

Sorption enhanced production of hydrogen in industrial processes using two chemical loops

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ABSTRACT

We analyze in this work a number of process concepts that involve the production of hydrogen (from natural gas reforming or shifting CO-rich gases) enhanced by the carbonation of CaO. This reaction removes CO₂ and shifts equilibria towards the formation of H₂. A second chemical loop is used to regenerate the sorbent back to CaO and produce a rich stream of CO₂. One of such generic systems is the Ca-Cu looping process (see Fig. 1, left), which has so far been developed for H₂ production and power generation [1-3]. The basic process scheme consists of a sequence of three reaction steps. In the first stage, an enriched stream of H₂ is produced by the sorption enhanced reforming (SER) of natural gas in the presence of a reforming catalyst, a CaO-based sorbent and a copper-based solid (that acts as inert in this stage). In the next stage, the Cu-based material is oxidized with air at a moderate temperature to avoid the decomposition of CaCO₃ through partial calcination. In the final stage, the calcination of the CaCO₃ is accomplished by means of the exothermic reduction of CuO with a gaseous fuel at atmospheric pressure. This critical reaction step has been recently demonstrated at TRL4 [4] under the FP7 ASCENT project, which aims at demonstrating under industrially relevant conditions the Ca-Cu looping process (and other two pre-combustion CO₂ capture technologies) that rely on the use of high temperature solids.

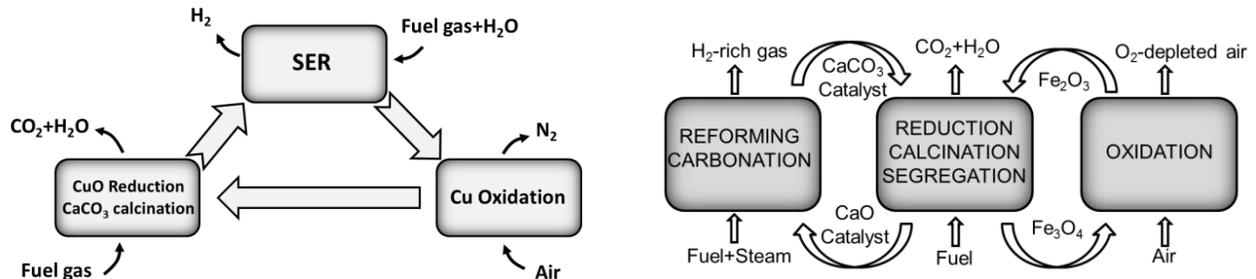


Figure 1. Schemes of hydrogen production processes enhanced by CaO carbonation and combined with a second chemical loop to calcine CaCO₃ and produce a rich stream of CO₂.

Martínez et al. [5] have recently assessed the integration of the Ca-Cu looping into a state-of-the-art ammonia production plant, exploiting the inherent advantage of providing almost pure streams of hydrogen and nitrogen as part of its products. As demonstrated, such integration

reduces the specific primary energy consumption per unit of NH_3 produced, even when accounting for the higher electric consumption associated to the Ca-Cu process. The Ca-Cu looping process has been also proposed for the production of a H_2 -enriched fuel gas by means of the sorption enhanced water gas shift (SEWGS) of blast furnace (BFG) gas in steel mills [6]. The operation is carried out in an arrangement of interconnected fluidized-bed reactors at atmospheric pressure, which allows for a solids' segregation step to be introduced that will reduce significantly the solid circulation between reactors. Around 27% of the BFG can be decarbonized in the SEWGS reactor with this process, decreasing in this way the CO_2 emissions associated to its use within the steel mill.

We compare recent advances in the Ca-Cu looping process with the performance of an alternative sorption enhanced reforming process that uses the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ chemical loop for the regeneration of the CO_2 -sorbent (see Fig. 1, right). In this case, the enthalpy of reduction of Fe_2O_3 to Fe_3O_4 is slightly endothermic and the energy required for the simultaneous reduction/calcination reactions is transported as sensible heat by hot solids that circulate from the oxidation reactor [7]. The large heat-transfer capacity and the good performance at high temperatures (up to 1200°C) of the iron oxides allows the operation to be carried out with reasonable circulation of solids (within the typical ranges of CFB boilers). In this work, mass and energy balances of the hydrogen production processes shown in Fig.1 are compared when used in stand-alone hydrogen production plant from natural gas or in a steel mill for decarbonizing the exhaust gases in this process. Optimum operating conditions in each case are conveniently assessed, and process performance is discussed in terms of H_2 production efficiency, specific primary energy consumption per unit of CO_2 avoided and/or overall feasibility of the configuration proposed.

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