Integration of a fluidized-bed Ca-Cu chemical looping process in a steel mill

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Abstract

An integrated full system to decarbonize a steelworks plant is discussed, using high temperature Ca-Cu chemical looping reactions. A H₂-enriched gas is produced through sorption enhanced water-gas-shift (SEWGS) of blast furnace gas (BFG) using a CaO-based CO₂ sorbent. The resulting CaCO₃ is regenerated with heat from CuO reduction with N₂-free steel mill off-gases. The high temperature operation allows for an effective integration of a power steam cycle that replaces the steel mill power plant. The proposed fluidised-bed process facilitates a solids segregation step to separate the O₂ solid carrier from the CO₂ sorbent. The CaO-rich stream separated could be used in the steelmaking process thereby removing the lime plant. Balances of a steel mill integrated with the Ca-Cu process are solved and compared with those obtained for a reference steelworks plant with post-combustion CO₂ capture through amine absorption. Using exclusively steel mill off-gases in the Ca-Cu process can reduce CO₂ emissions by 30%. Moreover, the H₂-gas could produce about 10% of additional iron through a Direct Reduced Iron process. In contrast, by adding natural gas for CuO reduction, almost all the BFG can be decarbonised and an overall CO₂ capture efficiency in the steel plant of 92% can be achieved.

Keywords: CO₂ capture, steelworks, blast furnace gas, CaO, CuO/Cu, looping

Notation

e_{CO_2}	CO ₂ emissions
P_{el}	Net electric consumption in the steel mill
q	Primary energy consumption

Greek symbols

η	Electric efficiency
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Acronyms

APH	Air preheater
ASU	Air separation unit
BF	Blast furnace
BFG	Blast furnace gas
BOF	Basic oxygen furnace
BOFG	Basic oxygen furnace gas
CCS	Carbon capture and storage
CLC	Chemical looping combustion
COG	Coke oven gas
DCC	Direct contact cooler
DRI	Direct reduced iron
ECO	Economiser
EVA	Evaporator
FR	Fuel reactor
FWH	Feedwater heater
HP	High pressure
HRC	Hot roll coil
LP	Low pressure
MEA	Methylamine
NG	Natural gas
RH	Reheater

SC	Steam cycle
SER	Sorption enhanced reforming
SEWGS	Sorption enhanced water gas shift
SH	Superheater
SPECCA	Specific primary energy consumption per unit of CO ₂ avoided
TRL	Technology readiness level
WGS	Water gas shift

1. Introduction

Steelmaking is the main energy-consuming industry in the world, accounting for 27% of the total CO₂ emissions from industrial processes [1]. Over the last decades, the world steel production has experienced a great increase and it is expected to keep on rising in the next years. As a mature industry, steelmaking has done a substantial effort in order to reduce its energy demand from 23 GJ per tonne of liquid steel produced in 1970 to 20GJ/t in 2015 for modern steelworks, through energy efficiency, process optimization and fuel substitution measures [2,3]. However, the specific CO₂ emissions for the main existing routes of steel production from raw minerals have passed well beyond the limit of what is considered a climate-sustainable process and breakthrough technologies are therefore needed in order to significantly reduce the CO₂ emissions associated to this industry [4].

Around 70% of the steel produced nowadays is obtained via the combination of the blast furnace (BF) and basic oxygen furnace (BOF) route [5]. Ironmaking is responsible for 80% of the total carbon input in a BF-BOF steel mill, but only less than 30% of the CO₂ emitted is attributed to this part of the process [6]. Most of the by-product gases, i.e., the blast furnace gas (BFG), coke oven gas (COG) and basic oxygen furnace gas (BOFG), are used in different points of the steel mill as fuel gases in order to improve the energy efficiency of the process. Several alternatives have been proposed to improve the efficiency of the BF-BOF route, such as: increasing the size and productivity of the blast furnace or recycling a great amount of scrap at the BOF[7]. However, these innovations can only lead to a reduction of around 15% in CO₂ emissions compared to current levels of reference steel mills [8]. The direct reduction iron (DRI) route has been also developed to achieve further reductions in carbon emissions [7]. In this process, the reduction of iron ore is carried out in a solid state below the fusion temperature of pure iron, leaving gangue constituents (non-valuable minerals) in the sponge iron, which must be separated mainly in the electric arc furnace (EAF). Commercialized DRI technologies include the Midrex and Hylsa processes, which use natural gas rather than coal for iron ore reduction and eliminate the need for sintering and coke plants. The DRI process can reduce the CO₂ footprint of crude steel by 20-25% compared to the best performing BF-BOF steel production route [7,9].

Despite these innovations, only carbon capture and storage (CCS) has the potential to drastically reduce the CO₂ emissions far beyond what is nowadays possible in large stationary sources [4] and achieve the climate change mitigation targets (i.e., a 50% reduction in CO₂ emissions by 2050 and a 100% reduction by 2100) recently agreed at COP22 held in Marrakech in 2016 [10]. The deployment in steel production of the CCS technologies considered commercial-ready or already demonstrated at large pilot scale is nowadays hampered by the high cost for the CO₂ capture [11]. This cost is mainly related to the gas separation step and depends on the high costs of main equipment and utilities required (e.g. amine recovery unit and steam use in mature solvent-based systems, air separation unit (ASU) in oxy-fuel systems, cost/life ratio of functional materials in emerging membrane and solid sorbent systems, etc), and on the high operating costs (e.g. make-up flow of functional materials, pressure drops in multi-stage membrane separation process, solvent recovery in absorption columns, etc) [12]. The European Ultra-Low CO₂ Steelmaking (ULCOS) project has developed

novel CCS routes aimed at reducing by at least 50% the CO₂ emissions compared to the steelmaking benchmark [7]. The Top Gas Recycling (TGR) is one of the most promising technologies, which consists in injecting pure O₂ or enriched air instead of air into the furnace, thereby eliminating (or greatly reducing) the presence of N₂ in the BFG. As the concentration of CO₂ in the top gas is higher, its separation from the BFG in a subsequent stage is facilitated. The reducing gases (CO and H₂) are then recirculated back to the blast furnace, lowering the need for coke for the BF operation. CO₂ emissions can be reduced down to 76% compared to those produced by a conventional BF depending on the recycle rate used, although this value does not take into account the need for substitute fuels for other process operations and the additional energy required for the O₂ production [7]. Another CO₂ reduction programme is the Japanese COURSE50, which was focused on reducing carbon emissions by using alternative reducing agents such as, hydrogen, natural gas or biomass (instead of coke) and by developing chemical absorption and physical adsorption techniques to separate the CO₂ from the blast furnace gas [13].

The application of pre-combustion capture systems based on CO₂ separation [14] in steel industry, such as the Sorption Enhanced Water Gas Shift (SEWGS), can be particularly attractive to decarbonize the blast furnace gas (BFG), while a higher-LHV fuel gas is produced that can be easily integrated throughout the steel mill [15]. In the SEWGS, a high-temperature sorbent (typically a hydrotalcite-like material) that also acts as WGS catalyst removes the CO₂ from the gaseous phase as soon as it is produced [16]. The WGS equilibrium is then shifted towards a higher production of H₂ according to the Le Chatelier's principle. As a result, the almost total conversion of CO can be achieved at temperatures above 400 °C. The CO₂ sorbent is then regenerated by a thermal-swing procedure or by purging with steam at low pressure [17,18]. The demonstration of this process in multiple fixed beds at TRL6 is the objective of the ongoing EU project STEPWISE [19]. However, CaO-based materials have been also proposed as CO₂-sorbents in pre-combustion applications since the CaO carbonation rate is fast at temperatures above 600 °C, carbon deposition during the SER/SEWGS reactions can be considered negligible due to the presence of CaO and calcium-based solids can be acquired from a wide range of natural and cheap sources [20]. The main challenge for the scaling-up of the SEWGS technology (and in general of any calcium-looping system) is the need to find an efficient and low-priced method for the regeneration of the CO₂ sorbent.

The calcination of CaCO₃ is an energy-intensive reaction that requires temperatures of around 900 °C [21] to produce virtually pure CO₂ suitable for transport, reuse and/or permanent storage. Different process schemes have been envisaged to carry out the calcination of CaCO₃ under CO₂-rich atmospheres [22], such as the indirect heating using heat transfer surfaces [23–25], the use of hot Ca-rich streams of solids preheated in a combustion chamber [26–28] or the use of the sensible heat of high-temperature solids that come from a chemical looping combustion (CLC) system [29,30]. However, the only system developed so far to large pilot plant scale is the oxy-combustion carried out in a separate regenerator, which has been already demonstrated at TRL6 [31,32] for post-combustion applications and have shown itself to be highly competitive when

integrated in full-scale power plants [22]. The main disadvantage of the oxy-fuel combustion systems is the need for a costly and energy consuming Air Separation Unit (ASU).

In an attempt to avoid the ASU, Abanades et al. [33] originally proposed a packed-bed Cu/CuO chemical loop (i.e., the Ca-Cu looping process) to supply directly the heat needed to calcine CaCO_3 by exploiting the exothermic reduction of CuO with a gaseous fuel, producing in this way a highly concentrated stream of CO_2 and H_2O . Significant improvements in reactor modelling, thermal integration and materials durability have been made over the last years in the Ca-Cu looping process [34]. This concept has been experimentally validated at TRL4 [35,36] within the framework of the ASCENT Project [37]. The configuration of the Ca-Cu looping concept to reduce the emissions of CO_2 in a steel mill has been recently described by Fernandez et al. (2017) [38]. This novel process consists of three interconnected fluidised-bed reactors operating close to atmospheric pressure. In the first reactor, a significant part of the BFG is decarbonized by means of a SEWGS reaction in the presence of CaO- (CO_2 -sorbent) and Cu-based (WGS catalyst) particles. The resulting H_2 -rich gas stream contains about 25 vol.% of H_2 and less than 1 vol.% of CO and CO_2 in N_2 . This gas could be used as fuel to heat the coke oven, hot stoves or boilers (as happens in conventional steel mills), to generate power or to increase the production of steel in the plant through a Direct Reduced Iron (DRI) route. The CaCO_3 generated during the SEWGS stage is calcined in other reactor fuelled with Coke Oven Gas (COG) and/or with other N_2 -free fuel gas, and as a result a stream mainly composed of CO_2 and H_2O is produced. In this system, the exothermic reduction of CuO with the fuel gas and the sensible heat of high-temperature copper-based solids that come from an oxidation stage provide the heat required for the calcination of CaCO_3 . The reduced Cu-based particles resulting from the reduction/calcination stage are subsequently oxidized and heated up in an air reactor. The separation of both Ca- and Cu-based materials through segregation in the fuel reactor/calciner reduces considerably the circulation of solids in the system and increases the overall energy efficiency because the Cu-based particles act as thermal ballast in the SEWGS operation and in the transition from the SEWGS reactor to the fuel/reactor calciner. Moreover, an efficient segregation of the particles supplies the CaO needed for the steelmaking plant avoiding the need for a lime plant and the related CO_2 emissions.

This paper includes the simulation of the whole Ca-Cu system integrated in a steel mill with CO_2 capture. The effect on the reduction of the global CO_2 emissions of the whole steel mill using different fuel gases (i.e., steel mill off-gases or natural gas) fed into the Ca-Cu process has been carefully quantified in this work. Key performance indicators, such as the primary energy consumption, the net electric production or the CO_2 capture efficiency, have been calculated. Moreover, the amount of additional steel that might be produced through the DRI route with the H_2 -rich gas exported from the Ca-Cu process has been also estimated, evaluating its benefit into the global steelworks balances. Finally, the performance of a reference steel mill without CO_2 capture and with a post-combustion CO_2 capture system based on amine absorption have been also calculated for the sake of comparison with the steel mill integrated with the Ca-Cu looping process.

2. Process description of the reference steelworks

2.1. Steel mill processes

Data reported by the IEA in [39] have been used to carry out the mass and energy balances of the benchmark steel mill. The reference steel mill considered is based on the typical BF-BOF production route and it has an annual production of 4 million tonnes of hot rolled coil (HRC) per year, which is one of the several standard products that can be produced in a steel mill. Figure 1 shows a simplified layout of this reference steelworks plant, indicating the main processes involved in the plant as well as the gas streams interactions between these units.

Figure 1 Simplified layout of an integrated steel mill with a gas boiler steam power plant (adapted from [15]). Numbers in blue correspond to the energy flows of BFG/COG/BOFG expressed in MJ_{LHV}/t HRC

The core of this process is the blast furnace (BF) where iron ore (mainly Fe_2O_3) is reduced into iron metal in the presence of coke and coal as reducing agents. The raw materials (i.e. iron-bearing materials, coke and limestone) are charged through the top of the BF, while the molten iron and slag obtained as products are collected through the bottom. Therefore, the solid burden moves downwards meeting the hot temperature reducing gas that flows in counter-current fashion. The hot blast air (enriched with oxygen from an ASU) is preheated up to a high temperature between 900 and 1350°C in the hot stoves and is injected from the bottom part of the BF. The air blast provides the oxygen needed for coke/coal gasification and so produces mainly CO that reduces the iron ore to metal iron. The resulting blast furnace gas (BFG) is a low calorific value fuel gas (i.e., with a LHV of 3.21 MJ/Nm³) rich in N_2 and CO_2 (see Table 1) which is split downstream of the BF into two fractions as shown in Figure 1: one fraction is sent to the hot stoves to be used as a fuel for heating the

blast air fed to the BF, and the remaining BFG is sent to the gas cleaning section for eliminating entrained dust, cyanide and SO₂ compounds. Such cleaned BFG is used as fuel in the coke oven while the remaining excess BFG is sent to the power plant for producing electricity [40]. Coke introduced into the BF is produced in the coke oven, where coal is heated in the absence of air through heating walls consisting of flues with fuel nozzles and air boxes that supplies the heating flue gas. The resulting coke oven gas (COG) is a high calorific value fuel (i.e., with a LHV of 17.33 MJ/Nm³) rich in hydrogen, methane and other hydrocarbons (see Table 1). Typically, a small fraction of cleaned COG is used as fuel in the combustion chambers of the coke oven as indicated in Figure 1, whereas the remaining COG is used as fuel in the hot stoves of the BF and in other steelworks consumers such as the lime kiln or the hot rolling mill process [39]. Finally, the liquid hot pig iron collected from the BF is mixed with scrap iron before being introduced into the basic oxygen furnace (BOF), where carbon is oxidized to CO and CO₂ by injecting oxygen and removing any remaining impurity. Before being introduced into the BOF, the liquid pig iron is pre-treated to reduce the content of sulphur. The most widespread hot metal desulphurisation technology is based on the use of lime, which is produced in the lime kiln within the steelworks. The amount of additives such as chromium, nickel, titanium or manganese is adjusted downstream of the BOF through a secondary metallurgy process before the final casting, rolling and finishing operations. Based on the electric consumptions given in [39], total electric consumption of the reference steel mill is 400.1 kWh/t_{HRC} being the major power consumers the reheating and rolling mills, as well as the main air compressors of the BF and the ASU, which are responsible for 67.5 % of such electric consumption.

Energy flows (LHV-basis) of each gas distributed throughout the reference steelworks plant are indicated in Figure 1, which have been calculated from the balances in [39]. Table 2 summarises the energy consumption of the main steelworks processes considered in the reference steel mill calculated from [39]. In addition, the total CO₂ emissions for each steelworks process and those associated exclusively with the off-gases used within each unit are included in this table. The total CO₂ emissions and CO₂ emissions due to off-gas combustion (BFG and/or COG) practically match in most of the steelworks processes included in this table, which means that the CO₂ emissions are basically due to the combustion of BFG and/or COG with air to provide the energy needed in each specific process. However, in the case of the sinter plant and the lime production unit both CO₂ emissions are different, which means that there are other sources of CO₂ different from fuel combustion (i.e. coke breeze combustion in the sinter plant or limestone calcination in the lime plant). Composition and heating value of the COG, BFG and BOFG used within the steel mill are summarised in Table 1. As can be seen in Figure 1, a total amount of 3078 MJ/t_{HRC} of COG is produced within the coke plant. COG is mainly used as fuel in the combustion chamber of the coke oven (after being cleaned of tars, naphthalene, BTX, H₂S, ammonia and particulates) and also in the reheating furnace that heats up the slab before it enters the hot rolling mill to obtain the final product (i.e. 1470 MJ/t_{HRC}, as indicated in Table 2). Minor fractions of COG are used in the hot stoves of the BF (i.e. 125 MJ/t_{HRC} as seen in the figure) and in the lime kiln (i.e. 302 MJ/t_{HRC}) to produce the lime needed principally in the BOF. A total flow of 5077 MJ/t_{HRC} of BFG is produced in the BF. Excess BFG that is not needed within the steelworks (i.e. 2977 MJ/t_{HRC}) is sent to the power plant for producing

electricity. The basic oxygen furnace gas (BOFG) produced within the oxygen furnace is cleaned and entirely used in the power plant. The total energy consumption of the steel mill processes is 5178 MJ/t_{HRC}, whereas 3637 MJ/t_{HRC} is the thermal input to the power plant as indicated in Table 2. Finally, as indicated with dashed lines in Figure 1, there is a fraction of COG, BFG and BOFG flared to the atmosphere that cannot be recovered for reuse in the plant. Concretely, 73.5, 72.6 and 267.8 MJ/t_{HRC} of COG, BFG and BOFG, respectively, are flared to the atmosphere according to the balances given in [39]. These flared gases have been neglected when accounting for the total gas production in the Ca-Cu plant, as explained in the next section.

Table 1 Composition and heating value of the COG, BFG and BOFG produced within the steel mill [39]

	Coke Oven Gas (COG)	Blast Furnace Gas (BFG)	Basic Oxygen Furnace Gas (BOFG)
<i>Composition (%vol.)</i>			
CH ₄	23.04	--	--
H ₂	59.53	3.63	2.64
CO	3.84	22.34	56.92
CO ₂	0.96	22.10	14.44
O ₂	0.19	--	--
N ₂	5.76	48.77	13.83
H ₂ O	3.98	3.15	12.16
CxHy	2.69	--	--
LHV [MJ/Nm ³]	17.33	3.21	7.47

Table 2 Energy consumption and CO₂ emissions of the different units in the reference steel mill considered [39]

	Fuel gas consumption [MJ _{LHV} /t _{HRC}]	Fuel-gas used	Total CO ₂ emissions [kg CO ₂ /t _{HRC}]	CO ₂ emissions associated with fuel gas combustion [kg CO ₂ /t _{HRC}]	Other sources of CO ₂ emissions (alternative to fuel consumption in previous column)
<i>Coke plant</i>	1383	COG, BFG	194.2	191.3	Flared COG
<i>Blast furnace hot stoves</i>	1636	COG, BFG	416.7	416.7	Flared BFG
<i>Sinter plant</i>	81	COG	250.9	3.2	Coke breeze, limestone
<i>Lime production plant</i>	302	COG	71.6	12.0	Limestone calcination
<i>Slab reheating furnace</i>	1470	COG	58.5	58.5	--
<i>Pulverised coal drying</i>	24	COG	0.98	0.98	--
<i>Other uses*</i>	282	COG	11.2	11.2	--
<i>Diffuse CO₂ emissions**</i>	--	--	56.3	--	--
Total steel mill processes	5178	--	1060.4	693.8	--
<i>Power plant</i>	3637	BFG, BOFG	933.2	933.2	--

*COG used for torpedo heating, ladle heating, and BF and BOF flare

**Diffuse CO₂ emissions in hot metal desulphurisation, ladle metallurgy and hot rolling mill (CO₂ emissions associated with flared BOFG are included in this term)

2.2. Steam cycle power plant

The power plant considered for the steelworks is based on a sub-critical steam cycle (SC) (by far the most common power generation technology in European steel mills), where BFG and BOFG (2977 MJ/t_{HRC} and 660 MJ/t_{HRC}, respectively, according to [39]) are burnt with air constituting a total fuel thermal input of 461.5 MW

(LHV-based). Main process assumptions used for calculating the power plant are given in Table A1 in the appendix.

Two different configurations have been considered as reference steam cycle power plants, depending on whether post-combustion CO₂ capture is considered in the flue gas exiting the boiler or not. In the steam cycle power plant without CO₂ capture, the flue gas at the air/fuel preheater outlet is directly emitted to the atmosphere through the stack. In this case, the low pressure section of the steam turbine operates with an outlet pressure of 0.048 bar. Due to the low condensation temperature (around 32°C), the steam cycle needs a total number of 5 feedwater heaters, four operating at low pressure (including the deaerator) and one at high pressure. A total flow of 137 kg/s of superheated steam at 565°C and 153 bar is produced, which is sent to the high pressure steam turbine. Steam is then reheated at 40 bar and 565°C and expanded in the low pressure turbine. Net electric output of the power plant is 193.1 MW, which corresponds to 422.9 kWh/t_{HRC}. Compared to the electric consumption of the steel mill (400.1 kWh/t_{HRC}), there is an excess of electricity in this scenario that can be exported to the grid as will be explained in more detail in the results section.

The second benchmark power plant includes a post-combustion CO₂ capture process based on a MEA absorption process (Figure 2), in which the cooled flue gases are treated after the gas air preheater (APH) and the direct contact cooler (DCC) as shown in this figure. To compensate the pressure losses introduced by the MEA absorption process, a fan is included downstream the DCC just before the absorption column of the MEA process. The CO₂-lean flue gas exiting the absorption column is sent to the stack (stream #7), whereas almost pure CO₂ is obtained in the stripper column that is cooled down and sent to the CO₂ compression unit.

A backpressure steam turbine configuration has been adopted in this case, working with an outlet pressure of 2 bar (stream #13 in Figure 2). All the steam available exiting the steam turbine is sent to the reboiler of the stripping column of the MEA absorption process to supply the heat needed for regenerating the amine. Condensed water at 1.5 bar from the stripper reboiler is sent back to the feedwater preheater line of the steam cycle (stream #12). The specific heat duty for MEA regeneration has been considered equal to 3.03 MJ/kg_{CO2}, according to [39]. Table 3 summarises the mass flow rates, temperature, pressure and composition of the main process streams in Figure 2.

Figure 2 Flowsheet of the reference power plant with post-combustion CO₂ capture coupled to an integrated steelworks

Table 3 Mass flow rate, temperature, pressure and composition for the main streams of the reference SC power plant shown in Figure 2

Stream no.	$T [^{\circ}\text{C}]$	$p [\text{bar}]$	$G [\text{kg/s}]$	Composition [%mol.]						
				Ar	H ₂	CO	CO ₂	O ₂	N ₂	H ₂ O
1	28.5	1.10	173.14	--	3.54	25.35	21.44	--	45.74	3.93
2	150.0	1.10	173.14	--	3.54	25.35	21.44	--	45.74	3.93
3	200.0	1.05	159.07	0.92	--	--	0.03	20.73	77.29	1.03
4	250.0	0.99	332.21	0.49	--	--	25.79	3.00	66.05	4.67
5	101.0	1.01	332.21	0.49	--	--	25.79	3.00	66.05	4.67
6	49.4	1.11	332.21	0.49	--	--	25.79	3.00	66.05	4.67
7	51.8	1.01	250.2	0.57	--	--	6.26	3.49	76.91	12.77
8	25.0	150.0	93.7	--	--	--	100	--	--	--
9	565.0	153.0	137.06	--	--	--	--	--	--	100
10	355.1	40.0	136.52	--	--	--	--	--	--	100
11	565.0	36.0	136.5	--	--	--	--	--	--	100
12	191.0	180.0	137.07	--	--	--	--	--	--	100
13	110.0	1.50	119.71	--	--	--	--	--	--	100
14	181.5	2.00	119.71	--	--	--	--	--	--	100

3. Steelworks plant integrated with the Ca-Cu process

The Ca-Cu looping process aims at reducing the CO₂ content in the off-gas from the blast furnace steel mill and so produce a H₂-enriched gas that can be used as fuel in the steelworks processes, thereby reducing the

CO₂ emissions to the atmosphere. This pre-combustion CO₂ capture concept was recently analysed in a previous paper [38], where different options regarding the reactor temperatures, the air/Cu ratio at the oxidation reactor inlet and the segregation efficiency in the reduction/calcination reactor were assessed. This process is based on an arrangement of three atmospheric fluidised bed reactors, as depicted in Figure 3.

Figure 3 Simplified scheme of the Ca-Cu looping process considered

The first reaction stage consists of the sorption enhanced water gas shift (SEWGS) of the BFG, where the BFG and steam are fed into the reactor together with a stream of solids containing CaO that reacts with the CO₂ present in the gas according to reaction (1) (reaction enthalpy at 298 K calculated using formation enthalpies in [41]). As a result, the water gas shift (WGS) reaction of the CO present in the BFG is favoured (Eq.(2)), and generates a product gas containing up to 30-35% vol. of hydrogen (dry basis, the balance being mainly N₂) and less than 1% vol. of CO₂ and CO. Solids exiting this SEWGS stage are sent to a second reactor, where the regeneration of the CO₂ sorbent occurs. The heat needed for the CaCO₃ calcination is supplied by the sensible heat and the exothermic reduction of a CuO-based material coming from the third oxidation reactor. A 'N₂-free' fuel gas containing H₂, CO and/or CH₄ is desirable as a reducing gas in the reduction/calcination stage so that the CO₂-rich gas obtained at this stage outlet can be easily purified and compressed before being sent for storage. Therefore, the COG generated in the coke oven of the steelworks, which is rich in CH₄ and H₂ (see Table 1) and almost free of N₂, is suitable for this stage. Natural gas can be also used as fuel in this reduction/calcination stage in order to increase the amount of BFG that can be processed in the SEWGS stage. The operating temperatures needed to ensure the complete CaCO₃ calcination in this reduction/calcination range between 870 and 900°C, depending on the amount of CO₂ generated at the reactor outlet [42]. During

the reduction/calcination, the reactor operates as a bubbling bed to facilitate the reactions involved in this stage and the separation by segregation of the CaO- and Cu-based solids, as explained below. Finally, a large fraction of the solids exiting this reduction/calcination reactor are sent to an air reactor that operates as a CFB. Air is fed into this reactor to produce the necessary amount of CuO for the reduction/calcination stage. As explained in [38], during the oxidation stage the reactor operates at under-stoichiometric air/Cu ratio (i.e. the Cu is not completely oxidised into CuO) at a temperature slightly above that of the reduction/calcination reactor (i.e. around 900°C) in order to maximise the thermal efficiency of the process. The energy needed in the reduction/calcination stage for heating the solids from the SEWGS reactor and for CaCO₃ calcination is therefore supplied by the sensible heat obtained from cooling the high temperature solids from this oxidation reactor and by the exothermic reduction of the CuO present in this solids stream.

One of the main advantages of the Ca-Cu process is that the CaO needed in the steelworks can be obtained separately in the reduction/calcination reactor. In order to reduce the energy demand in the reduction/calcination reactor, the limestone make-up flow is introduced into the SEWGS reactor where it is preheated by the heat released from the carbonation and WGS reactions [38]. The differences in solid densities and and/or particles sizes should allow for an effective separation through segregation between the CaO and Cu-based particles [43,44]. In this way, there is no need for a lime plant in the steelworks plant.

In the steelworks plant integrated with the Ca-Cu looping process all the COG produced within the steel mill (i.e. 3078 MJ/t_{HRC}) is assumed to be used as fuel in the reduction/calcination reactor of the Ca-Cu plant. This determines the amount of Ca-based sorbent that can circulate between the SEWGS and reduction/calcination reactors, and so the amount of BFG that can be fed to the SEWGS reactor. In this way, only a fraction of the total amount of BFG produced in the steel mill can be fed to the Ca-Cu process, where a H₂/N₂-rich fuel is obtained that can be used as a low-carbon fuel in the steelwork processes or exported from the plant for other uses (e.g. for additional steel production in a DRI purposes or electricity production). The fraction of BFG not used in the Ca-Cu process and the BOFG produced in the basic oxygen metallurgy are burnt in the steel mill to replace the COG used for the reduction of CuO. Superheated steam is produced within the Ca-Cu process due to the recovery of heat from the SEWGS reactor and from the high temperature gas streams available throughout the process, which is sent to a steam turbine power plant for the production of electricity.

With respect to the consumption of limestone in the reference steel mill, about 0.279 t CaCO₃/t_{HRC} are needed (calculated from reference [39] assuming that limestone is 100% CaCO₃) which is distributed among the lime plant (i.e. 0.14 t/t_{HRC}), the sinter plant (i.e. 0.13 t/t_{HRC}) and the blast furnace (i.e. 0.01 t/t_{HRC}). As one of the objectives of the Ca-Cu process is separating the CaO produced in the lime plant, a limestone make-up flow

of 0.14 t/t_{HRC} has been considered in the Ca-Cu process. Since the lime plant is not needed with the Ca-Cu process, the fuel gas energy consumption of 302 MJ/t_{HRC} associated with this unit (see Table 2) is avoided, and the total fuel gas energy demand in the steel mill with the Ca-Cu process is reduced from 5178 to 4876 MJ/t_{HRC}. Moreover, the electric consumption associated with the lime plant (i.e. 2.6 kWh/t_{HRC}), which is associated to the air blower, the fans for the evacuating the flue gas from the kiln and the electric motors for driving the solid conveyors, is also avoided. As a result, the total electric consumption of the steel mill is reduced to 397.5 kWh/t_{HRC}.

A detailed configuration of the Ca-Cu process integrated within the steelworks is depicted in Figure 4. As noticed in the figure, two suspension preheaters, similar to those used in cement industry, are assumed to be used for preheating the carbonated solids from the SEWGS reactor (stream #25) up to 600°C before being introduced into the reduction/calcination reactor. The high temperature CO₂-rich stream from this reactor and the N₂-rich gas from the oxidation reactor are used as heating sources in the suspension preheaters. The assumptions used for carrying out the calculations of the Ca-Cu process are summarised in Table 4. The steam cycle and the CO₂ compressor calculations have been made using the same parameters as those in the reference power plant, shown in Table A1 in the appendix.. Table A2 summarises the mass flow, temperature, pressure and composition of the main process streams highlighted in Figure 4.

As can be seen from the process flowsheet shown in Figure 4, there are four main heat sources in the Ca-Cu looping process: (i) the SEWGS reactor (where the heat available from the WGS and carbonation reactions and from the cooling of the circulating solids is available); (ii) the H₂-rich gas from the SEWGS reactor (which is cooled from 600°C down to 70°C before being partially recirculated to the steel mill); (iii) the CO₂-rich gas from the reduction/calcination reactor (downstream of the suspension preheaters that needs to be cooled down to 80°C before the CO₂ compression unit); (iv) the N₂-rich gas from the oxidation reactor (downstream of the suspension preheaters that is cooled to 80-90°C before being emitted to the atmosphere through the stack).

Superheated steam with the same parameters of the benchmark plants is produced with the available heat in the SEWGS reactor and from the cooling of the H₂- and CO₂-rich gases. The reheater section is also assumed to be located in the SEWGS reactor. In the proposed steam cycle there is one evaporation level and the condenser operates at a pressure of 0.048 bar. The steam cycle has five feedwater heaters including the deaerator, which operates with an inlet temperature of 140°C. In order to maximise the heat recovery from the CO₂-rich stream in the low temperature range (i.e. below 180-210°C), an external low temperature feedwater heater is placed in parallel to the low-pressure preheating line of the steam cycle. In this external water preheater, almost half of the water after the condenser extraction pump is heated up to 140°C before being fed to the deaerator. The sensible heat of the CaO solid purge at 880°C taken from the reduction/calcination segregator has not been recovered within the steam cycle.

Figure 4 Configuration of the Ca-Cu process coupled with the integrated steel works and the steam cycle power plant (Numbers in blue in the gas flows from the steel plant correspond to the energy of BFG/COG/BOFG expressed in MJ/thrc)

Figure 5 shows the temperature-heat curve for the heat sources available in the plant shown in Figure 4. The largest amount of thermal power transferred to the steam cycle is provided within the SEWGS reactor that makes available 250 MW from the total amount of 388 MW transferred to the steam cycle. Heat recovered for preheating the solids exiting the SEWGS reactor before entering the reduction/calcination reactor corresponds to 51 MW, which allows dedicating a larger fraction of the COG thermal input to this reactor for CaCO_3 calcination. It should be noticed that the pinch point is located at the entrance of the ECO (i.e. between the rich- CO_2 stream #10 in Figure 4 and the water fed to the ECO). The suspension preheaters considered in the flowsheet are direct gas-solid heat exchangers, and therefore the temperature of the solid and gas phases at the outlet of such preheaters is the same.

(a) CO_2 -rich gas

(b) SEWGS reactor and H_2 -rich gas

Figure 5 Temperature-heat transferred diagrams for the different heat sources of the process shown in Figure 4

4. Methodology and performance indicators definition

The data needed to solve the mass and energy balances of the main components of the reference steel mill (i.e. the energy consumption of the different units in the steel mill and the CO_2 emissions linked to each unit)) have been taken from a recent IEAGHG report [39] and listed in Table 2.. The power island integrated within the steelworks (both for the reference case without CO_2 capture and that including post-combustion CO_2 capture with MEA) has been solved using the in-house GS (Gas-steam cycle) code, developed at the Department of Energy of Politecnico di Milano [45]. This code assumes ideal behaviour for the solids, gases and liquids and calculates the thermodynamic properties by means of the NASA polynomials [46] using the database available in [47]. Only pure water and steam are considered as real fluid and their properties are calculated through the IAPWS97 thermodynamic database. The assumptions used for calculating the power island have been summarised in Table A1. The Ca-Cu looping process and the steam cycle integrated with the different gas streams and units of this process have been also solved using GS according to the assumptions given in Table 4. Finally, the CO_2 compression unit has been calculated using Aspen Plus and the Peng Robinson equation of state. The calculation of this compression unit was based on the information given in Table A1.

Table 4 Main assumptions used for calculating the requirements of the Ca-Cu process plant integrated with the steel mill and the steam cycle

<i>Ca-Cu process</i>	
Operating temperature of the SEGWS reactor [°C]	600
Temperature of feed gas to the SEWGS reactor [°C]	250
Operating temperature of the reduction/calcination reactor [°C]	880
Temperature of the fuel fed to the reduction/calcination reactor [°C]	600
Operating temperature of the oxidation reactor [°C]	900
Temperature of the air fed to the oxidation reactor [°C]	300
Overall pressure drop in each Ca-Cu reactor and cooling section [kPa]	25.0
CaO conversion to $CaCO_3$ in the SEWGS reactor [%]	20.0

Steam-to-carbon ratio at SEWGS reactor inlet [-]	1.0
Cu-material segregation efficiency in the reduction/calcination reactor [%]	100
Molar Cu-to-CaO at oxidation reactor inlet	0.038
% wt. Cu ₂ O in the solid bed reduction/calcination reactor material [%]	4.4
Calcination efficiency in the reduction/calcination reactor [%]	100
<i>Auxiliaries consumption</i>	
Mechanical-electric efficiency of ID/FD fans [%]	94.0
Isentropic efficiency of ID/FD fans [%]	80.0

For evaluating the performance of the reference steelworks plant and the steel mill integrated with the Ca-Cu looping process, different performance indicators have been defined:

- *Direct fuel consumption* or fuel gas energy consumption in the steelworks [in MW_{LHV} or MJ_{LHV}/t_{HRC}] is the energy provided by the combustion of the different off-gases (i.e. BFG, COG, BOFG or H₂-rich gas) within the steel mill. It can be expressed in absolute terms or per tonne of final product (HRC) produced in the steel mill, and it has been calculated on LHV basis. Coal consumption in the coke plant or in the BF of the steelworks have not been accounted for in this direct fuel consumption, being invariant in the different configurations assessed.
- *Indirect fuel consumption* (q_{in}) [in MW_{LHV} or MJ_{LHV}/t_{HRC}] is the primary energy consumption associated with the net electricity consumption (P_{el}) of the steelworks, and it is calculated by means of Eq. (3). The net electricity consumption in the steelworks considers the total electric consumption of the steel mill processes and the electricity produced in the power plant. This P_{el} can be negative when the electricity produced in the power plant is larger than that needed in the steel mill and there is an electricity export to the grid. In this case, the indirect fuel consumption values would be negative, indicating a credit of primary energy.

$$q_{in} = \frac{P_{el}}{\eta_{ref,el}} \quad (3)$$

For the definition of the indirect fuel consumption, a reference electric efficiency $\eta_{ref,el}$ must be defined depending on the fuel and the technology used for generating the electricity delivered from the grid to the steelworks. The European energy mix of 2014 has been taken as the reference electricity production scenario for the steel mills calculated in this work. An average electricity production efficiency for the EU-28 equal to 45.9% has been considered, according to the electricity scenario calculated in [48], which corresponds to 23% of coal-based electricity, 10% from gas (natural gas, oil gas and refinery gas), 34% of nuclear power and 33% from renewables.

- *Equivalent fuel consumption* (q_{eq}) [in MW_{LHV} or MJ_{LHV}/t_{HRC}] is the sum of the direct (q) and indirect (q_{in}) fuel consumptions in the steel mill.
- *Direct CO₂ emissions* (e_{CO_2}) [in kg_{CO2}/t_{HRC}] correspond to the amount of CO₂ directly emitted to the atmosphere from the whole steel mill (i.e. the CO₂ emitted through the steel mill processes and the CO₂ emitted from the power plant).

- *Indirect CO₂ emissions* ($e_{CO_2,in}$) [in kg_{CO₂}/t_{HRC}] correspond to the CO₂ emissions associated with the net electricity consumption P_{el} of the steelworks (in kWh/t_{HRC}). This is calculated according to Eq. (4), where $e_{ref,el}$ (given in kg_{CO₂}/kWh) refers to the specific CO₂ emissions of the reference power production technology considered. The emission factor for the average European energy mix taken as the reference scenario is 0.262 kg_{CO₂}/kWh [48].

$$e_{CO_2,in} = P_{el} \cdot e_{ref,el} \quad (4)$$

- *Equivalent CO₂ emissions* ($e_{CO_2,eq}$) [in kg_{CO₂}/t_{HRC}] is calculated as the sum of the direct (e_{CO_2}) and indirect ($e_{CO_2,in}$) CO₂ emissions from the steel mill.
- *CO₂ avoided* is calculated by means of Eq. (5) considering the equivalent CO₂ emissions and with respect to the reference steelworks plant without CO₂ capture described before.

$$CO_2 \text{ avoided} = \frac{e_{CO_2,eq-ref} - e_{CO_2,eq}}{e_{CO_2,eq-ref}} \quad (5)$$

- *Specific Primary Energy Consumption for CO₂ Avoided* ($SPECCA_{eq}$) [in MJ/kg_{CO₂}] is calculated by means of Eq. (6) and it calculates the additional equivalent fuel consumption that is needed in the steelworks with CO₂ capture to avoid the emission of one kg of CO₂ into the atmosphere with respect to the steelworks plant without CO₂ capture.

$$SPECCA_{eq} = \frac{q_{eq-ref} - q_{eq}}{e_{CO_2,eq-ref} - e_{CO_2,eq}} \quad (6)$$

5. Discussion

Table 5 and Table 6 summarise the gas consumption throughout the plant and the electric balance and global performance indicators, respectively, for the reference steel mill with and without CO₂ capture and for the steel mill integrated with the Ca-Cu process. For the reference steel mill with and without CO₂ capture, the direct energy consumption of the steam cycle power plant is 3636.8 MJ/t_{HRC}, corresponding to the BFG not used in the steel mill and all the BOFG produced in the BOF, as already explained in Section 3. Regarding the reference steel mill without CO₂ capture, electricity production in the power plant is 422.9 kWh/t_{HRC}, which fulfils the electricity demand of the steel mill (400.1 kWh/t_{HRC}), leaving a small amount of electricity that is exported to the grid (i.e. 22.8 kWh/t_{HRC}). When integrating the MEA absorption system in the power plant of the steelworks (Figure 2), the net electric production of the power plant is noticeably reduced by almost 50% due to the energy consumed in the reboiler of the stripper column. As explained in section 2.2., a backpressure configuration for the steam turbine of the power plant is adopted when performing CO₂ capture with a MEA system. In this way, all the steam exiting the back-pressure turbine is condensed in the reboiler of the stripper column to supply the energy needed to regenerate the amine. Since the outlet pressure of the turbine has been increased in this case

with respect to the power plant without CO₂ capture, the electricity produced is reduced from 193 MW in the condensing configuration to 98 MW in the backpressure one. Therefore, the electricity produced in this case is not enough for fulfilling the electricity demand of the steel mill and 185.4 kWh/t_{HRC} will need to be imported from the grid.

In the Ca-Cu process integrated within the steel mill, 1498 MJ/t_{HRC} of BFG are introduced into the SEWGS reactor that will leave 3579 MJ/t_{HRC} of BFG available for the different processes in the steel mill (see energy results in Table 5). Considering also the energy available in the BOFG, the total amount of energy in the BFG and BOFG that can be used within the steel mill is 4239 MJ/t_{HRC}. However, as explained in section 3, the fuel gas energy demand of the full steel plant is 4876 MJ/t_{HRC} (excluding the consumption of the lime plant), and therefore additional energy will be needed to fulfil the energy requirements of the steel mill processes. A fraction of the H₂-rich gas produced in the SEWGS reactor of the Ca-Cu process is therefore recirculated to the steel mill to cover this fuel gas energy demand (Figure 4), and the remaining 671 MJ/t_{HRC} that has not been used will be exported from the steelworks plant. For comparison purposes in terms of performance, this excess of low pressure H₂-rich gas is considered to be converted into additional electricity in the steam cycle with an efficiency of 42%, which will be accounted for calculating the net electricity consumption of the steel mill P_{el}. The electricity production in this case is 328.4 kWh/t_{HRC}, which is not enough to fulfil the electric demand of the steel mill processes (i.e. 397.5 kWh/t_{HRC} without the electric consumption of the lime plant [39]). Such electricity production is higher than in the benchmark steelworks plant with CO₂ capture, which results in a lower electricity import from the grid and so a lower equivalent energy consumption.

Results about the CO₂ balance in the benchmark steelworks cases with and without CO₂ capture as well as in the steelworks integrated with the Ca-Cu process are indicated in Table 7. It can be seen from the CO₂ emissions in the steel mill processes that the direct CO₂ emissions for the steel mill integrated with the Ca-Cu process amount to 1096.5 kgCO₂/t_{HRC}. These emissions are noticeably larger than those in the reference steelworks (693.8 kgCO₂/t_{HRC}), where COG and BFG were used to fulfil the fuel gas energy demand of the steel plant. From the composition and LHV of the steel mill gases shown in Table 1, it can be seen that BFG and BOFG have a larger CO₂ emission factor (in kgCO₂/MJ_{LHV}) than COG due to the larger CO and CO₂ content of these gases and their lower LHV. Therefore, when using exclusively BFG and BOFG in the steel mill processes as in this case, the CO₂ emissions increase. The CO₂ emissions associated with the 637 MJ/t_{HRC} of H₂-rich gas used as fuel in the steel mill processes amount to only for 2.1 kgCO₂/t_{HRC} due to the reduced content of CO and CO₂ in this gas (i.e. 0.14 and 0.32 % vol. respectively).

As for CO₂ emissions from the power plant, 931.2 kgCO₂/t_{HRC} are emitted in the reference steelworks without CO₂ capture, which are associated with the use of BFG and BOFG as fuel in the steam cycle boiler. In the benchmark steelworks plant with CO₂ capture using a MEA absorption unit, about 79.2 % of the CO₂ emitted in the power plant would be captured considering the specific consumption of 3.03 MJ/kgCO₂ for regenerating the MEA in the stripper column reboiler. As a result, direct CO₂ emissions in the power plant fall to 194.5 kgCO₂/t_{HRC} (corresponding to 905.8 kgCO₂/MWh) as indicated in Table 7. In the power plant integrated with the

Ca-Cu process depicted in Figure 4, direct CO₂ emissions are practically zero (i.e. 2.10 kg_{CO2}/t_{HRC}), associated exclusively to the H₂-rich gas exported from the plant that is used to produce additional electricity. When considering the indirect CO₂ emissions from the electricity imported to the plant, the equivalent CO₂ emissions amount to 936.9 kg_{CO2}/t_{HRC} for the reference steelworks with the MEA absorption process and to 1116.7 kg_{CO2}/t_{HRC} for the steelworks plant integrated with the Ca-Cu process, which correspond to 42.1 and 31.0 % of CO₂ avoided, respectively.

As can be seen from the results shown in Table 7, the CO₂ capture efficiency achieved in the full steel mill when integrating the Ca-Cu process is limited because only a fraction of the BFG produced is decarbonised. From the balances shown in Table 5, when all the COG is used as reducing gas, only 29.5% of the total BFG can be decarbonised in the SEWGS reactor, whereas the remaining 70.5 % that contains 970.7 kg_{CO2}/t_{HRC} is used directly as fuel gas in the steel mill processes. In order to achieve a significant reduction in the CO₂ emissions of the full steelworks process, a complete decarbonisation of the BFG should be therefore carried out by processing additional fuel in the reduction/calcination reactor of the Ca-Cu process. It is therefore analysed a scenario where natural gas (NG) is also introduced in the reduction/calcination reactor together with the COG to completely decarbonise the 5077 MJ/t_{HRC} of BFG produced in steel mill. In this case, the fuel gas energy demand of the steel mill processes can be fulfilled with the H₂-rich gas produced in the SEWGS and the BOFG. The results obtained for this case are listed in the last column of Table 5, Table 6 and Table 7. The NG composition assumed for the calculations is 89% CH₄, 7% C₂H₆, 1% C₃H₈, 0.11% C₄H₁₀, 2% CO₂ and 0.89% N₂ [12], with a LHV of 46.482 MJ/kg. It should also be pointed out that in this case the operating temperature of the reduction/calcination reactor needs to increase to 885°C in order to maintain the same temperature difference with respect to the calcination equilibrium as in the previous case, since the use of NG increases the CO₂ partial pressure in the outlet gas. As shown in Table 5, the NG thermal input needed in the reduction/calcination stage is 6658 MJ/t_{HRC} (corresponding to 844.5 MW_{th}, LHV based) which is mixed with 3078 MJ/t_{HRC} of COG. Taking into account the BFG processed in the SEWGS reactor, a total direct fuel consumption of 14813 MJ/t_{HRC} will be needed in the Ca-Cu process, which leads to an electricity production of 892.0 kWh/t_{HRC}. Additional electricity can be produced from the H₂-rich gas exported from the Ca-Cu process as in the previous case, which translates into a total electricity production of 917.4 kWh/t_{HRC}. This amount of electricity is enough to satisfy the electric consumption in the steel mill, resulting in an electricity output of 517.2 kWh/t_{HRC} as indicated in Table 6. The direct CO₂ emissions in the steel mill processes fall down to 136.9 kg_{CO2}/t_{HRC} in this case, which correspond basically to those of the BOFG (i.e. 123.8 kg_{CO2}/t_{HRC}) since those associated to the H₂-rich gas are substantially low (i.e. 0.003 kg_{CO2}/MJ). Considering the emissions of the power plant, the total direct CO₂ emissions are 137.6 kg_{CO2}/t_{HRC}, which represents more than 91.5% of CO₂ emission reduction in the whole steel mill (i.e. steel mill processes and power plant) with respect to the benchmark plant.

When accounting for the indirect CO₂ emissions associated with the electric output (see Table 7), the equivalent CO₂ emissions in the steelworks become almost zero (i.e., about 1.4 kg_{CO2}/t_{HRC}). The credits

associated with the electricity exported to the grid (i.e. $-136.2 \text{ kg}_{\text{CO}_2}/\text{t}_{\text{HRC}}$) compensate for the direct CO_2 emissions to the atmosphere, resulting in an almost carbon neutral system that exports around 237 MWe to the grid. However, the SPECCA will be higher than in the reference steelworks with post-combustion CO_2 capture using MEA (4.30 vs $2.39 \text{ MJ}/\text{kg}_{\text{CO}_2}$ as indicated in Table 7) since the additional primary energy consumption needed in this scenario will be twice that of the reference steelworks without CO_2 capture.

Moreover, the H_2 -rich gas produced in the Ca-Cu looping process that is not recirculated back to the steel mill processes can be exported to produce additional iron through a direct reduction iron (DRI) process (by means of the reaction, $\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$). In this scenario, the additional iron produced could be incorporated in the steel making process (i.e. in the BOF) to increase the HRC production capacity of the plant. It must be highlighted that this option is not feasible for the benchmark steelworks since there is no excess H_2 production, so it can only be performed by implementing a purpose-built fired tubular reformer unit for producing the H_2 for the DRI process. To introduce this possibility in this analysis, it is assumed that the mass and energy balances of the Ca-Cu process and the power plant do not change with respect to those shown before, so that the same excess of H_2 -rich gas is produced (see Table 5). In this way, both the energy and the electric consumptions associated to the BOF and the rest of the units located downstream (i.e. ladle metallurgy, caster, reheating and rolling processes) will increase. For the sake of simplicity, it has been assumed that these energy and electric consumptions will increase in proportion to the amount of additional HRC produced. The additional energy consumption will be fulfilled with NG (as happens in the reheating furnace for producing the slab for the rolling mill). On the other hand, the additional electric consumption will be satisfied by electricity imported from the grid, which will result in an increase in the total electric consumption of the plant.

The results obtained for this scenario are summarised in Table 8. When COG is exclusively the fuel gas in the reduction/calcination reactor, $0.416 \text{ Mt}_{\text{HRC}}/\text{yr}$ of additional HRC can theoretically be produced assuming a complete hydrogen conversion in the DRI reactor. This represents an increase of 10.4 % over the baseline HRC production of the reference steel mill. As a result, the fuel gas energy demand of the steelworks increases by $178.3 \text{ MJ}/\text{t}_{\text{HRC}}$ with respect to the consumption $4876 \text{ MJ}/\text{t}_{\text{HRC}}$ given in Table 5 for an annual HRC of 4 million tonne, achieving a total consumption of $5055 \text{ MJ}/\text{t}_{\text{HRC}}$. The addition of extra NG will satisfy the fuel gas energy demand in the ladle metallurgy, caster and rolling processes. The electricity imported from the grid also increases by $99.1 \text{ kWh}/\text{t}_{\text{HRC}}$ with respect to the previous scenario where the H_2 -rich gas exported from the plant was used to produce extra electricity. On the whole, equivalent CO_2 emissions result in $1152.9 \text{ kg}_{\text{CO}_2}/\text{t}_{\text{HRC}}$, which are $36.2 \text{ kg}_{\text{CO}_2}/\text{t}_{\text{HRC}}$ more than in the previous scenario without DRI production, due to the higher indirect CO_2 emissions associated with a larger electricity import and the direct CO_2 emissions associated with the additional NG needed. In the case where COG and NG are used as reducing gas, the amount of H_2 -rich gas exported from the steel mill that could be used for DRI production is less than in the case where exclusively COG is used in the reduction/calcination reactor. Therefore, only $0.135 \text{ Mt}_{\text{HRC}}/\text{yr}$ of additional HRC could be annually produced, which represents barely 3.4 % of the annual HRC production of the reference steelworks.

Finally, it must be highlighted that an alternative decarbonising scenario could have been achieved in case a common reference steelworks plant with two blast furnaces were considered. One of the limits of the proposed decarbonising scenario is that a significant amount of NG is needed to achieve high CO₂ capture rates close to 91.5% in the steelworks. However, in case a reference steelworks with two blast furnaces were considered, one of the blast furnaces could be adapted to be oxygen blown with top gas recycling, producing in this way a N₂-free BFG. In this case, such N₂-free BFG could be used as fuel in the reduction/calcination reactor of the Ca-Cu process, avoiding the need of additional NG and so boosting the energy conversion efficiency of the process, as well as the CO₂ avoided rate for the case with only COG used in the Ca-Cu process.

Conclusions

In this work, a novel reactor configuration of the Ca-Cu looping process has shown to be theoretically viable to fully decarbonise a full steelworks plant. The process is designed to decarbonise the blast furnace gas and obtain a H₂/N₂-rich fuel in a sorption-enhanced water gas shift reactor, using coke oven gas and natural gas as fuels for sorbent regeneration. Mass and energy balances of a reference steel mill plant integrated with this pre-combustion CO₂ capture process have been solved and compared with the balances obtained with a post-combustion MEA absorption system. It has been shown that by using exclusively the COG, around 30% of the BFG can be decarbonised in the Ca-Cu looping process. When an efficient segregation of the solids can be implemented, the CaO required for the steelmaking process may arise from the deactivated sorbent stream leaving the CO₂ capture Ca-Cu system, avoiding the need for a lime plant and the related CO₂ emissions.

For a steelmaking plant with a post-combustion MEA absorption system, the electric production of the power plant is around half of the electricity produced in a reference steel plant without CO₂ capture (i.e., from 422.9 to 214.7 kWh/t_{HRC}), due to the energy consumed in the reboiler of the stripper column. In this case, about 185 kWh/t_{HRC} needs to be imported from the grid to fulfil the electricity demand of the steel mill (i.e., typically 400 kWh/t_{HRC}). In the Ca-Cu looping process, the net electricity production of the power plant is 328.4 kWh/t_{HRC} that results in less electricity imported from the grid. It has been analysed the possibility of using the excess of H₂-rich gas in the Ca-Cu steel plant to produce additional iron through a direct reduction iron (DRI) process. It has been demonstrated that it is possible of increasing the production capacity of the steel plant by around 10.5% without installing a purpose-built and high-cost NG reforming plant. Moreover, this study has looked at the possibility of attaining a CO₂ capture efficiency of about 91.5% in the whole steelworks plant when the BFG is completely decarbonised by using NG in the reduction/calcination stage. In this scenario, almost zero CO₂ emissions amounting to 1.4 kg_{CO2}/t_{HRC} can be achieved mainly due to the fact that the credits from the CO₂ emissions associated with the export of electricity compensates for the direct CO₂ emissions from the full steelworks.

Once the potential of integrating the proposed Ca-Cu process scheme into a steel mill has been demonstrated, future research efforts should be devoted to the study of an appropriate segregator design, able to separate efficiently a pure stream of calcined limestone (i.e., free of Cu particles) to be integrated directly in the steel

production process without affecting the final steel quality. Moreover, the stable operation of the three interconnected fluidized bed reactors system needs to be demonstrated at a sufficient scale for this process. Finally, the chemical and physical stability of Cu-based materials with a proper Cu content should be evaluated for hundreds of oxidation/reduction cycles under the strict operating conditions of the reduction/calcination and oxidation stages of the Ca-Cu process.

Acknowledgements

Authors acknowledge the financial support from the European Union Seventh Frame Programme FP7 under the project ASCENT (Grant agreement no. 608512).

Appendix A. Additional information

Table A1. Main assumptions used for calculating the steam cycle power plant in the reference steelworks with and without CO₂ capture

<i>Gas Boiler</i>	
Air/fuel pressure to the burners [bar]	1.05/1.10
Pressure drop of the flue gas in the furnace [kPa]	4.0
Pressure drop of the flue gas in the convective pass [kPa]	2.0
Pressure drop of the flue gas in the Ljungström air preheater (APH) [kPa]	1.0
Oxygen concentration in flue gas [% vol.]	3.0
Air preheating temperature [°C]	200
Flue gas temperature at economizer outlet [°C]	250
Fuel feeding temperature to the boiler [°C]	150
<i>Steam cycle</i>	
Boiler feedwater temperature [°C]	190
Boiler feedwater pressure [bar]	180
Live steam temperature SH/RH [°C]	565/565
RH steam pressure [bar]	36
SH outlet pressure [bar]	153
Pressure losses in RH tubes [% of inlet pressure]	10
SH/RH piping thermal losses [°C]	2
Condensation pressure in the condensing steam cycle [bar]	0.048
Condensation pressure in the backpressure steam turbine* [bar]	2
Number of preheaters (including the deaerator)	5 (3**)
Heat loss in each heat exchange section [% of heat transferred]	0.5
Feedwater pump hydraulic efficiency [%]	85.0
Mechanical-electric efficiency of feedwater pump [%]	90.6
Steam turbine mechanical efficiency [%]	99.6
Electric generator efficiency [%]	98.5
Auxiliaries for condenser heat rejection [% of heat transferred]	0.8
<i>Auxiliaries consumption</i>	
Mechanical-electric efficiency of ID/FD fans [%]	94.0
Isentropic efficiency of ID/FD fans [%]	80.0
<i>MEA CO₂ absorption process</i>	
Heat duty of the stripper reboiler [MJ/kgCO ₂]	3.03
Pump consumption [kWh/kgCO ₂]	0.03
Steam pressure for the stripper reboiler [bar]	2.0
Pressure drop in the absorber [kPa]	10
Fan isentropic efficiency [%]	85.0
Fan mechanical-electric efficiency [%]	95.0
<i>CO₂ compression</i>	
Number of inter-cooled compression stages [-]	5
Isentropic efficiency [%]	84.0
Electric-mechanical efficiency [%]	94.0
Pump hydraulic efficiency [%]	75.0
Pump electric-mechanical efficiency [%]	94.0
CO ₂ pressure at compressor discharge [bar]	89.1
Final CO ₂ pressure [bar]	150.0

*Valid only for the power plant integrated with post-combustion CO₂ capture with MEA

**Number of feedwater heaters in the power plant with post-combustion CO₂ capture with MEA

Table A2. Flow rates, temperature, pressure and composition for the main streams in Figure 4

Stream no.	T [°C]	p [bar]	G [kg/s]	N [kmol/s]	LHV [MJ/kg]	Gas composition [%mol.]									Solid composition [%wt.]					
						Ar	CH ₄	C+	H ₂	CO	CO ₂	O ₂	N ₂	H ₂ O	CaO	CaCO ₃	Cu	Cu ₂ O	CuO	Al ₂ O ₃
1	25.0	1.01	80.0	2.64	2.40	--	--	--	3.63	22.34	22.10	--	48.77	3.15						
2	214.8	1.26	99.6	3.73	1.91	--	--	--	2.57	15.81	15.64	--	34.52	31.46						
3	400.0	1.08	48.5	2.57	3.42	--	--	--	26.56	0.14	0.32		50.13	22.86						
4	183.3	1.04	48.5	2.57	3.42	--	--	--	26.56	0.14	0.32		50.13	22.86						
5	70.0	1.01	48.5	2.57	3.42	--	--	--	26.56	0.14	0.32		50.13	22.86						
6	25.0	1.01	9.7	0.99	39.48	--	23.04	2.69	59.53	3.84	0.96	0.19	5.76	3.98						
7	600.0	1.26	9.7	0.99	39.48	--	23.04	2.69	59.53	3.84	0.96	0.19	5.76	3.98						
8	726.4	1.09	96.9	2.92	--	--	--	--	--	--	57.61	--	1.96	40.43						
9	579.1	1.06	96.9	2.92	--	--	--	--	--	--	57.61	--	1.96	40.43						
10	210.0	1.04	96.9	2.92	--	--	--	--	--	--	57.61	--	1.96	40.43						
11	80.0	1.01	96.9	2.92	--	--	--	--	--	--	57.61	--	1.96	40.43						
12	25.0	1.01	133.3	4.65	--	0.91	--	--	--	--	0.03	20.41	79.10	2.55						
13	300.0	1.21	133.3	4.65	--	0.91	--	--	--	--	0.03	20.41	79.10	2.55						
14	900.0	1.05	105.1	3.77	--	1.12	--	--	--	--	0.04	1.80	93.90	3.15						
15	396.1	1.00	105.1	3.77	--	1.12	--	--	--	--	0.04	1.80	93.90	3.15						
16	82.5	1.01	105.1	3.77	--	1.12	--	--	--	--	0.04	1.80	93.90	3.15						
17	565.0	153.0	109.5	6.08	--	--	--	--	--	--	--	--	--	100						
18	565.0	36.0	109.1	6.06	--	--	--	--	--	--	--	--	--	100						
19	140.0	8.0	51.5	2.86	--	--	--	--	--	--	--	--	--	100						
20	285.5	180.0	105.8	5.87	--	--	--	--	--	--	--	--	--	100						
21	285.5	180.0	98.9	5.49	--	--	--	--	--	--	--	--	--	100						
22	138.5	1.26	19.6	1.09	--	--	--	--	--	--	--	--	--	100						
23	25.0	1.01	17.9	0.18	--									--	100	--	--	--	--	
24	880.0	1.20	10.0	0.18	--									100	--	--	--	--	--	
25	600.0	1.10	394.7	5.99	--									66.01	33.99	--	--	--	--	
26	671.4	1.10	394.7	5.99	--									66.01	33.99	--	--	--	--	
27	726.4	1.10	394.7	5.99	--									66.01	33.99	--	--	--	--	
28	900.0	1.05	8224.4	142.10	--									91.34	--	--	1.47	3.33	2.66	
29	880.0	1.02	8196.3	140.38	--									92.77	--	0.03	4.49	--	2.70	
30	70.0	1.01	23.6	1.25	3.42	--	--	--	26.56	0.14	0.32	--	50.13	22.86						
31	35.2	150.0	75.0	1.72	--	--	--	--	--	--	97.37	--	2.63	--						

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