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An experimental characterization of Calcium Looping integrated with concentrated solar power

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ABSTRACT

Carbon Capture and Sequestration (CCS) and renewable energy sources are both essential to mitigate the CO_2 emissions in the near future. Calcium Looping (CaL) is an important post-combustion carbon capture technology that has reached the maturity of the pilot plant stage. On the other side Concentrated Solar Power (CSP) is a fast-growing renewable technology in which solar energy, concentrated up to several MW m^{-2}, can be used to produce electricity or to drive an endothermic chemical reaction. The integration between a CSP system and a CaL cycle, in order to use a renewable source to supply the energy required by the calciner, would strongly improve the performance of the CaL process by overcoming some of its main drawbacks. However, the role that highly concentrated radiation can have on the sorbent properties in the CaL cycle is still matter of investigation. In this study, the CaL-CSP integrated process is experimentally investigated through the use of a directly irradiated Fluidized Bed (FB) reactor. Simulated concentrated solar radiation featured a peak flux on the FB surface of approximately 3 MW m^{-2} and a total power of about 3 kW_{th}. Several calcination and carbonation tests have been performed on samples of a commercial Italian limestone, in order to establish the evolution of the sorbent capacity of CO_2 capture at increasing number of cycles. The properties of the limestone samples were further investigated by means of microstructural characterization. The comparison between results obtained with and without the use of the solar concentrated flux to thermally sustain calcination provides useful information on the potential of solar driven CaL and on the measure to overcome some of its potential limitations.

1. Introduction

Authoritative outlooks anticipate a transitional era during which achievement of global warming and CO_2 emission reduction targets could be achieved by a combined shifting toward renewable energy sources and a rational use of fossil fuels with implementation of Carbon Capture and Storage (CCS). Calcium Looping (CaL) stems out as one of the most promising and mature post-combustion CCS technologies, which can be effectively implemented in existing combustion plants. It is based on the alternated temperature-swing uptake and concentrated release of CO_2 in flue gas by a Ca-based sorbent (e.g. limestone). In the carbonator reactor, CO_2 in the flue gas generated from a combustion plant is captured by CaO at around 650–700 °C following an exothermic reaction. Thus, the carbonator emits a CO_2-depleted flue gas and a spent sorbent consisting of a mixture of reacted $CaCO_3$ and unconverted CaO. The spent sorbent is eventually fed to a calciner where endothermic regeneration is carried out at around 850–950 °C. This step yields a CO_2-rich flue gas (ready for further processing and final storage) and regenerates the CaO-based sorbent. The heat required to sustain the endotherm of the calcination step is usually supplied by burning auxiliary fuels in the calciner in an oxyfiring mode, so as to avoid dilution of the CO_2-rich stream generated in the calciner. This option requires coupling of the CaL plant with an ASU (air separation unit) to provide O_2-rich feeding to the calciner. CaL is most typically carried out in a Dual Interconnected Fluidized Bed (DIFB) reactor arrangement, which enables effective solid transfer from one reactor to the other and a convenient environment for the progress of the heterogeneous gas–solid reactions. The CaL technology, documented by a vast literature [1–5], has reached the maturity of the pilot plant stage [6–7].

Operating the calciner as an oxyfiring combustor represents a major drawback of the CaL basic cycle, which may be overcome by integration between the CaL cycle and Concentrating Solar Power (CSP) systems [8–15]. In this case the heat required for the calcination step is directly provided by the abundant and inexpensive solar source, and the overall

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thermal throughput of the power plant is increased accordingly [16]. Integration between CaL and CSP has been encouraged by the expanding application of fluidized beds (FB) to CSP as solar receivers or solar multiphase reactors [17–20]. Dense solid suspensions can absorb and withstand highly concentrated radiative fluxes of several MW m^{-2} typical of CSP systems in either the solar-tower or beam-down versions. This feature enables operation of solar collectors/reactors at high process temperature and large thermal efficiencies. Use of FB in CSP systems is encouraged by excellent thermal properties of dense gas-solid suspensions [21]: large heat transfer coefficients and thermal diffusivities promote collection and transfer of the incident solar energy with minimal local overheating. The potential of FB reactors has already been recognized and reported by several research groups [22–24] and FB have been positively tested at laboratory scale for generation of solar fuels and chemicals [25–29]. The interaction between the incident radiative flux and FB can occur in an indirect way, as the radiation is collected in a cavity whence the incident power is transferred to the FB, or in a direct way, as the FB is directly irradiated through openings or transparent walls and windows. Direct absorption of solar energy permits higher operating temperatures [30]: directly-irradiated FB reactors can be operated at process temperatures high enough to perform thermochemical storage with high energy density and production of solar fuels [31–33]. A critical issue in solar FB reactors is represented by the overheating of bed surface that can be induced by the highly concentrated solar radiations. This can indeed affect the efficiency of FB as thermal receivers and cause possible sintering and/or degradation of the fluidized particles, with the consequent reduction of the efficiency of thermochemical cycles. Unconventional fluidization, e.g. by uneven and unsteady fluidization, has been proposed as a mean to promote thermal equalization while limiting parasitic energy losses [21,34–35]. Integration of CaL and CSP ("solar CaL") has been considered as early as in the beginning of seventies [24,36–40] to prove that solar energy can be conveniently used to calcine limestone in a FB reactor. Moreover a lab-scale FB reactor, equipped with a high-pressure Ar arc to simulate the source of solar energy systems, has been used to uptake CO_2 from ambient air with Ca-based sorbents [41–42].

In the present study, the "solar CaL" process has been investigated in experimental tests consisting of iterated calcination/carbonation cycles in a directly irradiated lab-scale FB reactor. Results are compared with those obtained in "non-solar CaL" experiments carried out without simulated solar radiative heating. In the latter case the FB reactor was thermally sustained by controlled electric heating. The comparison is helpful to shed light on the possible effect that uneven localized energy supply to the bed exerts on temperature non-uniformity and, in turn, sintering and deactivation of the sorbent upon iterated cycles. To this end, sorbent samples recovered at the end of CaL tests have been characterized from the standpoint of microstructural properties.

2. Experimental

2.1. Experimental apparatus

The experimental apparatus used in the present study is reported in Fig. 1. It consists of a FB reactor with an internal bed diameter of 0.102 m and a height of 0.1 m. The choice of a bed aspect ratio (internal diameter-height ratio) approaching unity was intentional, in order to promote internal solids circulation patterns characterized by the establishment of a single vortex ring [43]. The windbox section is 0.15 m high. The upper part of the FB reactor is connected to a conically-shaped section, 0.4 m high, which represents the freeboard of the FB reactor. The upper section of the freeboard is confined by a ceramic glass optical window through which the simulated solar radiation reaches the bed. The window has a thickness of 4 mm and a maximum operating temperature of 700 °C. The transmittance of this glass is about 0.9 in the spectral range between 340 μm and 2350 μm. An air purge stream was intermittently used to clean the external side of the window. The conical shape of the upper freeboard ensures that there is no restriction to the radiative flux. Moreover it promotes effective settlement of the particles projected by bubble bursts [43] so that the transparent window can be kept clean. The gas discharge port is located at mid-level in the freeboard conical section so that entrainment of solid particles ejected by bubble bursting and impact of finer particles with the upper transparent window are minimized.

The solar concentrated radiation is simulated by an array of three short-arc Xe-lamps of 4 kW_{el} each, coupled with elliptical reflectors (Optiforms E1585). The use of Xe lamps to simulate the solar spectrum is well established in the literature since the differences with the solar spectrum are quite small, especially in the visible spectral range. The filtering effect of the window can be considered negligible and affects only the tails of the spectrum. The characterization of the simulated radiation was performed by following an experimental procedure described in a previous study [35] which makes use of a thermal infrared camera (Optris PI-400, 7.5–13 μm, 382 × 288 pixels, maximum frame rate 80 Hz), to record the spatial distribution of the incident radiative flux, and of a water cooled radiometer (Vatell TG-9000) to measure the radiative flux. The distribution of the spatial flux of each lamp on the FB surface was obtained independently from the others, and finally the three distributions of spatial flux were superimposed to obtain the overall distribution of heat flux (Fig. 2). Surface mapping of radiative power indicates a peak flux of approximately 3000 kW m^{-2}, a value typical of research-oriented applications of CSP to high-temperature thermochemical energy storage [30]. The average flux over the whole reactor cross-section is equal to 390 kW m^{-2}, which corresponds to a total irradiated power of about 3.2 kW.

The reactor is also surrounded by two semi cylindrical radiant heaters consisting of electrical resistances embedded in ceramic fiber (Watlow Ceramic Fiber Heaters, maximum power 5 kW at 240 V) which accomplish two main tasks: i) heating of the reaction chamber, and ii) insulation of the internal chamber from the environment. A gas preheater (Osram Sylvania Threaded Inline Heaters, maximum power 1.6 kW at 170 V), made of a stainless steel pipe with a serpentine-coil element as electric heater, may also be used to heat up the inlet gas stream up to 750 °C depending on the experimental requirements. The semi cylindrical heaters are driven by an ON/OFF PID controller connected to a K-type thermocouple located inside the bed, whereas gas preheating was regulated by acting on applied voltage by means of a rheostat. Preheating of the fluidizing gas was used for better control and fine tuning of bed temperature. Finally, two mass flow controllers were used to supply air and CO_2 at the desired concentration.

The reactor is equipped with two K-type thermocouples located inside the FB: one, 0.01 m above the gas distributor, measured the bulk bed temperature (T_{down}); the second, located 0.08 m above the gas distributor, provides a measure of bed overheating close to the irradiated surface (T_{up}). The infrared camera (Optris PI-400, 7.5–13 μm, 382 × 288 pixels, maximum frame rate 80 Hz) is used to measure the surface temperature of the bed. The calibration range enables temperature detection in the 200–1500 °C interval, once a proper value of emissivity is set for the emitting surface.

The spectral range detected by the infrared camera does not overlap with the emission spectrum of the short-arc Xe-lamp, so the error related to the part of the incident radiation which is reflected by the fluidized particles can be considered negligible. However the infrared camera cannot measure the bed surface temperature when the optical window is mounted on the reactor, as the window material absorbs the infrared radiation in the 7.5–13 μm spectral range. Monitoring CO_2 concentration at the exhaust is accomplished with an Advance Optima ABB AO2020 (Uras 14, 0–100%$_v$) analyzer. Gas sampling is accomplished via a 6 mm stainless steel (ID 4 mm) probe, inserted in the reactor through one of the four outlet pipes and located at a level of 0.15–0.20 m above the bed surface. A suction pump is calibrated to sample at a rate of 0.050–0.060 $Nm^3 h^{-1}$. A steel wool filter is interposed between the pump and the reactor to avoid that fine solid particles reach the analyzer.