

Conceptual design of a Ca-Cu chemical looping process for hydrogen production in integrated steelworks

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Abstract

A novel configuration of the Ca-Cu looping process is proposed for the production of a H₂-enriched fuel gas from blast furnace gas (BFG). CO from BFG is converted with H₂O to CO₂ and H₂ in a sorption enhanced water gas shift (SEWGS) stage where CO₂ is simultaneously removed from the gas using a CaO-based sorbent. A Cu/CuO chemical loop supplies the energy required for the regeneration of the CaO carbonated during the SEWGS via the exothermic reduction of CuO with coke oven gas (COG) (and/or other N₂-free off-gas from the steel mill). The resulting Ca-Cu looping process comprises three reaction stages: SEWGS, Cu oxidation, and a simultaneous CuO reduction/CaCO₃ calcination stages. These are carried out in an arrangement of interconnected fluidized-bed reactors operating at atmospheric pressure. The use of fluidized beds facilitates the feed of a continuous make-up flow of limestone (precursor of the CaO needed for the CO₂ capture) and the generation of the associated purge of CaO needed in the steel mill. Moreover, this configuration allows for a solids' segregation step to be introduced, which improves the energy performance of the process since the Cu-based solids would act as thermal ballast in the SEWGS reactor. A conceptual design of this process is presented for a set of boundary conditions in order to demonstrate the theoretical feasibility of the process and to find the operational window that will ensure optimal performance in terms of energy and CO₂ capture efficiency. A reference case is analyzed in more detail by assuming that the SEWGS is carried out at 600 °C and the regeneration of the sorbent is carried out at 870 °C using as fuel gas the coke oven gas (COG) from the steel mill. Considering sub-stoichiometric conditions in the oxidation stage to limit the maximum temperature at 900 °C, 27% of the BFG can be decarbonized in the SEWGS reactor producing 110 Nm³ of H₂ per tonne of steel. Under these conditions, a CO₂ capture ratio of 31% with respect to the total carbon emissions in the steel mill can be achieved. Apart from the H₂ produced, more than 60% of the thermal input of the Ca-Cu process ends as high temperature heat generated in the SEWGS reactor and as sensible heat in the exhaust gases that could be efficiently recovered by producing high pressure steam to generate electricity in the steel mill power plant.

Keywords: Hydrogen, steelworks, CO₂ capture, sorption enhanced water gas shift, chemical looping combustion

1. Introduction

A drastic reduction in anthropogenic CO₂ emissions is needed before 2050 in order to achieve the climate change mitigation targets [1] that have been set as long term objectives after COP21. The iron and steel industry is the largest energy consuming manufacturing sector worldwide and contributes about 5-7% of the total anthropogenic CO₂ emissions [2]. Modern steelworks have been highly optimized and today they are being operated very close to their thermodynamic limits in terms of carbon use. It is therefore extremely difficult to further reduce CO₂ emissions as they are inherently linked to the extensive use of carbon containing fuels in the different parts of the iron and steel making process [3]. CO₂ Capture and Storage (CCS) can lead to a drastic reduction in CO₂ emissions far beyond that currently achievable in the steelmaking industry [1, 3]. In this field, significant R&D initiatives are ongoing in Europe through the Ultra-Low CO₂ Steelmaking (ULCOS) project [4, 5] and in Japan through the COURSE50 project [4, 6]. The conventional post-combustion capture amine-based chemical absorption technologies are in principle suitable for the capture of CO₂ from steel mills [2, 7]. However, the varying characteristics (e. g. composition, flowrate and location) of the different off-gases generated across the multiple parts of the iron and steelmaking process make it difficult to install capture systems aimed at a high reduction of CO₂ emissions [8, 9]. Moreover, if the steel mill off-gases are used in a combined cycle for high efficiency power generation, a low amount of low pressure steam is available for solvent regeneration from the power plant and limited CO₂ capture efficiencies can be achieved while keeping high thermodynamic efficiency [10].

The implementation of pre-combustion capture systems on the blast furnace gas (BFG) appears to be an attractive option to achieve higher carbon capture rates in the steelmaking process [11], since BFG contains 60-80% of the total carbon entering the steel mill in the form of CO and CO₂ [2-4]. At the same time, a decarbonized H₂-enriched fuel gas is produced suitable for use in the power plant and in the main process heaters (hot stoves and coke plant). Among the pre-combustion CO₂ capture processes, the Sorption Enhanced Water Gas Shift (SEWGS) [12] seems to be particularly suitable for application in steel mills [10, 13] and it is the subject of the ongoing EU demonstration project STEPWISE [14]. In SEWGS processes, almost pure hydrogen is produced from CO and H₂O through the water gas shift reaction, while the CO₂ is removed from the gas phase as soon as it is produced [15]. So far, this concept has been envisaged to be mainly implemented in a system of multiple fixed beds operating in parallel that remove the CO₂ at high temperature (up to 550°C) and pressure (up to 30 bar) [15-18]. The sorbent usually proposed for the CO₂ capture in the SEWGS process is hydrotalcite-based clay, which also acts as water-gas-shift catalyst, being regenerated either by a thermal-swing technique or by reducing the pressure and purging with steam [16, 18].

Calcium-based materials have also been widely proposed in the literature as CO₂ sorbent [19-21] for enhancing the thermodynamics of catalytic processes aimed at H₂ production from methane (Sorption Enhanced Reforming, SER) [22-24] or from syngas (SEWGS) [13, 25, 26]. These solids can be obtained from a wide range of abundant, natural and inexpensive sources, such as limestone or dolomite and their presence in SER and SEWGS processes minimizes coke formation and diminishes the steam requirements [23]. When CO₂ is captured using these materials, CaCO₃ is formed and its subsequent regeneration demands temperatures around 900 °C. The calcination of CaCO₃ is highly endothermic and needs to be carried out under a CO₂-rich atmosphere if the process is aimed at very low CO₂ emissions (i.e. in order to generate a rich stream of CO₂ suitable for purification, compression and storage).

Different alternatives have been proposed in the literature as a means of providing the large amount of heat required for the calcination of CaCO₃ in pre-combustion capture SER/SEWGS and in post-combustion capture Calcium looping systems. This heat can be directly supplied using an oxy-combustion system [27-30], indirectly through high temperature heat transfer surfaces [31-34] or by the direct contact with hot solids from an air-blow combustion chamber [35-37]. Another alternative is to use a chemical looping combustion (CLC) system, typically proposed for the CO₂ capture in power generation [38], in which oxygen is transferred from air to the fuel by using an oxygen carrier (typically a metal oxide) [39]. This avoids the dilution by nitrogen of the combustion products and generates a gas highly concentrated in CO₂, making the CO₂ capture easier and cost-effective [40]. The CLC concept was adapted to form part of the “unmixed reforming” concept [41], in which the exothermic oxidation of Ni with air supplies the energy required for the decomposition of CaCO₃, thereby regenerating the Ca-based sorbent needed for the next cycle. Carrying out simultaneously both oxidation and calcination reactions in one single stage allows a higher energy efficiency to be achieved as the heat is directly transferred from the oxygen carrier to the calcium carbonate. However, the CO₂ generated in the calcination with this system is emitted highly diluted with N₂, which means that CO₂ capture is not feasible without further separation steps [42]. Recent CLC configurations have been proposed to calcine CaCO₃ so that the CO₂ capture can be carried out by means of indirect heating using the high heat-transfer capacity of NiO [43] or iron oxides [44] that come from an oxidation step at temperatures above 1000°C.

A Ca-Cu chemical looping process was recently proposed [45] for enhancing the production of H₂ with CO₂ capture, in which the heat needed for calcination is supplied by the exothermic reduction of CuO to Cu with a gaseous fuel. The theoretical advantages of such combined chemical loops are similar to those of “unmixed reforming” processes, i.e. there is no need for heat transfer surfaces in the reactors, as the heat for the CaCO₃ calcination is supplied in situ by the exothermic heat of CuO reduction. However, the key difference is that in the Ca-Cu processes the CO₂ released during calcination of CaCO₃ is not diluted with N₂ but generated in a concentrated stream of CO₂ and H₂O_(v), which are the reaction products of reducing CuO with a

suitable gaseous fuel. A variety of experimental demonstrations using high-performance materials with direct application to the Ca-Cu looping process have been reported in recent years [46-53]. To date, most of works investigating the Ca-Cu looping process have been focused on developing systems composed of fixed-bed reactors [54-64]. A considerable progress has been made recently in the study of CLC systems in fixed beds [65-69]. These configurations facilitate the performance at high pressure, which allows higher energy efficiencies to be achieved [70] and avoid the need of downstream solid-gas separation devices [40]. However, CLC fixed-bed systems require adequate heat management strategies in order to avoid hot spots and approach the complete conversion of gases and solids [71, 72]. Moreover, several reactors performing in parallel that need a large number of high-temperature valves are needed to ensure a continuous operation [58, 73]. Detailed model simulations including the thermal integration of the Ca-Cu looping process on a large scale have demonstrated the feasibility of this process for H₂ production [58, 62] and for power generation [57] with competitive efficiency penalties with respect to NGCC systems without capture. Other application of the Ca-Cu chemical loop in post-combustion capture systems has also been assessed [74], although the use of significant amount of methane in the fuel reactor, ultimately converted with an efficiency typical of a steam cycle instead that of a combined cycle, will most probably prevent this application from being competitive against other capture technologies suited for natural gas.

This work proposes a novel Ca-Cu process scheme for the production of a H₂-enriched fuel gas of direct use in a steel mill or elsewhere via the SEWGS of blast furnace gas (BFG) with integrated CO₂ capture by CaO. The Cu/CuO chemical loop allows the calcium-based sorbent carbonated in the SEWGS stage and the limestone required for steel production to be calcined in a rich atmosphere of CO₂ using coke oven gas (COG) and/or other N₂-free off-gases available in the steel mill. The process is carried out in an arrangement of fluidized-bed reactors, in which a solids segregation step is introduced in order to obtain separately the CaO required for the ironmaking process and to improve the performance of the process since the copper-based particles would act as thermal ballast in the SEWGS stage, as explained below. This novel configuration has been envisaged to reach a substantial reduction of carbon emissions in the steelmaking process if the rich streams of CO₂ generated in the process are purified and safely stored. A full conceptual design of the Ca-Cu looping process is presented in this work for a set of boundary conditions that will allow its application in a representative steel mill. Reasonable assumptions concerning the reactions involved in each stage of the process have been made using literature data on similar chemical looping combustion and calcium looping systems. A sensitivity analysis of the main operating parameters has been carried out to demonstrate the theoretical viability of the process and to determine the operational window that will ensure optimal performance in terms of energy and CO₂ capture efficiency.

2. Process description

The Ca-Cu looping process proposed in this work for the CO₂ capture from blast furnace gas (BFG) comprises three main reaction stages, i.e. the sorption enhanced water gas shift (SEWGS) of BFG, the simultaneous CuO reduction/CaCO₃ calcination with a gaseous fuel and the oxidation of Cu with air. The general process scheme, which is presented in Figure 1, mainly consists of three interconnected fluidized-bed reactors operating at atmospheric pressure. The choice of fluidized beds in this application is based on the need to handle a continuous make-up flow of limestone (which is the precursor of the CaO needed for the reaction stage involving CO₂ capture by carbonation) and generate the associated purge of the CaO-rich material needed in the steel mill. These Ca flows will also allow the renovation of solids that may have been deactivated by impurities in the raw fuel gases coming from the steel mill (BFG, COG, etc). Most of the CLC systems proposed in the literature [40] are carried out in arrangements of fluidized-bed reactors, which allow for a good contact between gases and solids and facilitate the transport of the solids between the stages of the process. The CO₂ capture by means of calcium looping has also been shown to be feasible in interconnected fluidized beds for pre-combustion [75-77] and post-combustion [78-82] applications. Moreover, this configuration avoids the need for switching high-temperature valves (that are typically required for SER and CLC systems with fixed beds), facilitates suitable Cu/Ca ratios for the different reaction stages and allows the introduction of a solids separation step by segregation between the dense Cu-rich solids and the Ca-rich particles, as explained below.

In the first stage of the proposed process, a low pressure H₂/N₂ fuel gas (stream 2) is produced through the sorption enhanced water gas shift (SEWGS) from a low calorific value and carbon-rich blast furnace gas (BFG) (stream 1) in the presence of CaO, which acts as CO₂ sorbent. This stage is expected to operate at around 600°C. Under these conditions, both WGS (Eq. 1) and carbonation (Eq. 2) reactions are highly favoured, so that the almost complete conversion of CO and H₂O to CO₂ and H₂ can be expected, with a substantial CO₂ removal from the gas phase (in situ as soon as it is formed).



The product gas will contain around 30-35% vol. of H₂ on a dry basis (depending on the N₂ content of the BFG) and less than 1% vol. of CO and CO₂. This decarbonized H₂-enriched fuel gas, with an improved heating value with respect to the original BFG, can be used to provide heat for the steel mill processes (i. e., coke oven, stoves, boilers, etc, as it is done today with existing carbon-rich fuel gases), for power generation in a combined cycle after compression, or to produce steel through a Direct Reduced Iron (DRI) process avoiding the need for a dedicated steam reforming (FTR) plant [83]. Both the WGS and carbonation reactions are highly exothermic, so the excess in high temperature heat from the SEWGS stage can be efficiently used to produce steam for the steam cycle, that is typically employed in integrated steel mills for power generation.

After being separated from the product gas in a downstream cyclone, the carbonated particles are preheated by direct contact with hot process gases and sent to a second fluidized bed (the fuel reactor and calciner) where the regeneration of the CO_2 sorbent occurs. The heat required for the calcination is supplied by the exothermic reduction of a CuO -based material using any “ N_2 free” fuel gas containing CH_4 (Eq. 3), CO (Eq. 4) or H_2 (Eq. 5), (stream 8 in Figure 1). Low calorific value fuel gases generated across the iron and steelmaking process, such as the Coke Oven Gas (COG) or the Basic Oxygen Furnace Gas (BOFG), which contain significant amounts of CH_4 , H_2 and CO , being almost free of N_2 (see Table 1), are suitable for this operation. Natural gas can be also supplied to the fuel reactor/calciner to increase the amount of BFG that can be processed in the SEWGS. The typical temperatures required for the calcination of CaCO_3 (between 860°C and 900°C depending on the CO_2 content in the product gas [84]) match very well with the optimal operating temperature of fuel reactors of Copper-based CLC systems [40].

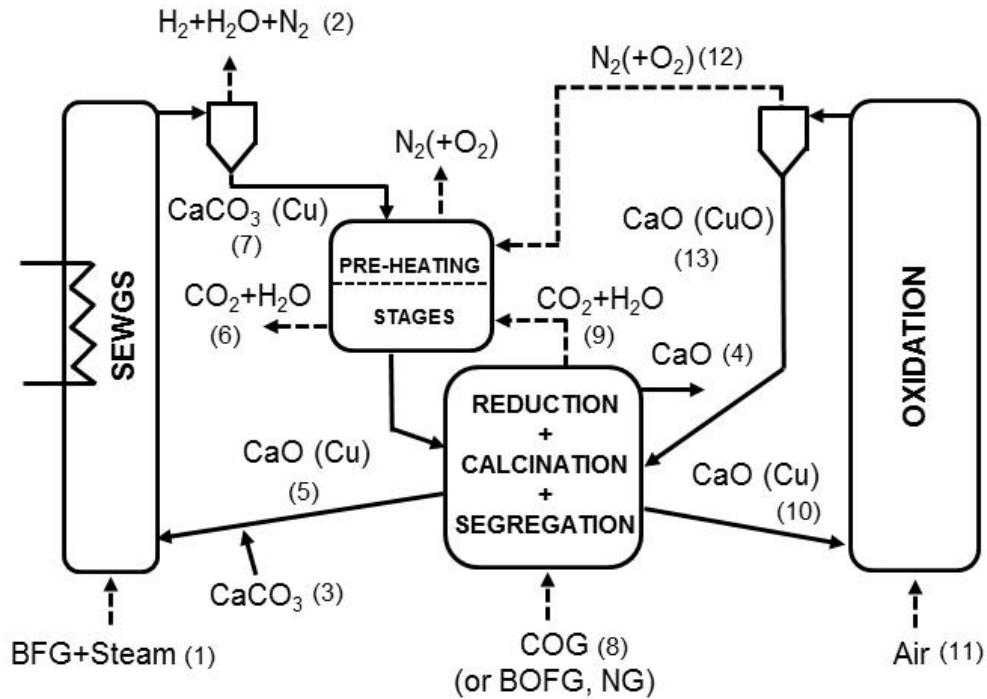
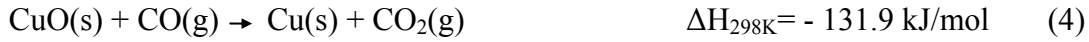
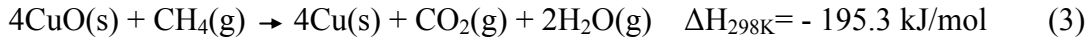


Figure 1. Scheme of the novel Ca-Cu looping process proposed for the CO_2 capture from blast furnace gas using fuel gases from steel mills.

The product gas (stream 9 in Figure 1) will be mainly composed of the CO_2 released from the CaCO_3 calcination and the CO_2 and H_2O resulting from the reduction of CuO with the fuel gas. To achieve a complete reduction of the copper oxide to Cu in a well-mixed fluidized bed, complete fuel oxidation cannot be achieved and low amounts of unburnt compounds resulting from the incomplete oxidation of the fuel gases will also be present in stream 9. In this case, as proposed for other CLC systems [40], an additional oxygen polishing step to complete the combustion of the non-converted compounds to CO_2 and H_2O or a low temperature CO_2 purification unit would be required in order to obtain a final concentrated stream of CO_2 and to recover the

unconverted fuel gases. Alternatively, a complete fuel oxidation may be achieved by accepting an incomplete copper oxide reduction in the fuel reactor/calciner.



The CaCO_3 required in the ironmaking process (around 280 kg CaCO_3 per tonne of steel [4]) can be fed into the system as make-up (stream 3 in Figure 1) to be calcined in the fuel reactor calciner without generating a separate source of CO_2 emission. From a thermodynamic point of view, the CaCO_3 make-up should be fed after preheating. While solids can be preheated downstream the SEWGS reactor in a gas-solid contactor such as a moving bed or a cyclone preheating tower typical of cement plants, part of the solids preheating may be performed by feeding the fresh CaCO_3 to the SEWGS reactor as illustrated in Figure 1, by exploiting the reaction heat of the WGS and carbonation reactions. The reduction of steam generated in the SEWGS reactor is more than balanced by the corresponding fuel saving in the fuel reactor/calciner per unit of hydrogen produced in the SEWGS assuming the limestone were fed to the calciner at lower temperature.

The separation of the solids by segregation, even if it is uncomplete, highly improves the energy performance of the process, since Cu solids would act as thermal ballast in the SEWGS reactor and the Cu fraction still oxidized at calciner outlet would oxidize part of the hydrogen produced in the same reactor. Perfect segregation between solids is challenging in continuous systems because axial concentration profiles appear when fluidising mixtures with very different particle properties [85]. However complete segregation is not necessary before the SEWGS, since the presence of Cu may be needed to catalyse the water gas shift reaction in addition to the CaO [86], which is the main reacting solid. Segregation is also very important to separate the lime required for the ironmaking process (virtually pure CaO) at the fuel reactor calciner outlet (see Figure 1). The ratios of solids densities and/or particle sizes are the main factors to achieve an effective separation of the solids by segregation [85, 87]. This is a similar operation to that envisaged for carbon strippers under study in other CLC systems with solid fuels to separate unconverted char from the oxygen carrier [40]. Under suitable fluidization conditions, very high separation efficiencies can be achieved (up to 95%, comparable to those obtained in CLC carbon strippers [40]), since the CaO particles (porous solids with an apparent density of around 1800 kg/m^3) will tend to rise, while the denser Cu-based particles (with an apparent density of around $3000\text{-}3500 \text{ kg/m}^3$) will sink in the reactor. Downstream of the fuel reactor calciner, the solid stream directed to a third fluidized bed (air reactor) for its subsequent oxidation (stream 10) is allowed to contain a fraction of CaO, since this material will simply be recirculated through the air reactor, which performs at relatively mild temperatures, avoiding CaO deactivation.

Most of the solids from the calciner are sent to the air reactor, which operates as a circulating fluidized-bed (CFB). Air is fed into this reactor to oxidise the Cu-based material that will be subsequently used in the fuel reactor calciner as heat source for calcination (stream 13 in Figure 1). In principle, the oxidation can be carried out with excess of oxygen (i.e., achieving complete oxidation of Cu into CuO in this reactor) or at under-stoichiometric conditions (i.e., without complete oxidation of Cu). Therefore, depending on the air-to-Cu ratio in the air reactor, the Cu-based material can be oxidised to Cu₂O or to CuO, Eq. (6) and Eq. (7). In any case, the oxidation reactor operates adiabatically, limiting the operating temperature to around 900°C in order to avoid loss of activity by sintering and/or agglomeration of both calcium and Cu-based materials. Cu-based materials with very high active content (higher than 60 wt.%) have been proven to be resistant to deactivation and agglomeration in long duration cyclic tests carried out at temperatures around 900 °C [88-90]. Several works have also demonstrated that calcination temperatures below 950 °C do not cause significant deactivation on Ca-based materials compared to the effect of carbonation/calcination cycles in the long term [91, 92]. The O₂-depleted air released at very high temperature from the air reactor (stream 12 in Figure 1) is a high-quality source of thermal power that can be used for preheating requirements and/or for producing high pressure steam that can be used for power generation in a steam cycle. After the separation of the solids from the product gas in a cyclone, they are fed into the fuel reactor calciner (stream 13) to complete the cyclic operation.



3. Process modelling assumptions

Mass and energy balances involved at every stage of the proposed Ca-Cu chemical looping system have been solved using an in-house code GS developed at the Department of Energy of the Politecnico di Milano [93]. A reference case study has been analyzed to assess the performance of the proposed concept as well as to demonstrate its potential for being integrated in steelworks. Moreover, a sensitivity analysis of the key design variables has been carried out to determine the operational window that leads to optimal performance in terms of energy consumption and CO₂ capture efficiency. Balances have been solved taking as reference 1 tonne of steel produced in the integrated steel mill. Flow rates and the composition of the gas streams (i.e. BFG, COG and BOFG) coming from the steelworks have been taken from the reference BF-BOF based integrated steel mill balances reported by the IEA in [4]. In this reference plant, approximately 1609 Nm³ of blast furnace gas (BFG), 179 Nm³ of coke oven gas (COG) and 88 Nm³ of basic oxygen furnace gas (BOFG) are produced from the main stages of the iron and steelmaking process [4]. The composition of these steel mill off-gases are listed in Table 1. Regarding the solids, about 20% of the Ca-based material is assumed to be converted to CaCO₃ in the SEWGS reactor and the Cu-based solids consist of 60 wt.% of CuO over alumina. The relatively high CaO capacity

is justified by the high make-up flow of fresh limestone fed into the process, which results in a very active sorbent circulating through the SEWGS reactor (e.g. according to the definition proposed by [94] a maximum average CaO conversion of around 27-29 % should result for the conditions of this work). The main reference plant assumptions adopted in this study are summarized in Table 2.

Table 1. Composition and lower calorific value (LHV) of the main off-gases from the integrated steel mill used for the calculations [4].

	Blast Furnace Gas (BFG)	Coke Oven Gas (COG)	Basic Oxygen Furnace Gas (BOFG)
Composition (%vol)			
CH ₄	--	23.0	--
Other HC	--	2.7	
CO	22.3	3.8	56.9
CO ₂	22.1	1.0	14.4
H ₂	3.6	59.5	2.6
H ₂ O	3.2	4.0	12.2
N ₂	48.8	5.8	13.8
O ₂	--	0.2	--
LHV [MJ/Nm ³]	3.21	17.33	7.47

Table 2. Operating conditions of the Ca-Cu looping process in the reference case study.

Parameters	Reference values
Temperature in SEWGS, °C	600
S/C molar ratio in SEWGS	1
Temperature of inlet gases in SEWGS, °C	250
Temperature in Fuel Reactor, °C	870
Temperature of fuel gas at Fuel Reactor inlet, °C	600
Temperature in Air Reactor, °C	900
Temperature of inlet air in Air Reactor, °C	300
Molar Cu-to-CaO ratio in the SEWGS reactor	0.03
Molar Cu-to-CaO ratio in the air reactor	0.03
CaCO ₃ /Ca at SEWGS outlet	0.20
Molar Cu ₂ O/Cu ratio at Fuel Reactor outlet	0.045

4. Results

4.1. General discussion on the mass and energy balances of the Ca-Cu chemical loop

In this section possible operating windows for the two chemical loops used in the process are examined. The main process variables of the SEWGS reactor are the temperature and the steam to carbon ratio. In Figure 2 and Figure 3, the effect of these parameters on syngas composition and CO₂ capture efficiency is shown, on the basis of equilibrium calculations. The optimal operating conditions in view of these results should be defined on the basis of an economic trade-off between CO₂ capture efficiency (favored by a low temperature and a high S/C ratio), thermodynamic efficiency (favored by the opposite conditions) and reaction kinetics. From the results obtained, the assumed SEWGS operating temperature of 600°C and S/C=1 must be reasonably close to an economic optimum because they allow CO₂ capture efficiency from the BFG of about 95% with moderate steam consumption and at a temperature where both WGS and CaO carbonation are known to be sufficiently fast [13, 86, 95].

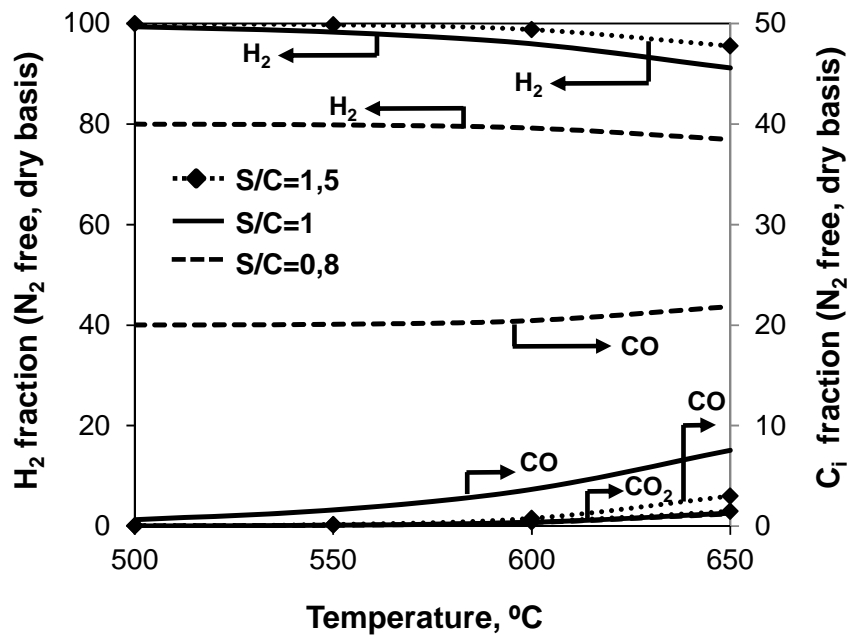


Figure 2. Effect of temperature and steam-to-carbon ratio on SEWGS equilibrium (at atmospheric pressure).

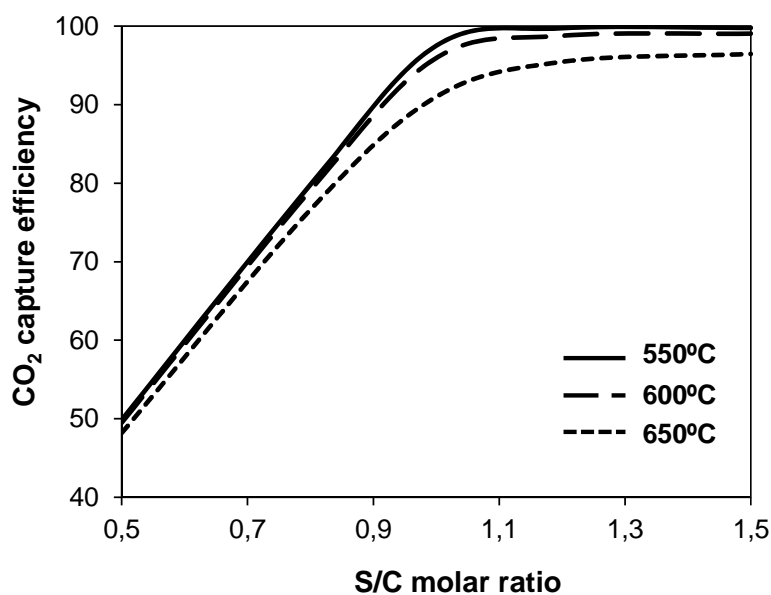


Figure 3. CO₂ capture efficiency on SEWGS equilibrium as a function of the steam-to-carbon ratio and temperature.

In the case of the CLC loop, an initial analysis can be based on the effect of the air-to-Cu ratio in the air reactor, for different solids compositions (determined by the Cu/CaO ratio). The amount of oxygen supplied to the air reactor (air-to-Cu ratio) and the inert content (here represented by the CaO in addition to the oxygen carrier support Al₂O₃) in the inlet solids stream affects the proportion of Cu/Cu₂O/CuO formed during the oxidation as well as the maximum temperature achieved in the air reactor. In Figure 4, the oxidation temperature (i.e. temperature at the adiabatic air reactor outlet) as a function of the air-to-Cu mass ratio at the inlet of this reactor for two different solid compositions is shown, assuming completely reduced Copper at the reactor inlet. As can be seen in Figure 4, the temperature achieved during Cu oxidation initially increases as the air-to-Cu ratio increases, as a consequence of the exothermicity of the oxidation reaction. For a sub-stoichiometric air-to-Cu ratio, the amount of air is not enough to oxidize Cu to CuO completely. For a low air-to-Cu ratio (O₂/Cu below about 1/4 on a mole basis) a mixture of Cu/Cu₂O is obtained at the air reactor outlet. For an intermediate air-to-Cu ratio (O₂/Cu between about 1/4 and 1/2), after all the copper has been oxidized to Cu₂O, fully oxidized CuO starts to form and a Cu₂O/CuO mixture is obtained in the solids population. In this zone, the temperature increases with the air/Cu ratio with a different slope. This is due to the different reaction enthalpies for the oxidation reactions (Eq. 6 and Eq. 7). Figure 4 also shows a discontinuity when passing from the Cu-Cu₂O system to the Cu₂O-CuO one, due to the fact that CuO starts to form when the O₂ partial pressure in the gas phase is sufficiently high. For example, considering the Cu/CaO=0.03 line, Cu is completely converted to Cu₂O for an air-to-Cu mass ratio of 0.55. At this condition, the temperature in the reactor is 905°C and the corresponding O₂ partial pressure in the gas phase, which is determined by the Cu/CuO/O₂ equilibrium, is 0.0004 bar. At this temperature, the equilibrium O₂ partial pressure for the Cu₂O/CuO/O₂ system is 0.02 bar. Therefore, some additional non-

reacting air has to be added to reach such O_2 partial pressure and to allow CuO formation. This inert air addition causes the small temperature drop visible in the figure, due to the sensible heat required to heat the inlet air at $300^\circ C$ up to the reactor temperature. The observed discontinuity is larger at higher temperatures because the $Cu_2O/CuO/O_2$ and $Cu/CuO/O_2$ equilibria involve higher O_2 partial pressure difference when the temperature increases [40]. The maximum temperature at air reactor outlet is achieved when Cu is fully oxidized to CuO , which occurs with different air-to- Cu ratio, based again on the equilibrium of the $Cu_2O/CuO/O_2$ system. The maximum temperature achievable also depends on the amount of inert solids in the system. The lower the amount of inert species, the higher the temperature (i.e. with higher Cu/CaO ratio in this case). After the maximum temperature has been reached, temperature falls as the air-to- Cu ratio increases, due to the increased thermal ballast of the excess air used. In light of this behavior, we can expect the targeted oxidation temperature in the air reactor to be achieved either by using a sub-stoichiometric (i.e. involving incomplete Cu oxidation) or an over-stoichiometric air/ Cu ratio.

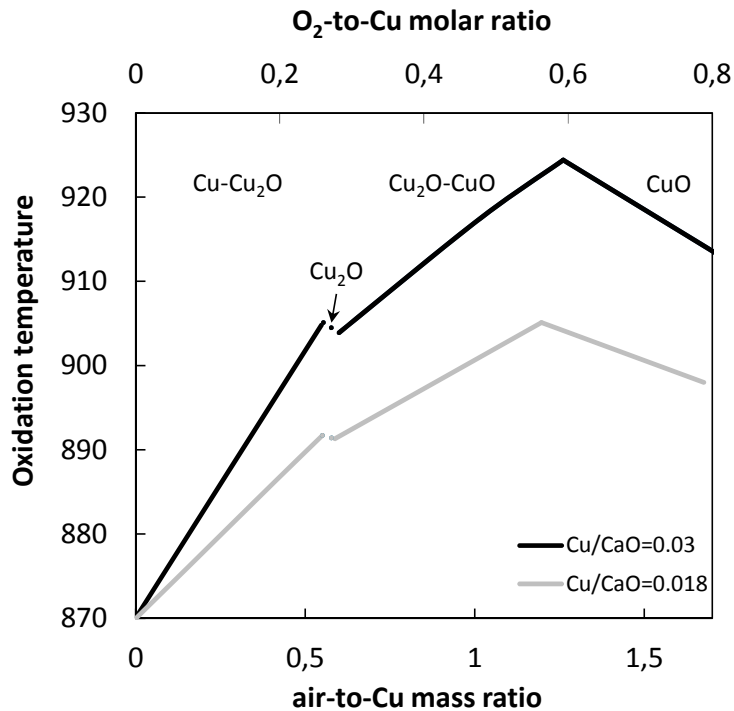


Figure 4. Effect of the air-to- Cu mass ratio and Cu -to- CaO molar ratio at the air reactor inlet on the oxidation temperature. Cu/CaO ratio of 0.03 corresponds to a solid stream flowing to the air reactor containing 3.2 %wt. of Cu , whereas a Cu/CaO ratio of 0.018 corresponds to a Cu content of 2.0 %wt.

In Figure 5, the heat provided to the fuel reactor/calciner per kmol of H_2 consumed as well as the solids circulation in the air reactor are shown for the assumed reference reactor temperatures and assuming complete reduction of the oxygen carrier. For each solids composition, the amount of air used in the air reactor (and therefore the composition of the copper-based solids at the fuel reactor/calciner inlet) is determined to

reach 900°C at the air reactor outlet at sub-stoichiometric and over-stoichiometric proportions (black and grey lines, respectively). On the left-hand side of the graph, the minimum amount of Cu in the solids can be appreciated. This amount corresponds to 1.5% of Cu, which depends greatly on the specific operating conditions assumed for the calculations (e.g. reactor temperatures, gas temperatures at the reactor inlets, Cu oxidation level at the air reactor inlet, amount of Al₂O₃ support in the oxygen carrier). This minimum Cu content corresponds to those conditions where the oxygen carrier has been fully oxidized to CuO in the air reactor so as to reach the desired temperature. Therefore, when operating at this condition of minimum Cu content, operating the air reactor either at sub-stoichiometric or over-stoichiometric air-to-Cu proportions result in the same amount of sensible and reaction heat provided in the fuel reactor/calculator. Starting from this point, when the Cu content is increased for sub-stoichiometric conditions in the air reactor (black lines), a lower air/Cu ratio is required in the air reactor and the fuel reactor/calculator is fed with a CuO/Cu₂O mixture with an increasing Cu₂O content. On the right hand side of the chart, the Cu content is sufficiently high to allow the targeted temperature in the air reactor to be reached with a lower air-to-Cu ratio, generating the Cu₂O/Cu mixture. At the boundary of these two zones, within a limited Cu content range of 2.4-2.5%, two solutions are possible as a consequence of the discontinuity observed in Figure 4 and the target air reactor temperature can be achieved with both the Cu₂O/CuO and the Cu/Cu₂O mixtures.

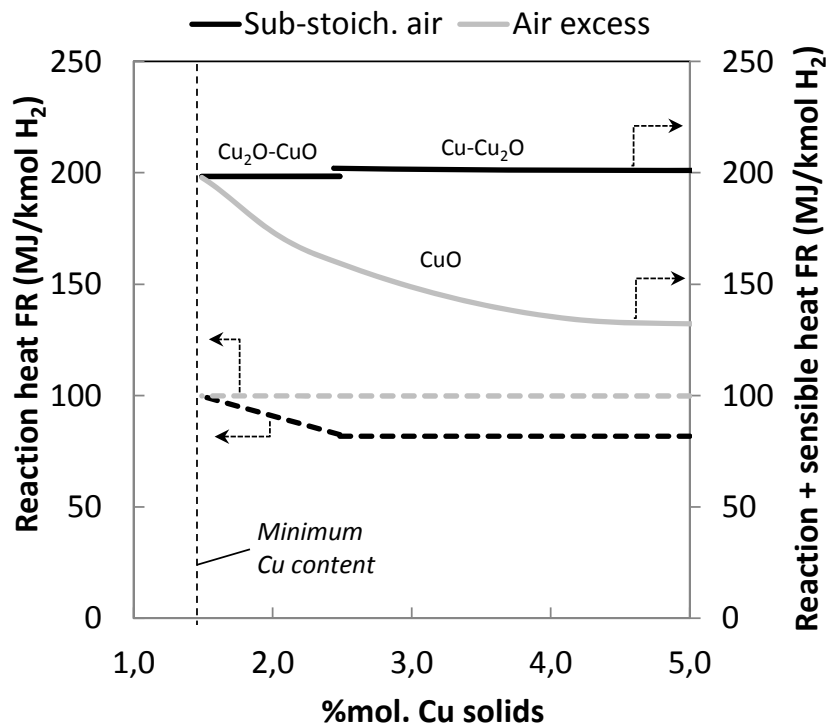


Figure 5. Heat provided in the fuel reactor/calculator (operated at 870°C) per kmole of H₂ consumed in this reactor as a function of the Cu molar content in the solids from the air reactor (operated at 900°C) operating with sub-stoichiometric (black lines) and over-

stoichiometric (grey lines) air-to-Cu ratios. The air reactor operates with an air inlet temperature of 300°C. Hydrogen is assumed to enter the fuel reactor at 870°C and to be fully oxidized to H₂O. Copper is assumed to be fully reduced by hydrogen in the fuel reactor/calcliner.

The energy provided to the fuel reactor/calcliner per kmole of H₂ consumed depicted in Figure 5 is representative of the useful heat available for sorbent regeneration from the fuel consumed in the fuel reactor. The sub-stoichiometric air-to-Cu conditions in the air reactor suggest that the total energy (reaction heat + sensible heat transported by the solids: continuous black line) available is barely affected by the solids composition. This heat (about 200 MJ/kmole_{H₂}) corresponds to the heating value of hydrogen, reduced by the sensible heat associated to air heating in the air reactor from its inlet temperature of 300°C to 900°C. Heat loss as air sensible heat remains constant throughout the entire operation range, except when there is a low Cu content, where a discontinuity again appears. Here, an additional excess of air is needed to achieve CuO formation and this hot excess air is responsible for an additional heat loss in the air reactor exhausts resulting in less energy being available from H₂ oxidation. In any case, the difference in the energy balance is rather small when the system is operated with the Cu₂O/CuO couple rather than with the Cu/Cu₂O one. This difference will completely disappear if air is fed to the air reactor at 900°C, eliminating the sensible heat associated with air heating. However, when over-stoichiometric conditions are employed in the air reactor, and therefore with the Cu/CuO couple over the whole range of Cu content explored, the chemical energy recovered from CuO reduction remains unaltered at around 100 MJ/kmol H₂, which corresponds to the enthalpy of reaction (5) at the temperature of 870°C. As the Cu content in the solids increases, a higher amount of energy is released from its complete oxidation into CuO and the amount of air needed for reaching the temperature of 900°C in the air reactor is therefore higher. As a consequence, the sensible heat associated to the air reactor exhaust gas rises with the Cu content, resulting in a continuous decay in the energy available from H₂ oxidation in the fuel reactor/calcliner.

In Figure 6, the energy provided to the fuel reactor/calcliner per kg of solids circulating in the CLC system and the solids circulation through the air reactor are represented. It can be seen that the higher the energy provided per kg of solids, the lower the solids circulation rate needed in the CLC loop to provide a given thermal power for the regeneration of the SEWGS sorbent. The total heat (reaction heat + sensible heat: continuous black line in this figure) provided by one kg of solids is almost independent of the Cu content in the solids when the system is operating in the Cu-Cu₂O zone. This is because the specific heat of the unreacted Cu with its support (that behaves as inert in such conditions and therefore transfers energy only through its sensible heat) is similar to the specific heat of CaO (0.846 kJ/kg-K vs. 0.855 kJ/kg-K), that also behaves as inert. Therefore, the heat carrying capacity is basically unaffected by the Cu content in this operating area. On the other hand, if the system operates in the Cu₂O-CuO zone, the energy carried by one kg of solids increases because all the Copper reacts in the CLC

loop. By decreasing the Cu content in the solids, an increasing amount of Cu is completely oxidized to CuO in the air reactor. In this way the chemical energy potential of the oxygen carrier is fully exploited. For the lowest feasible Cu content in the solids going to the air reactor and assuming sub-stoichiometric air-to-Cu proportions in this reactor, all the copper is oxidized to CuO and the energy transported per kg of solids increases by about 18% with respect to the conditions where Cu₂O and Cu coexist, resulting in an equivalent reduction of the solids circulation between the fuel and air reactors. A minimum solids circulation value of around 75 kg/m²·s (calculated assuming a superficial velocity of the gas at the air reactor outlet of 4 m/s) is found when working under these sub-stoichiometric conditions and at a minimum Cu content, which is higher than the solids circulation conditions typically found for large-scale CFB reactors. Hence, working with reasonable solids circulation values of CFB boilers of 10-20 kg/m²·s implies working with air excess and full oxygen carrier oxidation to CuO at the air reactor outlet, which results in an increased heat loss associated to the air reactor exhaust gas as observed in Figure 5.

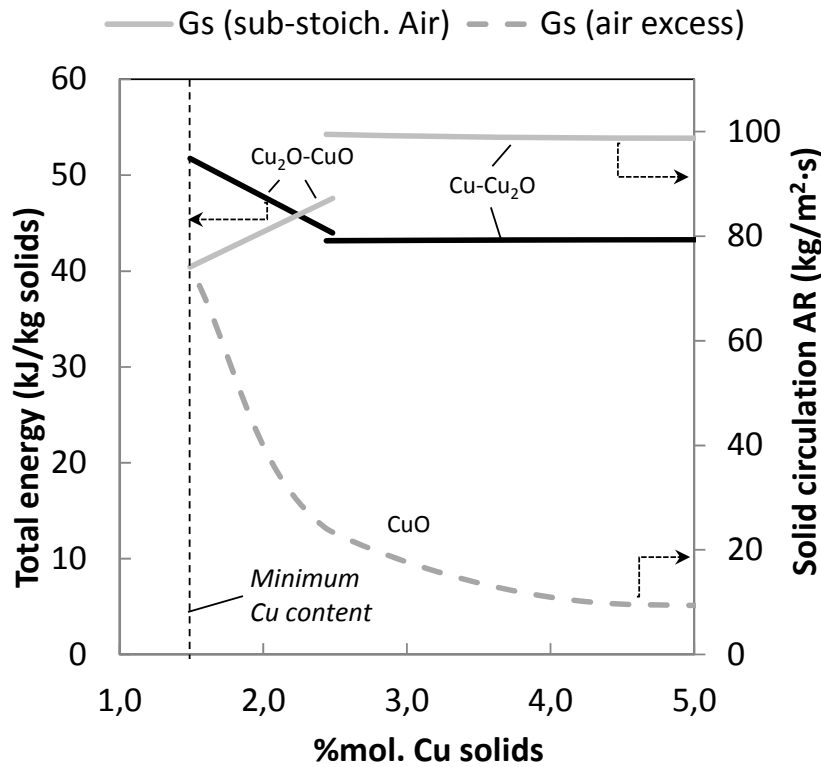


Figure 6. Heat provided to the fuel reactor/calcliner (operated at 870°C) per kg of circulating solids (primary ordinate axis) and solid circulation (secondary ordinate axis) in the air reactor (operated at 900°C) as a function of the Cu molar content in the solids from the air reactor. Heat to the fuel reactor is calculated with the air reactor operating with fully reduced Cu at the inlet and with an inlet air temperature of 300°C. Hydrogen is assumed to enter the fuel reactor at 870°C and to be fully oxidized to H₂O. Copper is assumed to be fully reduced by hydrogen in the fuel reactor/calcliner. Specific solids

circulation calculated assuming a gas superficial velocity at the air reactor outlet of 4 m/s.

4.2. Reference case description

Based on the analysis above, a reference case has been chosen that assumes that the reducing gas used in the fuel calciner is exclusively the COG from the integrated steel mill. Table 3 indicates the temperature, flow rate and composition of the solid and gas streams obtained by solving the mass and heat balances of the complete Ca-Cu looping process, on the basis of the assumptions of Table 2. The heat released from the oxidation of the COG in the fuel reactor will allow the CaCO_3 required in the ironmaking process and the CaCO_3 formed by the SEWGS to be calcined. In this case, it is considered that complete oxidation of COG occurs in the fuel reactor/calciner, while oxygen carrier conversion at this reactor outlet has been assumed to be equal to 0.05 (i.e. equivalent to a $\text{Cu}_2\text{O}/\text{Cu}$ molar ratio of 0.045 at the reactor outlet).

For each tonne of hot roll coil, a mass of 725 kg of gas (stream 1 in Figure 1) is fed to the SEWGS reactor, resulting from the mixing of 582 kg of BFG (around 27% of total BFG produced per tonne of steel in the steel mill) and 143 kg of steam used to achieve the target $\text{S}/\text{C}=1$. Performed at 600°C , the carbonation reaction (Eq. 2) will be sufficiently fast and, as can be seen in Figure 2 and Figure 3, a very high conversion of CO to H_2 (Eq. 1) and a CO_2 capture ratio of 99% is achieved. A mass of around 2529 kg (stream 5), mainly composed of CaO, arrives at the SEWGS reactor at 870°C coming from the fuel reactor calciner. Moreover, it is considered that the make-up stream of 282 kg of CaCO_3 (stream 3 in Figure 1) is fed to the process at the SEWGS reactor inlet at 250°C after being preheated using the low temperature heat available in the process, to be heated in this reactor up to 600°C and so reduce the heat demand in the fuel reactor/calciner. A mass of 354 kg of product gas is obtained at 600°C , containing around 26 vol.% of H_2 and a negligible content of CO_2 . This decarbonized fuel gas product could be delivered throughout the steel mill to provide heat and/or power, or to boost steel production by the DRI process with nearly zero CO_2 emissions, but such a level of detailed integration is beyond the scope of this conceptual study. However, the potential of this last application has been quantified by calculating the maximum amount of iron that could be produced from hematite (Fe_2O_3), if the H_2 produced in the proposed Ca-Cu process were fully oxidized. Considering the amount of H_2 in stream 2, a mass of about 183 kg of reduced iron could be additionally obtained following the DRI route in parallel to the conventional steel mill producing 1 tonne of finished steel. Since both WGS and carbonation reactions are highly exothermic, around 1.8 GJ must be removed from the SEWGS reactor in order to maintain the operation of this stage at 600°C . As mentioned before, this high quality energy can be efficiently recovered by producing high pressure steam to generate electric power in the power plant. This result clearly indicates the major benefits that the novel process can offer.

From the SEWGS stage, and after its separation from the product gas in a downstream cyclone, a mass of 3182 kg is obtained (stream 7), containing around 35 wt.% of

CaCO₃. In order to reduce the energy demand of the calcination stage, a two stage preheating system is proposed to increase the temperature of stream 7. This heating system can be either based on fluidized bed contactors or on suspension preheaters typically used in cement plants [96]. The high-temperature gas generated in the air reactor can be used in a first heating stage and the CO₂-rich gas obtained in the fuel reactor at 870°C can be used in the second stage to heat the solids up to temperatures of around 750°C avoiding any previous carbonate decomposition. In the first of the preheating stages, the use of a CO₂-free gas as a hot source in a temperature range of 600-660°C may result in the calcination of a minor fraction of the CaCO₃ if particles remain for prolonged times in contact with such gas. In case equilibrium compositions were achieved, it has been estimated that around 3% of the CaCO₃ entering into this preheater would decompose, which would result in a CCR decrease of 0.6%-points. However, due to the low operating temperatures in this preheater that would cause very low kinetics for the calcination reaction, the impact of the CaCO₃ decomposition in this first preheater on the global balances would be negligible and could be neglected. Consequently, for the reference case and without considering partial CaCO₃ calcination in this first solid preheating section, the sensible heat from these two hot product streams is sufficiently high to heat the solids fed to the fuel reactor up to 721°C .

Table 3. Temperature, mass and composition of the streams of the Ca-Cu looping process represented in Figure 1, assuming the conditions listed in Table 2.

Stream	1	2	5	7	8	9	10	11	12	13
T, °C	250	600	870	600	600	870	870	300	900	900
Mass, kg/t _{steel}	725	354	2529	3182	78	801	66228	997	770	66456
Moles, kmole/t _{steel}	27.2	18.7	44.3	47.1	8.0	24.0	1159.2	34.7	27.7	1145.0
Composition (wt.%)										
CaCO ₃	-	-	-	35.5	-	-	-	-	-	-
CaO	-	-	93.8	59.6	-	-	93.8	-	-	93.5
Cu	-	-	3.0	2.6	-	-	3.0	-	-	0.3
CuO	-	-	-	-	-	-	-	-	-	-
Cu ₂ O	-	-	0.3	-	-	-	0.3	-	-	3.4
Al ₂ O ₃	-	-	2.9	2.3	-	-	2.9	-	-	2.9
Composition (%mol)										
H ₂	2.6	26.3	-	-	59.5	-	-	-	-	-
CO	15.8	0.1	-	-	3.8	-	-	-	-	-
CH ₄	-	-	-	-	23.0	-	-	-	-	-
H ₂ O	31.5	23.1	-	-	4.0	39.6	-	2.6	3.2	-
CO ₂	15.6	0.3	-	-	1.0	58.5	-	-	-	-
O ₂	-	-	-	-	0.2	-	-	20.4	-	-
N ₂	34.5	50.1	-	-	5.8	1.9	-	76.1	95.6	-

C+	-	-	-	-	2.7	-	-	-	-	-
Ar	-	-	-	-	-	-	-	0.9	1.1	-

In the fuel reactor, solids from the SEWGS reactor (stream 7) are mixed with the solids stream coming from the air reactor, which contains the partially oxidized Cu material in the form of Cu/Cu₂O, as explained later on in this section. The heat necessary to heat up solids from the SEWGS reactor up to 870°C as well as to carry out the calcination of the CaCO₃ contained in this solid stream is supplied by the exothermic reduction of the Cu₂O with the COG (stream 8) together with the sensible heat contained in stream 13 that comes from the air reactor at 900°C. The COG is assumed to be fed into the fuel reactor at 600°C. The calcination reaction is limited by the CaCO₃/CaO/CO₂ equilibrium, which is strongly affected by the temperature and the partial pressure of CO₂ in the reaction atmosphere [84]. A minimum temperature of 870 °C ($P_{\text{CO}_2\text{eq},870^\circ\text{C}}=0.65$) in the fuel reactor is assumed in order to ensure the complete calcination of the CaCO₃ fed into this reaction stage with enough solids residence time in this reactor (i.e., around 3-5 min of solid residence time is needed according to [97] for this calciner temperature, which is 7°C above the temperature corresponding to the equilibrium for the CO₂ partial pressure of 0.59 bar present at the fuel reactor outlet). As mentioned before, it is considered that at 870 °C, the complete oxidation of the COG to CO₂ and H₂O is reached, while a small fraction of unconverted Cu₂O remains in the solid at the fuel reactor outlet. A mass of 801 kg (with a content of 58.5% of CO₂) is obtained as gaseous product (stream 9 in Figure 1) at 870 °C, from which CO₂ can be easily purified, and made suitable for transport and storage. The amount of CO₂ captured corresponds to approximately 31% of total CO₂ emissions from the reference integrated steelworks. The fuel reactor calciner operates as a bubbling bed and it must be designed to allow for a well-mixed section where the simultaneous CuO reduction and CaCO₃ calcination take place. Therefore, no segregation of either Cu- and Ca-based particles is assumed to occur in this section in the reference case. Therefore, the solids streams directed to the air reactor (stream 10) and to the SEWGS reactor (stream 6) will have the same composition. In a different section (or reactor, not shown here for simplicity), there will be an effective solids segregation in order to obtain a purge of 158 kg of pure CaO (stream 4 in Figure 1) for its use in the steel mill, as explained above.

A high proportion of inerts (CaO) circulating between the fuel reactor and the air reactor is proposed to increase the heat transport capacity of the solids leaving the air reactor (stream 13) to the fuel reactor. A chemical loop using iron oxides to carry out the CaCO₃ calcination could also arise as a promising alternative, since iron oxides have a very high heat transfer capacity [44]. However, their reduction with the COG in the fuel reactor is almost neutral ($\Delta H_{\text{red,H}_2}=-5.8$ kJ/mol) and the high temperatures achieved in the air reactor (higher than 1000°C) make it necessary to include a very effective segregation stage downstream the fuel reactor-calciner to avoid the feed of Ca-based solids to the air reactor and the subsequent decrease in their sorption capacity after a

few cycles. For the reference case and as indicated before, a Cu/CaO molar ratio of 0.03 is assumed in stream 10 that comes into the air reactor, which means a total Cu content of 3.2 wt.% in this solids stream. Under these conditions, the oxidation stage needs to be carried out with an air/Cu mass ratio of around 0.46 in order to limit the oxidation temperature at 900 °C, which falls in the Cu-Cu₂O region, as shown in Figure 4. In order to supply the air demanded for the Cu oxidation, a mass of 997 kg of air preheated at 300 °C (stream 11) is fed into the air reactor. Under these circumstances, a solid/gas mass ratio of around 66 would be needed in the air reactor, which corresponds to a solids circulation of around 99 kg/m²·s through the air reactor, assuming a gas superficial velocity of 4 m/s in this reactor. This solids circulation is significantly higher than the typical circulation rate in conventional CFB boilers and its feasibility should be experimentally verified. After the separation of the solids (stream 13) from the product gas in a downstream cyclone, they are directed to the fuel reactor to complete the chemical loop. A mass of 770 kg of O₂-depleted air (stream 12) is obtained as oxidation product, which is highly suitable for use in preheating stages and/or for heat recovery and power generation.

Energy introduced into the Ca-Cu chemical looping process with the COG and BFG streams is distributed among sensible and reaction heats as indicated in the Sankey diagram shown in Figure 7. In other words, energy introduced into the process ends up as chemical energy in the H₂ output, as high temperature heat inside the SEWGS reactor, as sensible heat in the gas streams from the whole process and as energy for calcining the fresh CaCO₃ introduced into the system (available as CaO for use in the steel plant). As can be seen in Figure 7, 69 % of the total thermal input introduced into the process is fed to the fuel reactor with the COG. The remaining 31 % of the total thermal input is BFG introduced into the SEWGS reactor, which represents around 27% of the total BFG produced in the integrated steelworks, as explained above. If the H₂ output from this process was used for the direct reduction of iron ore, the amount of direct iron produced from DRI might represent around 18.3 % of the steel produced in the integrated steelworks. As can be appreciated from Figure 7, a larger fraction of heat (i.e. almost 39.5 % of the total thermal input) is recovered as high temperature heat in the SEWGS reactor, which can be used for producing electricity. A significant energy output (11.3%) is used for CaO production, calculated as the reaction heat of CaCO₃ calcination. Chemical energy (LHV-based) from the H₂ produced is 26.8 % of the total thermal input introduced with BFG and COG, which measures the Cold Gas Efficiency (CGE) of the system. Finally, as appreciated in this figure, there is a noticeable fraction of sensible heat in the exhaust gases that can be still recovered after heating up incoming fuel gases up to the reactor feeding temperatures shown in Table 2. This residual heat accounts for 22.4 % of total fuel thermal input introduced into the process, and represents a potential heat source for steam production together with the heat recovered inside the SEWGS reactor. These heat sources account for more than 60% of the thermal power introduced with COG and BFG into the Ca-Cu process, highlighting the possibility of coupling the proposed process with a steam production system for

producing power in a steam turbine. Additional information about the performance of this reference case study can be found in Table 4.

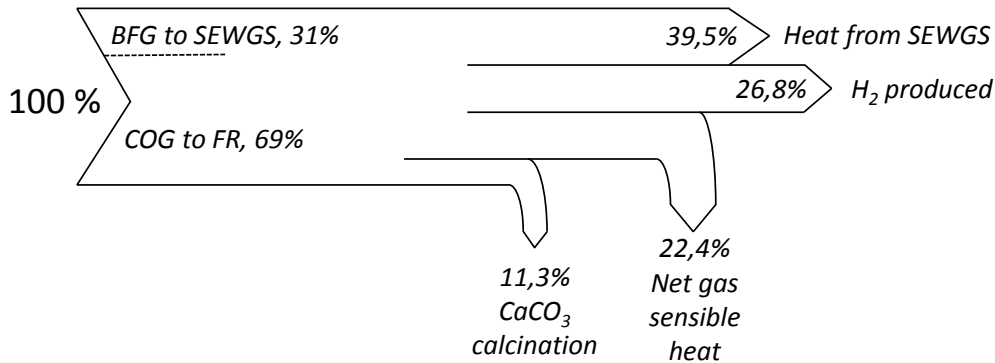


Figure 7. Sankey diagram of the energy balance of the process for the reference case conditions.

4.3. Sensitivity analysis

4.3.1. Effect of operating temperature in the fuel reactor calciner

One of the objectives of the proposed concept to ensure that CaCO_3 calcination occurs thanks to the energy released from reducing CuO or Cu_2O present in the solid material almost completely to Cu (i.e. maintaining the $\text{Cu}_2\text{O}/\text{Cu}$ ratio indicated in Table 2), as well as to the sensible heat released by cooling high temperature solids from the air reactor. As mentioned before, the operating temperature of 870°C chosen for the fuel reactor calciner of the reference case study was 7°C above that corresponding to the CaO/CaCO_3 equilibrium temperature for the CO_2 partial pressure in this reactor of 0.59 bar. To facilitate the calcination of CaCO_3 in this reactor and to reduce the residence time needed to achieve complete regeneration, a higher margin with respect to the equilibrium may be adopted. For example, a minimum temperature difference with respect to that of equilibrium of around $15\text{-}20^\circ\text{C}$ is proposed [98]. On the basis of this temperature margin, the effect of increasing the operating temperature in the fuel reactor calciner up to 880°C was analyzed. Table 4 summarises the results obtained from this analysis (referred to as Case Tcalc+ in the table). As can be appreciated, the effect of this increased fuel reactor temperature is reflected in the solids circulation between the air reactor and the fuel reactor, which increases by 50% due to the higher thermal input needed in this latest reactor to fulfill a higher operating temperature and to the lower temperature difference of the heat carrying solids which circulate between the fuel reactor/calciner and the air reactor. The gas/solid mass ratio at the air reactor inlet increases up to a value of 100 in this case, which means a solid flow of $150 \text{ kg/m}^2\cdot\text{s}$ in this reactor (calculated assuming a superficial gas velocity of 4 m/s) which is much higher than the usual operation range of this type of circulating fluidised bed reactor [99]. From an overall plant performance point of view, a negligible effect is observed

when increasing the operating temperature of the fuel reactor calciner. A global CGE of 26.5 % is obtained, considering the total fuel thermal input into the process. With respect to the CO₂ emissions from the whole integrated steel mill [4] (i.e. from the power plant, blast furnace and sinter plant), the proposed Ca-Cu chemical looping process under these conditions could capture almost 31 % of CO₂.

4.3.2. Effect of excess air in the air reactor

The effect of working with excess air in the air reactor was also analyzed (Case Air+ in Table 4). In this case, the conditions of the adiabatic air reactor working at 900°C are fulfilled by feeding in an air flow rate higher than that needed for the complete oxidation of Cu to CuO. In such operating conditions, excess air basically acts as a thermal ballast in this reactor reducing the outlet temperature. As can be appreciated in Table 4, the amount of air fed into the air reactor in this case (i.e. the air/FR fuel molar ratio) is twice that of the reference case, resulting in an air/Cu mass ratio of 2.1. As a consequence of these operating conditions, the solids circulation needed between the fuel reactor and air reactor is reduced noticeably to a value of 19.1 kg/m²·s (Table 4). However, hydrogen production in the SEWGS reactor decreases by 30 % and so does the CGE, which drops to 20.7%. This is due to the fact that, as shown in Figure 6, the sensible heat in the air reactor exhaust gases increases significantly, causing an increase in the gas sensible heat from 22.4 to 37.2% of the input heat. This indicates that an increasing fraction of the fuel heating value introduced in the fuel reactor is ultimately used to produce hot air from the air reactor, reducing the heat available for heating the solids. As a consequence, less CaCO₃ can be calcined in the fuel reactor/calciner and so less BFG can be converted in the SEWGS, which results in a decrease in the amount of H₂ produced.

4.3.3. Effect of fuel partial oxidation in fuel reactor/calciner

As already mentioned, the complete reduction of Cu₂O-CuO compounds into Cu in the fuel reactor calciner cannot be achieved by oxidizing completely the fuel used in this reactor. Low amounts of unburnt compounds coming from the incomplete combustion of fuel gas used in the fuel reactor calciner would be present in the exhaust gas if the complete reduction of Cu-based material into Cu occurs. The effect of the complete reduction of the Cu-based material in the fuel reactor/calciner on the global process performance was analyzed. The amount of unconverted compounds at fuel reactor exhaust is adjusted to achieve a CO₂ concentration of 90% on a dry basis, which is suitable for an efficient CO₂ purification unit with high CO₂ capture and a high recovery of the incondensable fuel species.

The performance results obtained for these operating conditions with fuel partial oxidation (POX) are shown in Table 4 and are referred to as Case FR-POX. A loss of a fraction of the chemical energy of the COG used as fuel in the fuel reactor calciner would entail a reduction in the amount of CaCO₃ that could be calcined in this reactor and therefore in the BFG that could be fed into the SEWGS reactor. Consequently, the amount of H₂ produced in this case would be reduced. According to the results shown in

Table 4, almost 3 % less of BFG could be processed with respect to the reference case, which would entail a reduction in the CGE to 25%. Moreover, since the system keeps on working in the Cu-Cu₂O zone at air reactor outlet, the solids circulation through this reactor would remain at a very high value of 99.6 kg/m²·s.

4.3.4. Effect of increased Cu/Ca ratio

In this case, the effect of working with a higher amount of Cu material in the circulating solids and with higher content of oxidized Cu in the fuel reactor/calciner was analyzed. In the reference case, the Cu₂O content at fuel calciner reactor outlet was limited to 0.045 moles of Cu₂O per mole of Cu (see Table 2), which results in a total Cu₂O content in the solids bed of the fuel reactor/calciner of around 0.3 %wt. Such a low fraction of oxidized oxygen carrier in the bed may require a very large solids inventory to achieve complete fuel oxidation. An increase in the amount of Cu₂O in the solid bed material of the fuel reactor calciner of around 4 %wt. was considered in this case for ensuring the complete conversion of COG in this reactor. Based on the modelling results reported in [100], it was estimated that such a concentration of oxidized Cu-based oxygen carrier in the fuel reactor should be enough to ensure complete fuel oxidation with a reasonable solids inventory. Moreover, in order to reduce the solids circulation rate between the fuel calciner reactor and air reactor, the molar Cu/CaO ratio in the solids was adjusted so that the air reactor operated close to the stoichiometric conditions (i.e. with complete Cu oxidation and no air excess in the air reactor). The results obtained for this case (referred to as ‘Cu/Ca+’) are included in Table 4.

As can be seen in Figure 6, working exclusively with CuO at the air reactor outlet maximizes the amount of oxygen transferred per unit of mass of solids circulating into the fuel reactor/calciner, which allows reducing the solid circulation needed in the system. From the results shown in Table 4 for this case, it can be seen that solids circulation at the air reactor outlet is greatly reduced by about 40% with respect to the reference case, reaching a value of 61.8 kg/m²·s. One of the negative effects of increasing the Cu/Ca ratio and the amount of Cu₂O at the fuel calciner reactor outlet is that a greater amount of Cu₂O is sent to the SEWGS reactor. In this reactor, Cu-based material acts as a thermal ballast decreasing the heat available from this reactor and oxidizing part of the H₂ formed. As a result, H₂ production diminishes and so does the CGE. As can be appreciated in Table 4, the CGE in this case is reduced by around 3%-points with respect to that of the reference case, reaching a value as low as 23.6%.

4.3.5. Effect of increased Cu/Ca ratio and solids segregation

When increasing the amount of Cu material in the circulating solids, the segregation of solids in the fuel reactor calciner becomes important to prevent oxidized Cu-based material passing into the SEWGS reactor and so maximizing the H₂ produced in the system. This analysis considers the possibility of separating the Cu/Al₂O₃ material completely from CaO in the segregator, so that pure CaO can be sent to the SEWGS.

Taking as reference the Cu/Ca⁺ case, because of the absence of Cu₂O or CuO at the SEWGS reactor inlet, H₂ production is noticeably raised by about 14% in this case with respect to the case Cu/Ca⁺, which results in a CGE as high as 27.1%. Moreover, due to the fact that exclusively CaO is sent to the SEWGS reactor the amount of heat recovered from this reactor is reduced as can be appreciated in Table 4.

Table 4. Main performance results for the reference case and those obtained from the sensitivity analysis on the operating temperature in the fuel reactor/calciner (case Tcalc+) and on the air excess (case Air+), as well as on partial oxidation of fuel in the fuel reactor calciner (case FR-POX) and on solid composition without and with segregation (Cu/Ca+ and Cu/Ca+segr cases respectively)

	Reference case	Tcalc+	Air+	FR-POX	Cu/Ca+	Cu/Ca+segr
Fuel reactor temperature [°C]	870°C	880°C	870°C	870°C	870°C	870°C
Cu-to-CaO molar ratio at air reactor inlet	0.031	0.031	0.031	0.031	0.036	0.039
Cu-to-CaO molar ratio at SEWGS reactor inlet	0.031	0.031	0.031	0.031	0.036	0
O ₂ content at air reactor outlet [%mol]	0	0	11.4	0	1.8	1.8
<i>Energy Balance</i>						
Thermal fuel input into the SEWGS reactor [MW _{LHV}]	1384	1367	968	1237	1424	1384
Thermal fuel input into the FR [MW _{LHV}]	3080	3080	3080	3080	3080	3080
Heating value of H ₂ produced [% of total fuel input]	26.8	26.5	20.7	25.0	23.6	27.1
Heat available from SEWGS reactor [% of total fuel input]	39.5	39.6	29.7	36.2	41.7	38.7
Sensible heat of gases [% of total fuel input]	22.4	22.5	37.2	21.4	23.5	23.0
Heat needed for calcining CaCO ₃ make-up in the FR [% of total fuel input]	11.3	11.7	12.4	11.7	11.2	11.3
Residual heating value of FR exhaust [% of total fuel input]	--	--	--	5.8	--	--
<i>General stream information</i>						
Solid/gas mass ratio at AR inlet	66.4	100.1	14.3	66.3	41.8	40.9
G _s at air reactor outlet* [kg/s/m ²]	99.8	150.2	19.1	99.6	61.8	60.4
Air/FR fuel molar ratio	4.3	4.3	8.8	4.1	4.9	4.7
Solids/FR fuel mass ratio	892.8	1322.2	400.9	830.7	650.3	604.5
Cu/Cu ₂ O/CuO content in solids from AR [%mol]	0.25/1.36/-	1.07/0.94/-	-/-/2.90	0.44/1.24/-	-/-/3.41	-/-/3.68
Cu/Cu ₂ O/CuO content in solids from fuel reactor calciner to AR [%mol]	2.69/0.12/-	2.69/0.12/-	2.69/0.12/-	2.89/-/-	0.21/1.64/-	0.03/1.87/-
Fraction of total BFG sent to SEWGS [%]	26.8	26.4	18.7	23.9	27.6	26.8
<i>General performance parameters</i>						
Hydrogen output at SEWGS outlet [MW _{LHV}]	1195	1180	836	1080	1065	1209
H ₂ production [m ³ N/t steel]	110	109	77	99	98	111
CO ₂ captured [kg CO ₂ at calciner outlet/ t steel]	617	612	505	552	628	617

CO ₂ capture ratio [% with respect to total CO ₂ emissions in steel mill]	31.2	31.0	25.6	27.9	31.8	31.2
Additional amount of Fe produced by direct reduction of Fe ₂ O ₃ with H ₂ produced [ton/ton steel]	0.183	0.181	0.128	0.165	0.163	0.185

* evaluated assuming a gas superficial velocity of 4 m/s at air reactor outlet

Conclusions

A comprehensive conceptual design of a novel Ca-Cu looping process for producing a H₂-enriched fuel gas via the sorption enhanced water gas shift (SEWGS) of blast furnace gas (BFG) using CaO as CO₂ sorbent has been carried out. Operating windows for the different reactions steps required in the process have been found to be consistent with the state of the art of the gas-solid reactions required in the process. On the basis of a reference case operated at reasonable conditions (i.e., the SEWGS stage performed at 600°C, regeneration of the Ca-based sorbent carried out at 870°C using as fuel gas exclusively COG from the steel mill, and the oxidation stage carried out under sub-stoichiometric conditions to limit the reactor temperature up to 900°C), it is estimated that around 27% of the BFG can be decarbonized in the SEWGS reactor, producing 110 Nm³ of H₂ per tonne of steel and reaching a CO₂ capture ratio of 31% with respect to the total carbon emissions in the steel mill. The SEWGS stage carried out at 600°C with a S/C molar ratio of 1 allows high H₂ yield in the product gas (up to 96 vol.%H₂, N₂ free and on a dry basis) and high CO₂ capture efficiency (around 95%) to be achieved with moderate steam consumption and reasonably fast reaction rates. The air-to-Cu ratio and the inerts content in the oxidation stage strongly affect the proportion of Cu/Cu₂O/CuO formed during the oxidation as well as the maximum temperature achieved in the air reactor. The targeted temperature in the air reactor of 900°C can be achieved either by performing under sub-stoichiometric or under over-stoichiometric conditions. At lower air-to-Cu ratios, the Cu is not completely oxidized to CuO, and therefore, the chemical energy potential of the oxygen carrier between the air reactor and the fuel reactor is not fully exploited. However, the heat loss associated to the exhaust gas of the air reactor decreases, since a lower flow of air is needed, resulting in an increase in the energy available from the COG oxidation in the fuel reactor/calciner. This means that higher amounts of CaCO₃ can be calcined, which allows a higher H₂ production in the SEWGS stage to be achieved. Nevertheless, the Cu oxidation under sub-stoichiometric conditions requires higher solids circulation rates in the CLC loop (around 100 kg/m²s) to provide a given thermal power for the CaCO₃ calcination, which are far above the typical rates for CFB boilers (between 10 and 30 kg/m²s). The analysis also shows that the increase in the Cu/Ca ratio in the circulating solids and assuming an effective segregation of the Ca- and Cu-based solids in the fuel reactor-calciner allow high H₂ production and high CO₂ capture ratios to be achieved with significantly lower solids circulation rates between the air reactor and the fuel reactor (around 60 kg/m²s). A Sankey diagram shows that around 27% of the energy introduced into the process ends as chemical energy in the H₂ output, while more than 60% of the thermal input ends as high temperature heat generated in the SEWGS reactor and as sensible heat in the exhaust gases that can be efficiently recovered in a steam cycle to generate electric power. These results confirm the potential of this novel Ca/Cu looping process as a pre-combustion CO₂ capture technology for H₂ production and power generation in steel mills.

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