feedstock to the process, as well as the pre-reforming of the desulphurised natural gas to convert the higher hydrocarbons were also included in the process layout and the heat and mass balance calculation.

A total number of 15 reactors was calculated by Martínez et al. (2014) for running a plant with a typical \( \text{H}_2 \) output of 30,000 \( \text{Nm}^3/\text{h} \), corresponding to three reactors operating in parallel in the SER stage, three in the Cu oxidation stage, three in the heating stage before reduction/calcination, and keeping one reactor for each of the remaining stages (i.e. rinse, depressurisation, pressurisation, calcination/reduction and cooling/reforming stages). Hydrogen production efficiencies as high as 76% were calculated in this work, including the penalties linked to the electricity import as well as the benefits for the steam exported. Compared with a reference \( \text{H}_2 \) production plant based on the well-established fixed tubular reformer (FTR) technology with MDEA for \( \text{CO}_2 \) absorption, the efficiency reached by the Ca-Cu looping based plant is around 4%-points higher than that calculated for the benchmark process. Moreover, global \( \text{CO}_2 \) capture efficiencies estimated were about 94%, which are well above the capture efficiency of 85% estimated for the benchmark (Martínez et al., 2014).

In a later work, Fernández and Abanades (2017c) evaluated the performance of the Ca-Cu looping reactors shown in Fig. 10 under conditions of reduced pressure for the SER stage with the objective of preventing \( \text{CaO} \) hydration from occurring in this stage. This work included a more elaborated reactor model for an accurate calculation of the temperature and concentration profiles within each individual stage of the Ca-Cu process with respect to the previous work by Martínez et al. (2014). An S/C ratio of 3, an inlet temperature of 700 °C and an operating pressure of 10 bar for the SER stage were proposed in this work for avoiding \( \text{Ca(OH)}_2 \) formation while obtaining a gas product with a \( \text{H}_2 \) content above 90 vol.% at this stage outlet. Operating pressures of \( \text{Cu} \) oxidation stage were proposed to be raised to 20 bar for limiting the \( \text{CO}_2 \) emissions during this stage. Considering an aspect ratio of 2 for the reactor (i.e., length/diameter = 2), reactor dimensions were estimated considering a maximum pressure drop of 10% of inlet pressure and the same stage duration of 15 min for all the Ca-Cu stages (i.e., SER, oxidation, heating, reduction/calcination, cooling/reforming). In this way, one reactor of 3 x 6 m for each of the Ca-Cu stages would be needed (neglecting the duration of the rinse, pressurization and depressurization stages needed at a larger scale). On the whole, hydrogen production efficiency remained invariable with respect to the value of 76% previously reported by Martínez et al. (2014).

Recently, a techno-economic analysis of a \( \text{H}_2 \) production plant using...
the Ca-Cu looping process has been published by Riva et al. (2018). The reactor layout proposed was simplified with respect to those previously considered and the cooling/reforming stage placed right after the reduction/calcination was avoided, resulting in the scheme shown in Fig. 11. In this process configuration, the off-gas from the purification unit is used as fuel in the calcination/reduction stage and the S/C ratio needed in the SER stage is therefore tuned for avoiding the need of additional fuel for this reduction step. A sharp front model, validated on the dynamic model published by Martini et al. (2016), was used for calculating the fixed bed reactors system. Each reactor was proposed to be divided into 4 sub-reactors with reduced length and diameter while keeping a constant length to diameter ratio of about 2, to reduce both the pressure drop across the fixed bed reactors and the total volume of the reactors, and therefore the amount of functional materials needed.

A sensitivity analysis was performed on the operating pressure of SER and oxidation stages in this work, demonstrating that reducing the operating pressure from 25 bar to 11 bar makes the global hydrogen efficiency to increase up to 79% when accounting for electricity and steam exchange with the surroundings. On the other hand, lowering the operating pressure leads to larger reactors volume and ultimately higher costs of H₂ production and of CO₂ avoided. Considering a H₂ output of 30,000 Nm³/h, the calculated cost for hydrogen production ranges between 0.178 and 0.181 €/Nm³ (operating SER stage at 25 and 11 bar, respectively), which is significantly lower than the calculated cost of 0.194 €/Nm³ for the benchmark hydrogen plant with CO₂ capture using a MDEA process. The estimated cost of CO₂ avoided is between 30 and 37 €/t, vs. 64 €/t of the benchmark.

5.2. Steel production with reduced CO₂ emissions through the Ca-Cu process

The implementation of CO₂ capture technologies on the gas generated in the blast furnace of a steel mill plant has been considered as one of the most promising routes for decarbonising the most common steelmaking route (i.e., blast furnace (BF) + basic oxygen furnace), since this gas contains 60–80% of the total carbon coming into the steel mill (Romano et al., 2013). Removing these carbon compounds from the N₂-rich blast furnace gas (BFG) allows producing a H₂-enriched gas that can be used as ‘low-carbon’ fuel in the power plant located within the steel mill premises and in the main heating processes of the steel mill (i.e., hot stoves and coke plant). For this specific application, the need of operating the BFG decarbonisation step at high pressure is not mandatory since the BFG is generated at moderate pressure in the BF and all the applications of this gas as fuel within the steelworks are at nearly atmospheric pressure. Moreover, the production of BFG in a typical BF-based steel mill producing 4 million tons of hot rolled coil (HRC) per year is around 1600 Nm³/tHRC (i.e., around 200 Nm³/s) (Santos, 2013), which is between 15 and 17 times the flow rate of gas processed in the SER stage of the Ca-Cu based hydrogen production plant of 30,000 Nm³/h of H₂ output analysed in the literature (Fernández and Abanades, 2017c; Martínez et al., 2014; Riva et al., 2018). The operation of a packed-bed reactor system for processing such a big flow rate of BFG in a Ca-Cu looping process would turn the operation at high pressure mandatory to reduce the size of the reactors and so the capital and operational costs of the system. However, the compression of the large flow rate of BFG in this case would be very energy-consuming, penalising the performance of the process.

Therefore, an arrangement of atmospheric fluidised bed reactors has
been proposed for operating the Ca-Cu process when focused on decarbonising the BFG in a steel mill (Fernández et al., 2017). A simplified scheme of this Ca-Cu process arrangement is shown in Fig. 12. In this reactor configuration, the production of the H2-enriched gas stage should be carried out in a circulating fluidised bed (CFB) reactor since bringing the huge BFG flow rate into contact with the CaO-rich solids can only be made in this type of reactor with very high gas throughput per unit of cross-sectional area. WGS and CaO carbonation reactions (Eqs. (2–3)) occur in the hydrogen production step of the Ca-Cu process (i.e., referred to as Sorption Enhanced Water Gas Shift stage, SEWGS in Fig. 12) since BFG does not contain significant amounts of CH4, being mainly composed of CO and CO2 diluted in N2. In this way, only two functional materials would be needed for running this Ca-Cu process configuration, namely the CaO-based CO2 sorbent and the Cu-based oxygen carrier. This reactor configuration allows the introduction of a solid separation step by segregation between the CaO and the Cu-based particles in the calcination/reduction reactor, which will provide the CaO needed for the ironmaking process and so will make the conventional lime plant in the steel mill unnecessary, while producing lime with no CO2 emissions. Moreover, the segregation of the particles will improve the performance of the Ca-Cu system since it reduces the Cu-based particles amount flowing from the reduction/calcination through the SEWGS reactor, where they act as a thermal ballast. A N2-free gas is needed as fuel in the reduction/calcination step in order to avoid diluting the CO2 generated with N2. The coke oven gas (COG), which is rich in H2 and CH4, is used therefore as feed gas in this stage. Moreover, as indicated in Fig. 12, there is a second hot solid stream fed to the calcination/reduction reactor in this scheme, which comes from an oxidation stage operating at higher temperature that supplies part of the energy needed for the CaCO3 calcination in the calcination/reduction reactor.

This Ca-Cu looping scheme was described for the first time by Fernández et al. (2017) that solved the balances to define the operating conditions window for each stage. The SEWGS reactor is proposed to be operated at 600 °C with a S/C ratio of 1. Solids exiting the SEWGS reactor need to be preheated as much as possible before being fed to the calcination/reduction reactor in order to reduce the heat demand in this reactor and so the need of Cu-based material. Operating temperatures for the calcination/reduction and Cu oxidation reactors were set at 870 °C and 900 °C, respectively, in order to limit Cu-based material degradation in the oxidation reactor and to have sufficient temperature difference between reactors to supply energy through circulating solids cooling. Based on the preliminary results obtained in this work, around 30% of the BFG produced in the steel mill could be decarbonised through this Ca-Cu reactor scheme using exclusively the available COG in the calcination/reduction reactor.

A detailed analysis of this process integrated into a steel mill has been performed by Martínez et al. (2018), who considered also the balances of the steel mill processes for evaluating the impact of integrating the Ca-Cu process on the reduction of the CO2 emissions in the steel mill. The integration of the heat available throughout the Ca-Cu process into a steam cycle for producing electricity has been also solved in this analysis, which elucidated the large reduction in electricity consumption that may be achieved compared with the reference steel mill process with a post-combustion CO2 capture process based on amine chemical absorption. The possibility of recovering a large fraction of the energy introduced with the fuel in the calcination/reduction reactor as high temperature heat in the SEWGS unit allows producing a large amount of steam for the steam cycle, which makes the electricity import to be reduced. Moreover, the possibility of increasing the steel production capacity of the plant up to 10.5% by means of a direct reduced iron (DRI) route using the excess H2-rich gas produced in the Ca-Cu process has been proposed. Considering the results from Martínez et al. (2018), the Ca-Cu process scheme shown in Fig. 12 has been demonstrated to be theoretically viable for fulfilling the almost complete decarbonisation of a steel mill when using additional natural gas as fuel in the calcination/reduction reactor. Around 92% of CO2 capture ratio could be reached in the whole steelworks, resulting in 1.4 kgCO2/tH2CO emitted in this case.

5.3. Ammonia production with inherent low CO2 emissions through the Ca-Cu process

The well-established ammonia production process is based on three main steps, namely (i) syngas production by steam reforming of natural gas by means of a two-step reforming process, (ii) conditioning of syngas for removing CO and CO2 through a two-step WGS reactor, a CO2 removal unit and a methanation step, and (iii) the ammonia synthesis loop itself. Most of the modifications and advancements made over the years to this well-established process concern the reforming step, looking for a reduction of the specific primary energy consumption per unit of ammonia produced and a plant capacity increase. However, due to the large energy demand needed for running the reforming reactions the specific primary energy consumption of the commercial process is still higher than the minimum (Appl, 2002).

Based on the improved performance of the Ca-Cu process as part of a standalone hydrogen production plant and the inherent co-production of pure streams of H2 and N2 as part of its products, the Ca-Cu process is a promising technology to be integrated in an ammonia production process. This application has been recently studied by Martínez et al. (2017), who proposed the schematic shown in Fig. 13. The synthesis gas production and conditioning steps used in a commercial ammonia production process are replaced by the fixed-bed Ca-Cu process shown in this figure that provides the H2 and N2 streams in the right proportion (i.e., 3:1) to be introduced into the NH3 synthesis loop. In addition to a PSA unit to purify the H2-rich gas from the SER stage, a second PSA unit is included for removing the small quantities of CO2 present in the N2-rich gas from the Cu oxidation stage.

Balances of a complete ammonia production plant based on the Ca-Cu looping process were solved by Martínez et al. (2017), considering the simplified sharp fronts approach described by Fernández et al. (2012c) for calculating the Ca-Cu reactors. Operating pressure of SER, oxidation and heating stages was considered equal to 23.5 bar, whereas the S/C ratio in the SER stage was tuned for providing the heat demand in the calcination/reduction stage by exclusively the off-gas from the hydrogen PSA unit. The conventional ammonia production process has been also calculated in the mentioned work for the sake of performance comparison. Based on the calculations performed, the ammonia production process integrated with the Ca-Cu process in Fig. 13 results in a primary energy consumption of 24 GJ/tNH3 which is 14% lower than
the energy consumption of the benchmark ammonia plant. This noticeable improvement is linked to the reduction of the natural gas input needed in the Ca-Cu based plant and the lower operating temperatures of the syngas production units (i.e. 856 °C at SER stage outlet and 1010 °C for the ATR outlet in the benchmark). Considering that the Ca-Cu process needs electricity to be imported from the grid, the global specific primary energy consumption is evaluated assuming that power is generated in a state of the art natural gas combined cycle, which results in energy consumption of 26.5 GJ/tNH₃ for the Ca-Cu based ammonia plant, vs. 27.6 GJ/tNH₃ for the benchmark ammonia production process.

6. Process design of Ca-Cu looping based power generation plants

Decarbonising the power production sector can be fulfilled through two different routes: (i) directly to the flue gas released to the atmosphere of the existing plant, which contains the carbon contained in the fossil fuel used as CO₂, or (ii) applying it to the fossil fuel before being burnt to generate a decarbonised fuel that is sent to the boiler or combustion chamber in the power production station. Inherent characteristics of each application lead to consider different aspects regarding the type of fuel used or the operating conditions needed in the CO₂ capture process. The application of the Ca-Cu looping process both as a post-combustion and pre-combustion CO₂ capture system has been also studied for power production plants.

When applied as a post-combustion CO₂ capture solution typically in coal-fired power plants, a three interconnected fluidised bed configuration operating at atmospheric pressure like the one depicted in Fig. 14 has been considered in the literature (Duhoux et al., 2016; Ozcan et al., 2015). Flue gas from the existing power plant is introduced into the carbonator reactor together with a solid stream containing CaO and CuO-based materials that comes from the oxidation step. In this reactor, carbonation of the CaO occurs at 650 °C whereas the CuO remains unaltered under these conditions. Solids containing CaCO₃ and CuO are then sent to the calcination/reduction stage where natural gas is used as fuel. Once the CaCO₃ has been regenerated into CaO, the solids containing CaO and Cu are sent to the oxidation reactor. The operating temperatures chosen for the calcination/reduction and oxidation reactors are 885–900 °C and 950 °C, respectively, to be able to circulate some solids from the high temperature oxidation reactor to the calcination/reduction one (indicated in dashed lines in Fig. 14) to fulfil part of the energy demand in this last reactor and so reduce Cu-based material and fuel needs.

When solving the balances for this application, the net electric efficiency of the whole process (i.e., existing power plant + Ca-Cu process + secondary steam cycle) ranges between 34.8–36.6 % depending on the amount of fresh sorbent make-up provided to the process (consisting in CaCO₃ and CuO-based particles) (Ozcan et al., 2015). These values show that efficiency improvements can be achieved with respect to conventional post-combustion Ca-Looping process, due to the absence of the ASU. However, the large amount of natural gas needed for CuO reduction (between 20 and 40% of the total input according to the balances solved by Ozcan et al. (2015)) involves a significant energy penalty, as such natural gas is ultimately converted into electricity with the efficiency typical of a steam cycle, which is intrinsically much less efficient (by roughly 15–20% points) than a combined cycle that is the reference power generation technology from natural gas. Therefore, energy penalty associated to CO₂ capture is shifted from electric consumption for oxygen production to inefficient conversion of high quality natural gas fuel. For the same configuration, it was estimated that separate loops between the carbonator-calcination/reduction reactors and the calcination/reduction-oxidation reactors were possible (i.e. by means of a segregation step within the calcination/reduction reactor as in the system shown in Fig. 12), solid circulation between reactors would be reduced by 10–20% while keeping the same electric efficiency (Duhoux et al., 2016). However, all these results are based on simplified process simulations and should be therefore further analysed through experimental and simulation works.

When used as a pre-combustion CO₂ capture process in a natural gas combined cycle (NGCC), the Ca-Cu process is operated in a fixed bed reactors system similar to that already described for hydrogen production plants, but the H₂-rich gas stream produced in the SER stage is used as fuel in the gas turbine of the combined cycle. The scheme of this Ca-Cu process application is shown in Fig. 15. H₂-rich gas from the SER stage is directly converted in the gas turbine with no further treatment and additional pre-reformed natural gas is used as fuel in the
The Ca-Cu looping process is a promising pre-combustion CO₂ capture technology which allows carrying out the energy-intensive sorbent regeneration with a moderate energy penalty. Although this novel technology can be performed in different reactor configurations, the feasibility of each reaction step has been experimentally demonstrated so far only in packed-bed reactors up to TRL 4-5. Moreover, significant progress has also been made in process modelling and simulation oriented to the generation of power and its integration in industrial processes, such as H₂, ammonia and steel production. However, further research is needed to facilitate the development of the Ca-Cu process at a large scale.

Regarding the functional materials, significant advances have been made so far, but future investigations need to focus on improving their long-term mechanical stability under shifting temperatures, pressures and redox atmospheres, as a necessary step for the scale-up of the technology. Moreover, chemical performance of the materials throughout extended number of cycles (i.e. thousands of cycles) and under industrial conditions (of pressure, temperature and gas composition) should be also studied.

As for the lab-scale validation of the Ca-Cu process, the different stages of the process should be tested under industrially relevant conditions (i.e., adiabatic reactors, particles in pellet form, SER stage at pressures above 20 bar, conditions that allow assessing the effect of the hydration issue on process performance, etc.). As with other emerging technologies, it remains important to evaluate the performance of the materials in the long term when exposed to harsh conditions after repeated cycles. It is also needed to better understand the response of the system when the chemical properties of the materials (kinetics, sorbent capacity, etc.) are partially lost, allowing for the process control design and the process model validation at larger scale.

In addition, some research gaps have been detected for the process design depending on the reactor type used. For the Ca-Cu packed-bed systems, reducing the volume of the reactors as much as possible allows reducing the pressure drops across the reactors and the amount of functional material, turning down in this way both operational and capital costs. However, the reduction of the reactors volume may be limited by fluid-dynamic and manufacturing constrains and the resulting short cycles may cause excessive stress for the valves, increasing the importance of the auxiliary purge, rinse, pressurization and depressurization stages, often neglected in process analysis reported so far. When focused on power production, process performance studies have always been designed to achieve the highest electric efficiency under full load operation, resulting in highly thermally integrated process configurations. However, the flexibility of the system and the effect of part-load operation on the performance of the Ca-Cu based power plant, whose importance is dramatically rising in the electric market, needs to be assessed and may make simpler and more flexible process configurations preferable over the highest efficiency process. For Ca-Cu fluidized bed systems, future challenges rely on the design and operation of reactor arrangements based on three interconnected fluidized beds, as well as on the deeper study on an efficient segregation step to separate the CaO- and Cu-based particles. Also, the technical feasibility of using alternative fuels (different from natural gas) as reducing agents in the calcination/reduction operation (for example, coal or biomass) might be evaluated in order to reduce operating cost, energy penalty and/or CO₂ emissions. Finally, economic analyses are needed to confirm the results recently published on power and hydrogen plants and to provide the first evaluation of the economic indicators for the Ca-Cu process integrated in ammonia plants and steel mills.

From the state of the art review carried out in this work, and from the limitations noted in previous paragraphs, it can be concluded that...
the Ca-Cu process has inherent limitations to drastically reduce cost and energy penalties in power plant applications, while it remains an important contender for future industrial systems requiring decarbonized hydrogen from carbon-based fuel gas streams.

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References


