**Advanced fixed-bed Ca-Cu looping process for the CO2 capture in steel mills**

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**Highlights**

* A novel process for H2 production by the SEWGS of blast furnace gas is proposed
* A Cu/CuO chemical loop supplies the energy required for the regeneration of the sorbent
* A process design has determined the operating windows for each stage of the system
* Results show theoretical viability of the process and potential for further development

**1. Introduction**

Steelmaking is the main energy-consuming industry in the world, accounting for 27 % of the total CO2 emissions from industrial processes [1]. CO2 Capture and Storage (CCS) is the only alternative that can lead to a drastic reduction in CO2 emissions far beyond that currently achievable in the steelmaking industry and achieve the climate change mitigation targets set as long term objectives after COP21 [2]. 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 [3], since BFG contains 60-80% of the total carbon entering the steel mill in the form of CO and CO2. The Sorption Enhanced Water Gas Shift (SEWGS) can be particularly suitable to decarbonize the BFG and produce a H2-enriched fuel gas that can be easily integrated throughout the steel mill [4]. In the SEWGS, a high-temperature sorbent (typically a hydrotalcite-like or a CaO-based material) removes the CO2 from the gaseous phase as soon as it is produced [5]. 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. CaO-based materials exhibit very high theoretical energy recovery and also have higher CO2 carrying capacities: up to 45% wt. in newly developed CaO materials compared to 8% for hydrotalcites. The main challenge for the scaling-up of the SEWGS is the need to find an efficient and low-priced method for the regeneration of the CO2 sorbent. The Ca-Cu chemical looping process, patented by CSIC in 2009 [6], is based on the “unmixed reforming” concept [7], but with the key difference that the heat needed for CaCO3 calcination is supplied in situ by the exothermic reduction of CuO to Cu with a gaseous fuel. Significant progress in reactor modelling, thermal integration and materials durability have been made over the last years in the Ca-Cu looping process [8]. This concept has also been experimentally validated in fixed beds at TRL4 [9]. In recent works [10], the Ca-Cu process has been proposed to decarbonize the off-gases of steel mills using an arrangement of interconnected fluidized-bed reactors operating at atmospheric pressure. In this work, an advanced configuration based on several fixed-bed reactors operating in parallel is proposed to integrate the Ca-Cu looping process in a steel mill. This configuration facilitates the performance at high pressure, which allows higher energy efficiencies to be achieved and avoids the need for downstream solid-gas separation devices.

**2. Process description**

The proposed Ca-Cu looping process follows a sequence of at least three reaction steps. A H2-rich gas is first obtained through a sorption enhanced water gas shift (SEWGS) process of BFG at 600-650ºC and 20 bar, while CO2 reacts with CaO to form CaCO3. In a second stage, Cu oxidation takes place at 20 bar with diluted air (about 3% of O2) by recirculating part of the N2 obtained as product to limit the temperature of the bed material below 880ºC, thereby minimizing the calcination of the CO2 sorbent (i.e., the CO2 slip during this stage). In the third stage, the necessary heat to calcine CaCO3 is directly supplied by the exothermic reduction of CuO-based solid with a gaseous fuel (that can be coke oven gas or external natural gas), thereby producing a highly concentrated stream of CO2 and H2O(v). An appropriate CuO/CaCO3 ensures that the heat generated during the CuO reduction is sufficient to decompose completely the calcium carbonate.

**3. Results and discussion**

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 the coke oven gas (COG) available in the steel mill as reducing gas in the reduction/calcination stage around 30% of the BFG can be decarbonized in the SEWGS reactor. An overall CO2 capture efficiency in the steel plant higher than 90% can be achieved if additional natural gas is used as fuel in the reduction/calcination reactor together with the COG. The proposed Ca-Cu looping process offers great CO2 capture rates with moderate energy consumption. A specific primary energy consumption for CO2 avoided (SPECCA) in the Ca-Cu looping process of 2.3 MJ/kg CO2 has been calculated, which is much lower than the energy consumed in the reference plant with CO2 capture using amine absorption (i.e. 4.3 MJ/kg CO2).

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