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Ca-Cu Chemical Looping Process for Hydrogen and/or Power Production

Isabel Martínez, Jose R. Fernández and Gemma Grasa

Abstract

It has been widely reckoned the potential of developing novel CO₂ capture technologies aiming at low-energy penalties and reduced cost as a solution for fighting against climate change. The Ca-Cu chemical looping process emerged as a promising technology for producing hydrogen and/or power with inherently low CO₂ emissions. The core of this concept is the calcination of the CaCO₃ by coupling in the same solid bed the exothermic reduction of a CuO-based material, improving the efficiency of the CO₂ sorbent regeneration step. Significant progress has been made since its first description in 2009, fulfilling the validation of the key stage under relevant conditions for the process in 2016. This chapter compiles the main advances in the Ca-Cu process regarding material development, reactor and process design and lab-scale testing, as well as in process simulation at large scale.

Keywords: CO₂ capture, sorption-enhanced reforming, calcium looping, chemical looping

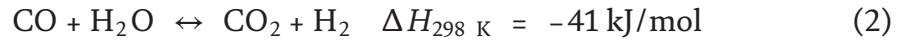
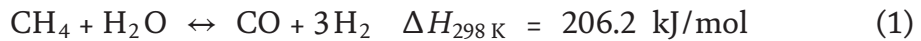
1. Introduction

It is globally accepted that there is an unequivocal relation between the increment of anthropogenic greenhouse gas (GHG) emissions to the atmosphere and the rise in the global temperatures [1]. CO₂ is considered the principal GHG due to the magnitude of its emissions in the global scenario (i.e. about 78% of total GHG emissions in the 2000–2010 period corresponded to CO₂), having reached a value of 36.2 Gton_{CO₂} in 2015 [2]. Fossil-fuel combustion is the responsible of about 90% of CO₂ emitted, being the heat and power sectors the major contributors to this share (i.e. about 35%). Among the industrial sectors with the largest CO₂ emissions, iron and steel manufacturing, cement production and other chemical industries (i.e. ammonia or lime production) are the most important. Drastic CO₂ emission reductions are needed to contribute in the stabilization of the global temperature rise to about 1.5°C above the pre-industrial levels, as recently agreed in the 22nd Conference of the Parties in 2016. In this context, CO₂ capture and storage (CCS) has raised as the only option for drastically reducing the CO₂ emissions in large stationary sources beyond the limits needed for fulfilling such ambitious target [1].

Hydrogen represents a proper alternative to fossil fuels due to its flexibility, fuel density and low carbon footprint. Currently, around 90% of the hydrogen produced worldwide (i.e. about 65 million tons per year) is used as raw material for ammonia

and methanol production [3]. However, fossil fuels represent the principal feedstock for hydrogen production worldwide, with around 96% of the global hydrogen produced from natural gas, fuel oil and coal. Hydrogen production with low carbon footprint has a great potential in fulfilling the stringent CO₂ emission cuts needed in the energy sector [4]. Therefore, the development of large-scale hydrogen production technologies including CO₂ capture that enable a reduced cost as well as an improved efficiency would greatly contribute to the climate change mitigation route [5].

In this context, the steam methane reforming (SMR) coupled with in situ CO₂ separation is gaining importance as a method for obtaining high-purity hydrogen in one single step [5]. This sorption-enhanced reforming (SER) proposes carrying out the reforming of methane in the presence of a CO₂ sorbent that reacts with the CO₂ as soon as it is formed, pushing the reaction equilibrium towards hydrogen production [6, 7]. Due to its good performance and favourable kinetics, CaO-based materials have been typically proposed as CO₂ sorbents in the SER process [7]. According to SER equilibrium (see Eqs. (1)–(3)), using CaO as a CO₂ sorbent allows reaching H₂ contents as high as 96 vol.% (dry basis) in a single step for temperatures about 650–700°C [6]. No water-gas shift (WGS) reactors are needed downstream the SER process since the CO content in the syngas produced is very low thanks to the presence of the CO₂ separation process. Moreover, since all the reactions occur in a single reactor, the energy released by the exothermic CaO carbonation reaction and the WGS reaction compensates the energy required for the reforming of CH₄, resulting in an almost neutral system that does not need from an external energy source as in conventional SMR.



One of the main issues of the SER process is the CaCO₃ regeneration step, which is a high endothermic reaction that needs to be performed continuously to allow for a cyclic operation. Several alternatives have been proposed in the literature for supplying the large amount of energy needed in the CaCO₃ regeneration step. Commonly, the direct combustion of a fuel in the same reactor in the presence of an O₂-rich atmosphere has been proposed [8, 9], which will allow producing a CO₂ stream that is not diluted with N₂ and so easy to be purified and compressed for its final storage. Other options have been proposed as an alternative to the high energy-consuming air separation unit (ASU) needed for supplying the pure O₂ required in this direct combustion option. For instance, the introduction of a high-temperature solid stream coming from a combustor in the calciner [10] or the use of an integrated high-temperature heat exchanger in the regenerator for transferring the heat indirectly from a high-temperature fluid [11, 12] have been proposed, but both options have not reached a sufficient development stage due to their limitations. As an alternative method for solving the problem of CaCO₃ regeneration in the SER process, the Ca-Cu looping process emerged [13]. This process proposes carrying out the calcination of the CaCO₃ by coupling in the same reactor the exothermic reduction of CuO with a gaseous fuel (i.e. containing CH₄, H₂ and CO). In this way, the coupling of the endothermic and exothermic reactions in a single step allows to supply directly the heat needed for CaCO₃ calcination without the need of costly heat exchange surfaces or energy-demanding units like the ASU, resulting in this way in a high-efficiency process.

2. Ca-Cu looping process: the concept

The Ca-Cu looping process was originally proposed in 2009 by Abanades and Murillo [13], and its basic scheme is based on the three main reaction stages shown in **Figure 1** [14]. The reactor configuration that fully exploits the advantages of the proposed concept is a series of fixed-bed reactors that operate in parallel at different pressure and temperature. Each fixed reactor passes through each stage of the Ca-Cu process in a sequential manner when changing the feed gas. Three functional materials are needed for operating this process: (i) a Cu-based material, (ii) a Ca-based CO₂ sorbent and (iii) a reforming catalyst (typically Ni-based).

The Ca-Cu process can be applied as a post-combustion CO₂ capture process in power plants, but the application having received more attention has been the developing of processes for the production of high-purity hydrogen and/or power [15]. At the beginning of the process, the Cu-based material and the reforming catalyst should be present in the bed in their reduced form, whereas the CO₂ sorbent should be fully calcined. The first stage of the process (referred to as 'A' in **Figure 1**) consists of a SER process, and it starts when natural gas and steam are fed to the reactor. The SMR, WGS and CaO carbonation reactions (Eqs. (1)–(3), respectively) occur during this stage. Pressure proposed to operate this SER stage ranges from about 10 to 25 bar depending on the main output of the process (i.e. hydrogen or power production). A H₂-rich gas is obtained at the outlet of this stage at high temperature, which should be cooled down to be used as fuel in a power production process or to be exported and used as feedstock for a downstream chemical process. SER stage finishes when all the CaO present in the solid bed is fully carbonated and there is no extra CaO to react with CO₂. The Cu-based material remains in its reduced form, unreacted, through this SER stage.

The second stage of the Ca-Cu process consists of the oxidation of the Cu present in the solid bed to produce the amount of CuO needed for the calcination of the CaCO₃. The oxidation stage (indicated as 'B' in **Figure 1**) starts when diluted air is fed to the fixed-bed reactor. This stage should be operated at controlled conditions of temperature and pressure to avoid temperature peaks within the reactor that lead to the prompt decomposition of the CaCO₃, as well as to avoid operational problems related to the Cu-based material (i.e. agglomeration and/or loss in reactivity) [16]. The operation strategy proposed for limiting such maximum allowable temperature has been reducing the temperature and the O₂ content in the diluted air stream fed to this stage. Recirculating a large fraction of the O₂-depleted gas at this stage outlet dilutes the O₂ content in the feed gas and increases the flow rate of the gas

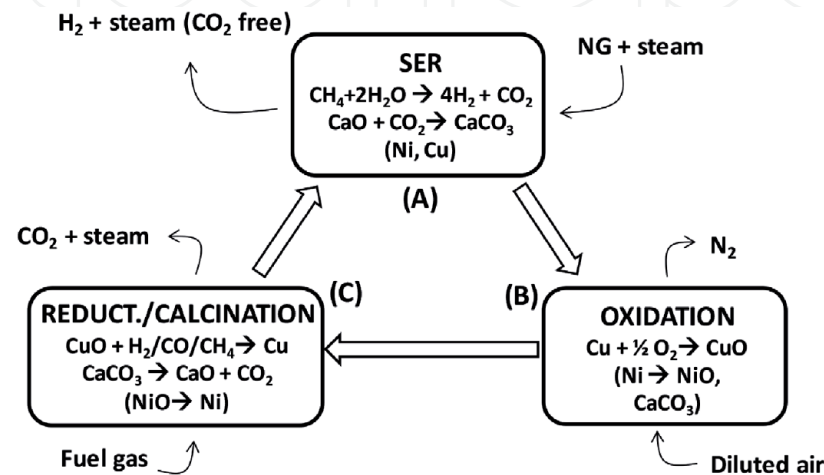
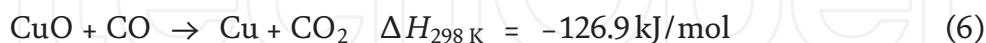
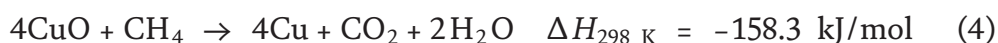


Figure 1.
Conceptual scheme of the Ca-Cu looping process.

fed to this reactor. This oxidation stage is operated at high pressure for reducing the driving force towards CaCO_3 decomposition. O_2 contents of around 3 vol.% and inlet gas temperatures of 150–300°C for this oxidation stage have been proposed as suitable for limiting the maximum temperature reached within the solid bed at 830–850°C [17]. The operation at high pressure allows using the non-recirculated O_2 -depleted gas at the reactor outlet for producing electricity in a gas turbine. The Cu oxidation stage finishes when all the Cu present in the solid bed is oxidized into CuO. At this moment, all the solid bed has been left at the temperature of the inlet gas (i.e. around 300°C), which is too low for the subsequent calcination/reduction stage to begin. The recirculated O_2 -depleted gas exiting the oxidation stage needs to be cooled down to about 300°C to be fed to the reactor, and it is passed through the fully oxidized bed to be cooled down while transferring its sensible heat to the solids, leaving them at a temperature of around 760–800°C suitable for the next reaction stage.

The last stage of the Ca-Cu process consists of the calcination of the CaCO_3 formed during the SER process by means of the energy released by the exothermic reduction of the CuO. This stage operates at atmospheric pressure to limit the maximum temperature needed to around 850–870°C. Typically, a mixture of H_2 , CH_4 and CO is proposed as feed gas in this stage, coming from either a hydrogen purification section or a separate reforming process. Proper CaO and Cu amounts are needed in the reactor to ensure that the energy released by CuO reduction is enough for fulfilling the energy requirement from CaCO_3 calcination as well as to reach the desired calcination temperature. The Cu/Ca ratio needed depends on the composition of the fuel gas used in this stage considering the reaction enthalpies of the reduction reactions with H_2 , CH_4 or CO (see Eqs. (4)–(6)). The maximum amount of Cu is needed when using CH_4 as reducing gas since it leads to the lowest exothermic reduction reaction per mole of CuO (i.e. a Cu/Ca molar ratio of 3.1 considering the reaction enthalpies at 850–870°C). On the contrary, the largest reduction enthalpy of the CuO with CO leads to the lowest Cu/Ca molar ratio needed of 1.3 [17].



3. Development of materials suitable for the Ca-Cu process

Three functional materials are needed for running the Ca-Cu process, namely, the CaO-based CO_2 sorbent, the Cu-based material and the reforming catalyst. Their proportion in bed will be determined by, on the one hand, the energy balance in the calcination/reduction stage in the case of Cu-based material/sorbent and, on the other hand, the CH_4 space velocity that a system is able to convert for the sorbent/catalyst ratio. In any case, it is important to maximize the active phase in every material, as the presence of inert in the reactor would negatively affect the efficiency of the process. In this section, a revision on the recent developments of CaO and Cu-based materials suitable for this process is included. As for the catalyst, conventional Ni-based reforming catalysts have been typically proposed for this process [15, 17], which have been successfully tested under suitable conditions for

the Ca-Cu process [18, 19]. It is important to assess the effect that the redox cycles have on catalyst activity and to determine the operational window in terms of CH_4 space velocity that a system sorbent/catalyst is able to convert.

3.1 Development of Ca-based CO_2 sorbents

In the recent years, intense work has been carried out in the field of synthetic CaO-based sorbents with the objective of overcoming the decay in CO_2 capture capacity that presents CaO-based sorbents derived from natural limestones and dolomites (see e.g. recent reviews [20–22]). Among the different strategies followed to produce materials resistant to sintering, the incorporation of the active phase (i.e. CaO) into an inert matrix is the most extended and validated synthesis method [23, 24]. The performance of the materials (referred to as CO_2 carrying capacity in g_{CO_2} absorbed per unit of CaO or sorbent weight) is commonly related to their pore structure/surface area and its evolution with the reaction cycles. The decay in sorption capacity is mainly a result of a sintering phenomenon that consists of the agglomeration of small CaO grains and the evolution of the pore structure towards higher pore diameters. It is important to highlight that it is not possible to directly compare the behaviour of materials tested under diverse reaction conditions as these will affect the materials performance in the long term (high number of reaction cycles) [25–27]. Anyway, there are valid trends that can be extracted from the results in the literature, as for example, that the maximum CO_2 carrying capacity of a sorbent is directly proportional to its CaO load [20] and that a minimum amount of inert matrix is required to maintain the pore structure and so reduce sintering.

A wide variety of synthesis methods (i.e. wet mixing, spray pyrolysis, sol-gel, co-precipitation, etc.) and inert supports (i.e. Al_2O_3 , MgO , ZrO_2 , SiO_2 , $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, etc.) have been studied in the literature for preparing synthetic CaO-based sorbents (see detailed reviews [20, 22] for an extended list of synthetic CaO-based sorbents). A recent paper by López et al. [24] evaluated the effect that sorbent inert support has on CO_2 carrying capacity and reactivity towards carbonation reaction. For this purpose, materials with different CaO amounts were prepared using two different inert supports (i.e. MgO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$). CaO/ MgO materials were prepared through co-precipitation (with CaO contents between 100 and 40%wt.), whereas materials with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as inert support were prepared via mechanical mixing and later calcination. The results indicated that a minimum amount of inert species was required to stabilize and to improve the CO_2 carrying capacity of the materials beyond the capacity of pure CaO. In **Figure 2**, the CO_2 carrying capacity of the different synthetic CaO-based materials prepared in [24] is depicted. A minimum amount of 10%wt. MgO improves the CO_2 carrying capacity of the material with respect to the performance of the co-precipitated CaO. Moreover, reducing the amount of CaO in the material diminishes the decay in the CO_2 sorption capacity along the initial cycles that is typical of naturally derived CaO-based materials. Taking into account that operation of the Ca-Cu process is thought to be carried out in fixed-bed reactors, the different functional materials should be in particle or pellet form. López et al. [24] prepared particles through an agglomeration process from the synthesized powder and demonstrated that the agglomeration process affected the textural properties of the materials, reducing the BET surface area and porosity with respect to the properties of the powder. Synthetic dolomites with a CaO/ MgO molar ratio of 2:1 and a particle size cut of 0.6–1 mm were obtained, which showed a CO_2 carrying capacity of about 0.28 $\text{g}_{\text{CO}_2}/\text{g}$ calcined material after 100 reaction cycles performing calcination under realistic conditions for the Ca-Cu process (i.e. at 900°C and 70%vol. CO_2).

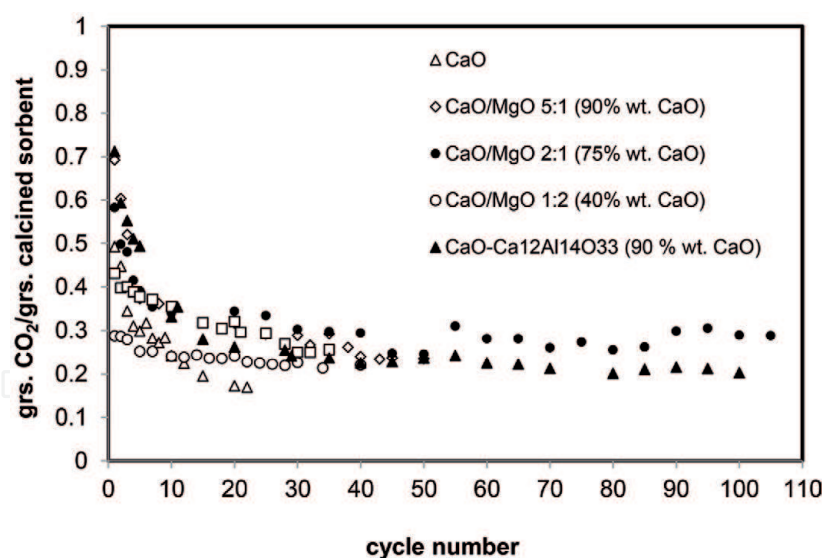


Figure 2.

Evolution of CO₂ carrying capacity with the number of cycles for different CaO-based materials (adapted from the information published in [24]). White symbols correspond to materials tested in powder form (<75 μm) and black symbols to materials in particle size cut of 0.6–1 mm.

Promising results have been reported in the literature for materials with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as inert support prepared through diverse synthesis routes under relevant calcination conditions for the Ca-Cu process (i.e. temperatures above 900°C in presence of CO₂ and steam). Pacciani et al. [28] reported a CO₂ carrying capacity of 0.17 g_{CO₂}/g calcined sorbent after 110 reaction cycles for a 85%wt. CaO, 15% wt. $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent prepared by co-precipitation. In another study, Koirala et al. [29] prepared different Ca-based sorbents with different Al/Ca molar ratios via single-nozzle flame spray pyrolysis. A CO₂ carrying capacity of 0.25 g_{CO₂}/g calcined sorbent was demonstrated after 100 calcination/carbonation cycles for a material with an Al/Ca molar ratio of 3:10 under severe calcination. Radfarnia and Sayari [30] used a citrate-assisted sol-gel technique followed by a two-step calcination method to produce an Al-stabilized sorbent that presented a CO₂ carrying capacity of 0.33 g_{CO₂}/g sorbent after more than 30 reaction cycles calcined at 930°C and 100% CO₂. An effort has been done by Kazi et al. [31] to produce efficient and stable CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbents via a cost-effective and easy scalable hydrothermal synthesis route, starting from low-cost hydroxide precursors. Through this method a highly stable sorbent presenting 0.21 g_{CO₂}/g calcined sorbent was synthesized, whose production has been recently scaled up within the framework of the FP7 ASCENT project [32].

3.2 Development of Cu-based materials

There is an important number of works focused on the development of Cu-based materials due to their application in chemical looping processes as oxygen carriers [16]. Different synthesis routes have been reported in the literature for these materials, as freeze granulation, impregnation, extrusion, spray drying, co-precipitation or mechanical mixing, using different inert supports (i.e. Al_2O_3 as the most common, but also MgAl_2O_4 , ZrO_2 , CeO_2 , TiO_2 and SiO_2 have been proposed), as widely reviewed by Adánéz et al. [16]. Cu-based materials with high Cu loads (i.e. about 60%wt. Cu) highly resistant to agglomeration and deactivation are those suitable for the Ca-Cu process. The recent interest of combusting solid fuels through CLOU process speeded up the development of materials with higher oxygen transport capacity (OTC) and therefore higher Cu contents [33]. However, despite some works reporting stable OTC along a reduced number of cycles

operated in fluidized bed under CLOU conditions for materials containing 80%wt. CuO on to MgAl_2O_4 [34], there are not many works published so far about highly loaded Cu materials specifically prepared for operation in fixed-bed reactors in pellet or large-particle form. A recent paper from Díez-Martín et al. [35] evaluated the maximum CuO load onto different inert supports (Al_2O_3 , MgAl_2O_4 , ZrO_2) that allowed chemically and mechanically stable materials along representative conditions for the Ca-Cu process. According to the results from this work, it was possible to produce chemically and mechanically stable pellet materials with Cu contents up to 65% wt. onto Al_2O_3 and MgAl_2O_4 from co-precipitated powders.

3.3 Development of combined CaO-CuO materials

With the objective of improving heat and mass transfer phenomena within the reduction/calcination stage of the process, there is an increasing number of works evaluating the synthesis of combined functional Ca-Cu materials [36–39]. Mechanical mixing of CaO and CuO powders was the selected synthesis route followed by Manovic and Anthony [40] for synthesizing for the first time this combined material. These authors prepared pellets by mixing CaO from calcined natural limestone with commercial CuO particles and Ca-aluminate cement as binder in a proportion that resulted in 45:45:10 mass fraction. Material performance was evaluated in a TGA apparatus along successive reduction/calcination and oxidation cycles. The Cu phase was totally converted during reduction (at 800°C in a CH_4 atmosphere) and oxidation in air, indicating that this could be a suitable material for the Ca-Cu process. Trying to explore the possibilities of the synthesis route, the same authors prepared core-in-shell materials with different CaO, CuO and Ca-aluminate cement proportions [41], maintaining the CuO in the inner core of the pellet. The OTC of the pellets indicated that a 25%wt. CaO in the core is sufficient to support the CuO and prevent the decay of its activity as an oxygen carrier. In other works, Quin et al. [39, 42] assessed the performance of materials composed by CaO and CuO supported on to MgO, Al_2O_3 or cement, prepared following diverse synthesis routes (wet mixing, sol-gel and mechanical mixing). The materials were tested in TGA and showed good reactivity along reduction and oxidation cycles using CH_4 and air, respectively. The presence of inert support allowed the combined material to maintain its CO_2 carrying capacity along cycles. This was especially clear for materials containing MgO on its structure, as this species greatly reduced the resistance to CO_2 diffusion during the carbonation stage. In contrast, the presence of Al_2O_3 produced $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ after reaction with CaO reducing in this way the amount of active phase for the carbonation reaction. As it happened for the sorbent and oxygen carriers, co-precipitation has been also a synthesis route explored to produce combined materials. Kierzkowska and Müller [38] prepared through this route combined materials with diverse CaO and CuO contents (CaO:CuO molar ratios of 1:1, 1.3:1 and 3.3:1) to be tested in a TGA along multiple carbonation/reduction/calcination/oxidation cycles. These cycles were performed isothermally at 750°C, carrying out carbonation in 40%vol. CO_2 in air, reduction in 10%vol. CH_4 in N_2 and oxidation 4.2%vol. O_2 in N_2 . According to this study, the best result was obtained for the material with a molar ratio 1:1 that maintained a CO_2 carrying capacity of 0.18 $\text{g}_{\text{CO}_2}/\text{g}$ material after 15 reaction cycles. In every case, the Cu phase reacted over 98%. Also these authors explored the effect that inert species might have on the chemical stability of the combined material, in this way they prepared via sol-gel materials supported on to Al_2O_3 , MgO and MgAl_2O_4 with CuO and CaO molar ratio of 1.3:1 and 3.3:1 [43]. As found by other authors, the presence of Mg in the support stabilized the CO_2 uptake and minimized carbon deposition. CuO- MgAl_2O_4 with a proportion of 1.3:1 was the material with the highest CO_2 uptake of 0.13 $\text{g}_{\text{CO}_2}/\text{g}$ material after 15 cycles of repeated carbonation/

calcination-redox reactions. In line with the efforts made to produce effective and economic sorbent materials, Kazi et al. [44] developed combined Ca-Cu materials via the hydrothermal synthesis route. A CO₂ carrying capacity of 0.15 g_{CO₂}/g material and an oxygen transport capacity of 0.07 g_{O₂}/g material after 50 reaction cycles in a TGA were reported for a material composed of 53%wt. CuO and 22% wt. CaO, being the rest Ca₁₂Al₁₄O₃₃. Conditions used for TGA tests were carbonation using a gas mixture of 15%vol. CO₂, 25%vol. steam in N₂ at 650°C, oxidation at 870°C with 25%vol. air in CO₂ and reduction at 870°C in a 40%vol. CO₂, 25% vol. steam in N₂.

4. Ca-Cu process lab-scale testing

The feasibility of the reaction steps of the Ca-Cu looping process has been experimentally confirmed in packed-bed reactors at laboratory scale during the recent EU-FP7 Project ASCENT [32]. Grasa et al. [18] focused the investigation on the SER stage using a commercial Ni-based catalyst and a CaO-Ca₁₂Al₁₄O₃₃ sorbent. After 200 reduction/oxidation cycles, the sorbent/catalyst system produced a gas with more than 90 vol.% H₂ on a dry basis (i.e. close to the maximum equilibrium value), operating with space velocities up to 2.5 kg CH₄ h⁻¹ kg cat⁻¹ (i.e. a gas velocity of 0.53 m/s inside the bed). The maximum space velocity at which the CH₄ is totally converted during the SER operation is determined by the CaO carbonation reaction. Sorbent carbonation reaction rates up to 4.42 × 10⁻² kmol h⁻¹ kg sorbent⁻¹ were calculated in the experiments.

The feasibility of the Cu oxidation stage was experimentally demonstrated by Alarcón et al. [45] under relevant conditions for the Ca-Cu looping process. Oxygen in the feed was diluted to 3%vol. with N₂ simulating the recirculation of a large fraction of the product gas from the oxidation stage outlet. The maximum temperature in the bed was kept below 800°C during the oxidation, which should prevent the agglomeration or sintering of the Cu-based material and highly reduce the loss of CO₂ by the partial calcination of the sorbent. Even at low starting temperatures in the reactor (of about 400°C), the oxidation of Cu occurred very fast taking place in sharp reaction fronts throughout the reactor. During the pre-breakthrough period, complete conversion of O₂ was observed despite of the very low O₂ content in the feed.

Fernández et al. [46] demonstrated at TRL4 the viability of the calcination of CaCO₃ by the in situ reduction of CuO with H₂ giving rise to a product gas composed of virtually pure CO₂ (after the condensation of H₂O). Tests were carried out in a fixed-bed reactor (1 m long and inner diameter of 38 mm) operating close to adiabatic conditions, loaded with commercial CaO- and Cu-based materials in pellet form (particle size of about 3 mm). The fixed-bed contained a Cu/CaO molar ratio of about 1.8, which is the theoretical value to accomplish the reduction/calcination with H₂ under neutrally thermal conditions. A fast and complete reduction of CuO with H₂ was observed even at relatively low initial solid bed temperatures (i.e. 400°C). However, only temperatures in the solid bed higher than 700°C allowed a simultaneous reduction/calcination operation, leaving uncalcined material in those zones at lower temperatures. Alarcón et al. [45] evaluated the effect of the fuel gas composition on the CuO reduction/CaCO₃ calcination operation. Different Cu/Ca molar ratios were used for this purpose to maintain neutral conditions in the reduction/calcination front. Mixtures of CO and H₂ showed high reactivity with the CuO-based material, resulting in the complete reduction of CuO to Cu in a sharp reaction front and the total oxidation of the gaseous fuel to CO₂ and H₂O. The Cu-based material was able to catalyse the reverse WGS reaction, favoured by the high temperature and the high CO₂ content in the atmosphere. Moreover, combined Ca-Cu oxides formed because of the multicycle operation at

high temperature, which slightly modified the chemical composition of the starting materials. These oxides carbonated in the presence of CO_2 , affecting the CO_2 sorption capacity of the solid bed. Recently, Fernández et al. [47] studied the reduction/calcination stage using pure CH_4 as reducing gas. The effect of the initial bed temperature and the inlet gas flow rate was evaluated. CuO reduction was favoured when using initial bed temperatures higher than 800°C , resulting in the complete oxidation of inlet CH_4 and the calcination of a large fraction of CaCO_3 . A low flow rate (i.e. $3 \text{ l}_\text{N}/\text{min}$ of CH_4) allowed a sufficient residence time of the CH_4 inside the reactor to be almost completely converted to CO_2 and H_2O . Temperature profiles higher than 900°C were measured, and large amounts of CO_2 resulting from CH_4 oxidation and CaCO_3 decomposition were observed. The relatively long breakthrough periods demonstrated that the reactivity of the CH_4 with the CuO -based material was significantly lower than that measured with H_2 .

Consecutive cycles of the three main reaction stages of the Ca-Cu looping process were made by Díez-Martín et al. [19] in a lab-scale fixed-bed reactor ($L = 0.2 \text{ m}$, I.D. = 18 mm) under relevant conditions of this process at a large scale. The solid bed contained the three functional materials required to run the process (i.e. a commercial Ni-based catalyst, a $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ sorbent and a $\text{CuO}/\text{Al}_2\text{O}_3$ material). The system was able to operate with space velocities of up to $13.5 \text{ kg CH}_4 \text{ h}^{-1} \text{ kg Ni}^{-1}$ during the SER stage at 675°C and 10 bar producing a gas with more than 93 vol.% H_2 (on a dry basis). The Cu-based solid exhibited fast reduction and oxidation kinetics, but it did not showed any appreciable reactivity towards CH_4 reforming during SER operation. Total O_2 conversion was observed during the Cu oxidation stage. Slightly higher amounts of CO_2 than those predicted by the CaO/CaCO_3 equilibrium were measured in the product gas during oxidation due to the carbon deposited during the breakthrough period of the previous SER step. The results obtained along several cycles were highly reproducible, demonstrating the proper chemical stability of the materials. Only a slightly decrease of the CO_2 sorbent capacity was observed. No mixed phases from the different active materials were detected, indicating the absence of any significant chemical interaction between the different solids loaded in the reactor.

5. Process analysis

5.1 Reactor design and modelling

The Ca-Cu looping process was mainly envisaged to be performed in several adiabatic packed-bed reactors operating in parallel. Fixed-bed reactors do not require solid filtering systems downstream since the formation of fines by attrition is avoided, and they allow the operation to take place in a more compact design at a high pressure. Moreover, H_2 and N_2 can be produced at a suitable pressure to be subsequently used in industrial applications and/or power generation. However, pressurized fixed beds require adequate heat management strategies in order to achieve the complete conversion of the solids and at the same time to avoid the formation of hot spots inside the reactors.

The first conceptual design of the overall Ca-Cu process was presented by Fernández et al. [17] in which a quite simple reactor model assuming narrow reaction fronts was used to describe the dynamic performance of every stage of the process. An ideal plug flow model with negligible axial dispersion was considered. Precise operating conditions for the process (i.e. temperature, pressure, steam-to-carbon (S/C) ratio, etc.) and material properties were defined. More rigorous reactor models were latterly developed to describe more precisely the

dynamic profiles obtained during every stage of the Ca-Cu process [48, 49]. These are basically 1D models in which a moderate axial mass and heat dispersion are considered and mass and heat transfer resistances between the gas and solid phases are neglected. The model developed by Fernández et al. [50] integrated the kinetic models for the SMR and CaO carbonation reactions occurring during the SER stage. These simulations demonstrated that operating at around 650°C, between 10 and 15 bar, S/C ratios between 3 and 5 and space velocities up to 3.5 kg/m² s, allows CH₄ conversions higher than 80% and a product gas with more than 90 vol.% of H₂ to be achieved. A similar reactor model was used to simulate the Cu oxidation stage [51]. In this work, it was theoretically demonstrated that a recirculation of around 80% of the product gas (to dilute the inlet O₂ content to 3–4 vol.%) restricts the temperature achieved in the oxidation front well below 850°C, thereby limiting the CaCO₃ calcination (whenever the operation is carried out at pressures higher than 10 bar). The CuO reduction/CaCO₃ calcination stage was also simulated in detail by Alarcon and Fernández [52] who demonstrated that appropriate proportions of CuO-based material (which depend on the composition of the reducing gas) provide the heat required for the direct calcination of the carbonated sorbent.

The three main reaction stages of the Ca-Cu process were also modelled in a more recent work by Martini et al. [49] using a relatively complex dynamic model and a simplified model that assumed narrow reaction and heat exchange fronts. The kinetics for the reactions occurring in all the stages of the Ca-Cu process were included. The maximum and minimum values achieved in both temperature and concentration profiles, as well as the reaction and heat exchange fronts velocities calculated using both models, were compared, showing a reasonably good agreement. The operability windows for each reaction stage were identified through sensitivity analyses of the main operating parameters (i.e. the CaO/Cu content in the bed, the composition of the inlet gases, the temperature and the pressure).

In a subsequent work, Fernández and Abanades [53] proposed a new operation strategy to minimize the number of reactors required, increase the CO₂ capture efficiency and avoid possible side reactions (e.g. CaO hydration) that might damage the mechanical characteristics of the Ca-Cu solids. **Figure 3** shows the reactor scheme proposed by these authors. The dynamic operation of the overall Ca-Cu process was simulated assuming that the initial conditions of each reaction stage were the result of the previous step. The simulations showed that the SER operation at 10 bar with temperatures lower than 730°C minimized CaO hydration and the emissions of CO₂. In the reduction/calcination stage, the feed of the fuel (mainly composed of the PSA off-gas resulting from the H₂ purification step downstream of the SER reactor) through the part of the bed that was at the highest temperature led to the complete conversion of the reducing gases. Only five reactors were found to be sufficient to operate the process (L = 6 m, I.D. = 3 m) and produce 30,000 Nm³/h of H₂, assuming a minimum length/diameter ratio of 2 and a maximum pressure drop of about 10% per stage, which are geometrical constraints and operational limits typically applied to CLC fixed beds [54].

5.2 Process assessment of large-scale Ca-Cu-based plants

The application of the Ca-Cu process having received more attention, due to its good performance in terms of efficiency and CO₂ emissions, is the production of high-purity hydrogen with inherent CO₂ capture. However, its application as CO₂ capture process in power plants has been also studied, both applied to the flue gas from a coal-fired power plant [55] and as a pre-combustion CO₂ capture process in a natural gas combined cycle (NGCC) power plant [56]. When applied to a coal-fired power plant, the Ca-Cu process led to a higher electric efficiency than the

When focused on large-scale hydrogen production, the performance improvements of the Ca-Cu technology with respect to the commercially ready SMR technology are not as tight as when focused on power production. Martínez et al. [58] evaluated for the first time the performance of a large-scale hydrogen production plant with CO₂ capture using the Ca-Cu process. The simple reactor model based on sharp reaction and heat exchange fronts described in [17] was used for solving the Ca-Cu reactors in this work, which completed the Ca-Cu scheme with the intermediate stages of rinsing, pressurization and depressurization that are needed in a large-scale process. Moreover, the presence of higher hydrocarbons and sulphur compounds in the natural gas used as feedstock made it necessary to include prereforming and desulphurisation stages in the model layout. A total number of 15 reactors was estimated in this work as those needed for running completely a Ca-Cu cycle (i.e. SER-rinse-oxidation-cooling-depressurization-rinse-reduction/calcination-pressurization), having three reactors operating in SER stage, three in the oxidation stage and three in the cooling stage before reduction/calcination, and keeping one reactor for each of the remaining stages. Hydrogen production efficiencies as high as 79% were calculated for the Ca-Cu-based hydrogen production plant in this work, which were reduced to 76% when including the penalties associated to the electricity consumption as well as the benefits for the steam exported.

A more compact reactor design for the Ca-Cu process for hydrogen production was proposed in a later work by Fernández and Abandes [53] who evaluated new operating conditions with the aim of reducing the number of reactors needed. SER stage was operated at a lower pressure (i.e. 11 bar) with an inlet S/C ratio of 3. It was proposed a configuration of only five reactors (i.e. one reactor per each of the Ca-Cu stages, SER, oxidation, cooling, reduction/calcination, cooling/reforming), whose length/diameter ratio was 2 (with a length of 6 m) and the maximum pressure drop allowed was 10% of inlet pressure. The hydrogen efficiency remained unvariable with respect to the value previously reported in [58]. Finally, these performance numbers were completed with an economic analysis by Riva et al. [59]. A rigorous model was used for calculating the fixed-bed reactor system, and it was carried out an optimisation of the pressure drop across the main heat exchangers needed in the plant, as well as across the fixed-bed reactors, with the aim of reducing the H₂ production cost. An economic analysis for a hydrogen production plant based on the Ca-Cu process was carried out for the first time in this work. Each of the four main reactors in the Ca-Cu process (i.e. SER, oxidation, cooling and reduction/calcination) is divided into four sub-reactors for reducing the pressure drop along the reactor and the total amount of functional materials needed to fill the reactors. A sensitivity analysis was performed on the operating pressure of SER and oxidation stages in this work, demonstrating that reducing the operating pressure to 11 bar makes the hydrogen efficiency increase up to 78% and to 79% (i.e. from 74 to 76% when operating at 25 bar) when accounting for electricity and steam exchanges with the surroundings. Considering a common calculation basis of H₂ production of 30,000 Nm³/h, the calculated cost of hydrogen for the Ca-Cu process ranges between 0.178 and 0.181 €/Nm³ (operating at 25 and 11 bar, respectively) which is below the cost of 0.194 €/Nm³ calculated for a benchmark hydrogen production plant based on the well-established SMR technology including CO₂ capture using a MDEA process [59].

One of the inherent advantages of the Ca-Cu concept is the possibility of producing almost pure streams of H₂ and N₂ as part of its products in the SER and oxidation stages, respectively. Such advantage makes it the perfect candidate to be integrated as part of an ammonia production process as recently proposed by Martínez et al. [60]. The schematic of an ammonia production plant based on the Ca-Cu process is shown in **Figure 4**(left). The synthesis gas production island used in the well-established ammonia production process (i.e. consisting of (1) two reforming steps, (2) two

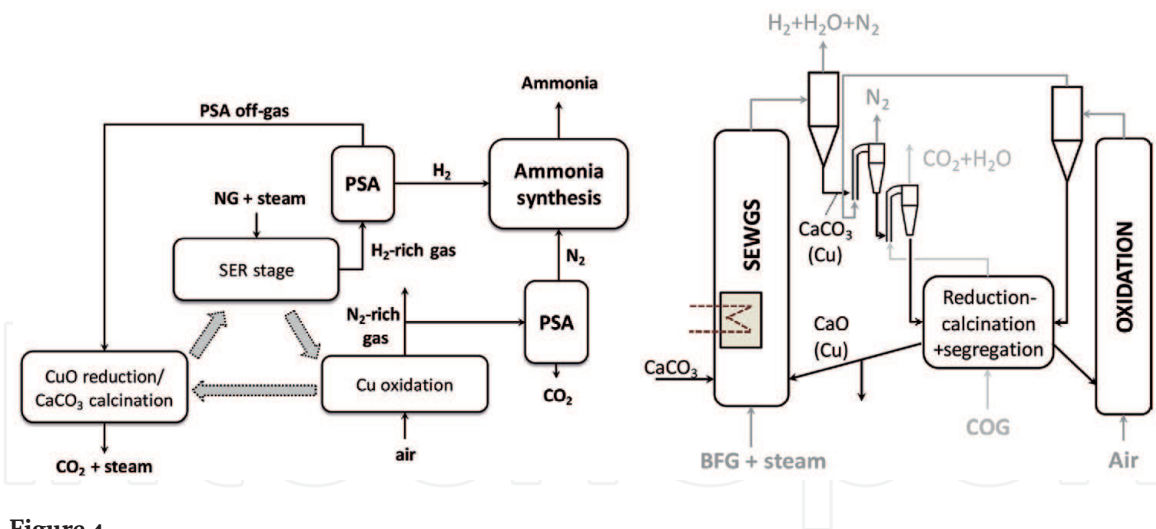


Figure 4.
 (Left) Schematic of the Ca-Cu process integrated into an ammonia production plant and (right) simplified Ca-Cu scheme for decarbonising off-gases in a steel mill.

WGS reactors, (3) CO₂ removal section and (4) methanation) is replaced by a fixed-bed Ca-Cu process providing the H₂ and N₂ streams in the right proportion (i.e. 3:1) to be introduced into the NH₃ production loop. Two purification steps would be needed in the Ca-Cu process to remove the impurities of the H₂-rich gas from the SER stage (i.e. unconverted CH₄, CO and CO₂) and from the N₂-rich gas from the non-recirculated gas from the oxidation stage (i.e. CO₂). Based on the analysis done in [60], the ammonia production process integrated with the Ca-Cu process allows reducing the primary energy consumption of a commercial ammonia production plant by around 14%, resulting in 24 GJ/ton_{NH₃}. Accounting for the electricity import needed, the advantage of the Ca-Cu-based ammonia plant is maintained. Further research is needed to evaluate the improvements in the ammonia synthesis loop, derived from a higher purity of the H₂/N₂ stream coming from the Ca-Cu process, as well as in the final ammonia production cost.

The potential of the Ca-Cu looping process as a decarbonizing process in the steelmaking sector has been also assessed. Fernández et al. [61] proposed scheme shown in **Figure 4**(right) for decarbonizing a substantial fraction of the blast furnace gas (BFG) produced in the steel mill. A three interconnected fluidized bed system configuration was proposed for this application. In this case, WGS and carbonation of CaO reactions (Eqs. (2) and (3)) occur in the H₂ production stage (i.e. SEWGS) since BFG is mainly composed of CO and CO₂ diluted in N₂, whereas coke oven gas (COG) is used as fuel in the reduction/calcination stage. The circulation of hot solids from an oxidation stage operating at 900°C supplies part of the energy needed for the CaCO₃ calcination. A segregation step is needed after the reduction/calcination stage to separate the pure CaO stream demanded by the steelmaking processes and to avoid too much Cu-based solids going to the SEWGS. Using exclusively COG as a fuel for the reduction/calcination, only 30% of the BFG produced in the blast furnace could be decarbonized, whereas adding NG to this reduction/calcination step allows attaining above 91% of CO₂ capture efficiency on the whole steel mill [62].

6. Concluding remarks

The Ca-Cu looping process is an emerging CO₂ capture process that points out an improved efficiency and reduced cost for H₂ production compared to well-established technologies. The functional materials needed for running the process are not a barrier for the progress of the technology, being already available with the proper

Cu and Ca contents. Further research in long-term stability of these materials would be needed in order to elucidate any problem related with activity loss or agglomeration problems. The key reaction stages of the process have been already tested at a sufficient scale under conditions relevant for the operation at a large scale, but investigation in multiple reactor system at a larger scale is needed for corroborating the promising results found at lab-scale.

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