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Preliminary Study on Sound Assisted Calcium Looping for TCES in CSP Applications

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Thermochemical energy storage (TCES) is considered as a promising technology to accomplish high energy storage efficiency in concentrating solar power (CSP) plants. Among all the alternatives, the calcium-looping (CaL) process, based on the reversible calcination−carbonation of $CaCO_3$, is one of the most promising solution due to the high energy density achievable and the extremely low price, nontoxicity, and wide availability of natural CaO precursors such as limestone. In this work, sound-assisted fluidization has been used to improve the carbonation of fine CaO particles (< 10 μm) at CSP conditions. In particular, CaL tests have been performed under ordinary and sound-assisted fluidization conditions in order to study the influence of the application of high intensity acoustic fields on the agglomeration of fine CaO particles. Tests have been carried out in a lab-scale experimental apparatus at CSP-CaL conditions. The effect of sound parameters (SPL and frequency) have been also highlighted.

1. Introduction

The main challenge for a short-term deeper penetration of renewable energy sources, such as solar energy, typically characterized by the intermittency of power production, is represented by energy storage (Salatino et al., 2016). In this framework, thermochemical energy storage (TCES) is one of the most promising technology to achieve high-energy storage efficiency in concentrating solar power (CSP) plants (Karasavvas et al., 2018). TCES basically consists of using the high temperatures achievable by CSP to drive an endothermic chemical reaction (Ortiz et al., 2018). The reaction products are stored separately to be employed when needed for carrying out the exothermic reverse reaction, which releases the heat previously used (Ortiz et al., 2018). Among the different alternatives, the calcium-looping (CaL) process, based on the reversible calcination−carbonation of $CaCO_3$, is considered to be one of the most viable candidates due to the high energy density achievable and the extremely low price, nontoxicity, and wide availability of natural CaO precursors such as limestone. Indeed, the carbonation/calcination reaction of CaO, with an equilibrium temperature of 895 °C (under a CO_2 partial pressure of 1 atm), has a high potential for TCES in the relatively high temperature range attainable in CSP tower plants (roughly between 600 and 1000 °C) and would allow also for a high energy storage density (about 3.26 GJ/m^3). As regards the reactor configuration, CaL is generally performed in two interconnected fluidized beds, one acting as carbonator and the other as calcinator (Valverde et al., 2013). It is noteworthy that the optimum conditions to carry out the CaL process strongly depend on the particular application, thus critically affecting the CaO multicycle performance (Alovisio et al., 2017). In particular, to achieve high overall efficiency for TCES and electricity generation in CSP plants, carbonation would be carried out at high CO_2 partial pressure and high temperature (around 850 °C, i.e. the highest achievable carbonation temperature, thus yielding high efficiency thermal to electricity efficiency of the power cycle), whereas, calcination could be performed at relatively low temperature (~700 °C) using a gas easily separable from CO_2, such as superheated steam or helium (thus reducing costs and allowing the use of already available solar receiver) (Alovisio et al., 2017).

Carbonation of CaO particles occurs in two phases. A first fast carbonation stage is characterized by the sorption of CO_2 on the free surface of the particles and proceeds under mass/heat transfer control (Valverde et al., 2013). The rate of this fast carbonation phase is not just controlled by the kinetics of the chemical

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reaction itself, but also by the transport of CO_2 and heat to the particles surface (Valverde et al., 2013). Then, after this fast stage, a thin layer of $CaCO_3$ covers the free surface of the sorbent particles and CO_2 sorption turns to be controlled by a much slower phase characterized by the diffusion of CO_2 through the solid $CaCO_3$ layer. In this framework, the use of fine particles (< 100 μm) can be a possible solution to reduce the intraparticle diffusion resistance on the reaction rate (Valverde et al., 2013). However, the use of fine particles, belonging to the C group of Geldart's classification (Geldart, 1986), poses issues concerning their intrinsic difficulty to be fluidized due to their strong interparticle forces (Viscusi et al., 2016), leading to agglomeration and channeling phenomena (Chirone et al., 2018), which in turns would remarkably hinder the reaction efficiency due to poor gas/solid contact and mass/heat transfer (Raganati et al., 2017). As a possible solution to these issues, it has been demonstrated that, from one hand, acoustic vibrations can promote the fluidization of fine particles (Ammendola et al., 2015) and, thus, improve the gas/solid contact efficiency by forcing particle vibrations, which reduces aggregation and disrupts gas channels (Valverde et al., 2013). From the other hand, sound waves induce also a number of phenomena taking place at the gas/solids interface, such as acoustic streaming, which contribute to enhance mass/heat transfer rates in gas/solids reactors (Valverde et al., 2013).

In this work, sound-assisted fluidization has been used to promote CaO carbonation at CSP conditions. In particular, tests have been performed under ordinary and sound-assisted fluidization conditions in order to study the influence of the application of high intensity acoustic fields on the agglomeration of fine $CaO/CaCO_3$ particles (< 10 μm). Tests have been carried out in a lab-scale experimental apparatus at CSP-CaL conditions. The effect of sound parameters (SPL and frequency) have been also highlighted.

2. Materials and methods

The sorbent used in this work is a limestone supplied by OMYA with a Sauter diameter of 3.61 µm, i.e. it belongs to Group C of Geldart's classification. All the tests have been carried out at atmospheric pressure in a lab-scale apparatus consisting of a fluidized bed column made of quartz (40 mm ID and 1500 mm high). The sound-generation system consists of a digital signal generator, a power audio amplifier rated up to 40 W, and a 8W woofer loudspeaker. Separate high purity N_2 and CO_2 cylinders (99.995% vol.) have been used to prepare the gas feed, using two mass flow controllers (Brooks 8550S) to set and control the inlet flowrates. A heating jacket (Tyco Thermal Controls GmbH) has been used to heat the column to the desired adsorption temperature. The temperature inside the reactor is monitored and controlled using a type K thermocouple connected to a PID controller. The column is provided with a pressure probe located at the wall, 5 mm above the gas distributor, to measure the pressure drops across the bed. The analysis system consists of a continuous analyzer, to monitor the outlet CO_2 concentration by means of an infrared detector (ABB AO2020, URAS 14) (Gargiulo et al., 2018).

Preliminary fluid-dynamic characterization

The limestone has been previously characterized from the fluid-dynamic point of view performing fluidization tests under both ordinary and sound-assisted conditions. N_2 has been used as fluidizing gas in order to prevent any intensification of the powder cohesiveness due to air moisture. For all the tests 100 g of limestone have been loaded in the fluidization column in order to obtain a bed height of about 15 cm. Pressure drops and bed expansion curves as a function of gas velocity have been measured in fluidization experiments carried out at different temperatures (25 - 800 °C) and using acoustic fields of different intensities (120−150 dB) and frequencies (50 - 300 Hz). Then, experimental data have been worked out to calculate the main fluidization parameters. In particular, the minimum fluidization velocity (u_{mf}) has been evaluated from pressure drop data and the average size of fluidized particles (d_p) has been evaluated from the experimental values of u_{mf} using a literature correlation (Raganati et al., 2017).

Carbonation/calcination tests

Pre-treatment: The $CaCO_3$ sample (100 g) is firstly subjected to a calcination step (T = 900 °C) for 2h under N_2 flow (115 NL/h), corresponding to a superficial gas velocity of 2.5 cm/s, which is about five times larger than the minimum fluidization velocity of the sorbent material, to obtain pure CaO. In particular, this pre-treatment has been carried out under sound-assisted conditions (150dB – 120Hz), corresponding to the optimal acoustic parameters obtained from the fluid-dynamic characterization, in order to obtain the starting materials under the same operating conditions for all the different tests.

Carbonation/Calcination cycles: After the pre-treatment stage, the sample is subjected to 10 carbonation/calcination cycles, where a cycle consists of a carbonation step followed by a calcination step. The carbonation step is carried out at 800°C using a mixture of 70% CO_2/30% N_2 vol/vol (115 NL/h) as inlet gas flowrate until the complete saturation of the bed. Then, this is followed by the subsequent calcination stage, which is also carried out at 800 °C but switching the inlet gas flowrate (115 NL/h) to N_2, up to complete decarbonation for regeneration of the sorbent. Carbonation tests have been carried out under both ordinary and sound-assisted fluidization conditions (120 – 150dB/50 – 300Hz); whereas, all the calcination tests have been carried out under sound-assisted fluidization conditions (150dB – 120 Hz).

3. Results and discussions

Preliminary fluid-dynamic characterization - The results of the fluid-dynamic characterization show that the application of the sound perturbation is necessary to achieve a fluidization regime. Indeed, as clear from the analysis of Figure 1a, under ordinary conditions the pressure drop curve is quite irregular and a proper fluidization regime cannot be reached due to agglomeration and channeling, as typical of cohesive powders (Raganati et al., 2018). In particular, the beneficial role of the sound assistance in a fluidized bed of fine powders is to induce a continuous break-up mechanism of the large aggregates present inside the bed into smaller fluidizable ones due to the action of external (drag and inertial) forces, which counteract the internal (cohesive) forces (Raganati et al., 2018). In other words, the acoustic perturbation makes it possible to fluidize fine cohesive particles in the form of aggregates (rather than as the original particles) that undergo a continuous mechanism of break-up and reaggregation. The results obtained also show that increasing temperatures lead to increased fluidization difficulty, as confirmed by the pressure drop curves shifting to the right (Figure1b) since the cohesiveness of the powder is enhanced at higher temperatures and more and more particles sticks together to form larger clusters (Raganati et al., 2018).

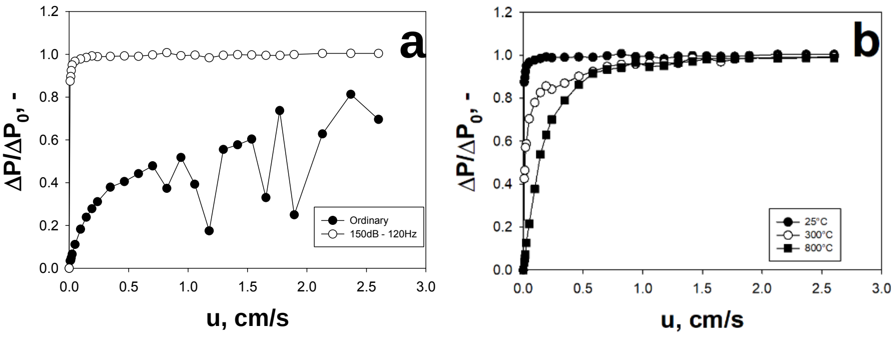

Figure 1: Pressure drops curves obtained: a) under ordinary and sound assisted fluidization conditions at 25 °C; b) under sound assisted fluidization conditions (150dB – 120Hz) at different temperatures.

With reference to the effect of the sound parameters, SPL has a beneficial effect on the fluidization quality. Indeed, d_p (35 – 25 μm) and u_{mf} (0.061 – 0.036 cm/s), as a consequence, are always decreased by passing from 120 to 150 dB. This evidence is due to the fact that with increasing SPLs more energy is introduced inside the bed, thus making the breakup of larger clusters more and more efficient (Raganati et al., 2018). Sound frequency has a non-monotonic effect on the fluidization quality: a nonlinear relationship has been observed between all the fluidization parameters and the sound frequency. Indeed, the curves of d_p and u_{mf}, as a consequence, are characterized by a minimum value (25 μm corresponding to 0.036 cm/s) at 120 Hz, i.e., the maximum response frequency. This behavior is due to the fact that the frequency directly affects the relative motion between clusters and subclusters, which, in turn, promotes the essential break-up and reaggregation mechanism (Raganati et al., 2018). In particular, for too high frequencies, the acoustic field cannot properly propagate inside the bed since the sound absorption coefficient is proportional to the square of sound frequency as sound propagates through the bed of particles. On the contrary, for too low frequencies, the relative motion between larger and smaller sub-aggregates is practically absent.

Cyclic carbonation/calcination tests - Figure 2, reporting the comparison between the CO_2 outlet concentration profiles obtained under ordinary and sound-assisted conditions, clearly shows that the acoustic perturbation remarkably enhances the carbonation performances. This is due to the fluidization quality being extremely poor and unstable under ordinary conditions; indeed, unable to overcome the cohesiveness of the fine sorbent particles, most of the inlet gas flows across the bed only through channels of minimum resistance (Raganati et al., 2018), thus allowing for a by-pass of an appreciable volume of gas and hampering both gas–solid contact and the carbonation efficiency. Indeed, the agglomeration phenomena affect both the gaseous (CO_2) and solid ($CaCO_3$) reactants taking part to the carbonation reactions. As for the gaseous side, due to agglomeration a small fraction of the inlet CO_2 takes part to the reaction, most of it by-passing the bed through the channels. Accordingly, most of the gaseous reactant, CO_2, exit the bed without reacting with CaO (Raganati et al., 2016). As for the solid side, agglomeration also remarkably reduces the actual availability of sorbent surface to the carbonation reaction. Indeed, due to agglomeration, a large portion of the sorbent surface is completely precluded to the fluid phase. Therefore, the general result of the sorbent agglomeration is a continuous and sudden increase of the CO_2 outlet concentration.

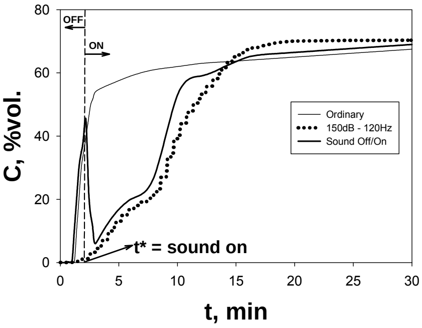

Figure 2: CO_2 outlet concentration measured during carbonation for an ordinary fluidization test, a sound-assisted fluidization test and for a test in which the sound was switched on at t = t. Inlet flow rate: 115 NL/h; Carbonation: T = 800 °C; 70%vol. of CO_2 in N_2. Calcination: T = 800 °C; 100%vol. N_2.*

On the contrary, the application of the sound makes it possible to hinder the agglomeration phenomena, enhancing the fluidization quality and providing better gas–solid contact and mass transfer coefficients (Raganati et al., 2015). Accordingly, channels are disrupted and more CO_2 can properly permeate the sorbent bed and take part to the carbonation reaction. Moreover, a larger surface of the sorbent can actually come into direct contact with the fluidizing gas and react with the CO_2 (Raganati et al., 2015). The application of the sound makes it possible to maximize the exploitation of the sorbent reactivity: even though fluidized in the form of aggregates, these fluidizing structures are not static but dynamic. In particular, they undergo a continuous mechanism of break-up and reaggregation, continuously renewing the sorbent surface exposed to the gaseous phase. It is also clear from Figure 2 that the difference between the ordinary and sound-assisted tests is more evident in the initial stage of the reaction. Indeed, the capability of the sound to increase the gas-solid contact efficiency, i.e. the enhancement of the sorbent surface availability, is particularly important in the initial kinetically controlled stage of the carbonation reaction, in which the carbonation conversion is ascribable to the sorption of CO_2 on the free surface of the sorbent particles (Valverde et al., 2013). After this initial phase, a thin layer of $CaCO_3$ (30-50 nm thick) begins to cover the free particle surface, and, consequently, the reaction turns to be controlled by a much slower phase characterized by the diffusion of CO_2 through the $CaCO_3$ layer (Valverde et al., 2013). In this much slower phase, the effect of the sound is less important since it is strictly related to diffusion mechanisms rather than to the availability of sorbent surface and, therefore, to the quality of the gas-solid contact.

Figures 3a and b report the results obtained in terms of carbonation conversion as a function of time and as a function of the number of cycles, respectively. In particular, the experimental data of CaO conversion during multiple cycles have been fitted using the semi-empirical equation (Perejón et al., 2016):

$$\frac{X_N}{X_1} = \frac{X_r}{X_1} + \left(\frac{1}{k(N-1)+\left(1-\frac{X_r}{X_1}\right)^{-1}}\right) \qquad (1)$$

where, X_N is the conversion in cycle N, X_r is the residual conversion, X_1 is the conversion in the first cycle and k is the deactivation rate constant. Consistently with the observed enhancement of the carbonation reaction (Figure 2), the carbonation conversion is obviously increased under sound-assisted conditions due to the better exploitation of both the gaseous (CO_2, which can properly permeate the sorbent without by-passing it unused due to agglomeration) and solid (CaO, which can come into direct contact with the CO_2 and doesn't remain unreacted) reactants. But, most interestingly, also the deactivation rate is reduced and the residual conversion is increased when sound is applied. Clearly, as widely documented (Blamey et al., 2010), the lime reactivity decreases with increasing the number of carbonation/calcination cycles due to the progressive reduction of the BET surface area as a result of material sintering during the calcination stages. However, since the sorbent has such small dimensions, something more happens. Indeed, in addition to sintering, which causes an intrinsic decline in sorbent surface over repeated cycles, the extreme agglomeration phenomena, due to the natural cohesiveness of the sorbent, contributes to a further reduction of the sorbent surface. Therefore, natural (due to calcination conditions) sintering plus natural (due to the fine sorbent particles) agglomeration lead to a faster carbonation conversion decline under ordinary conditions. On the contrary, when sound is applied, the agglomeration issue is solved and only sintering remains to cause the decline in carbonation conversion.

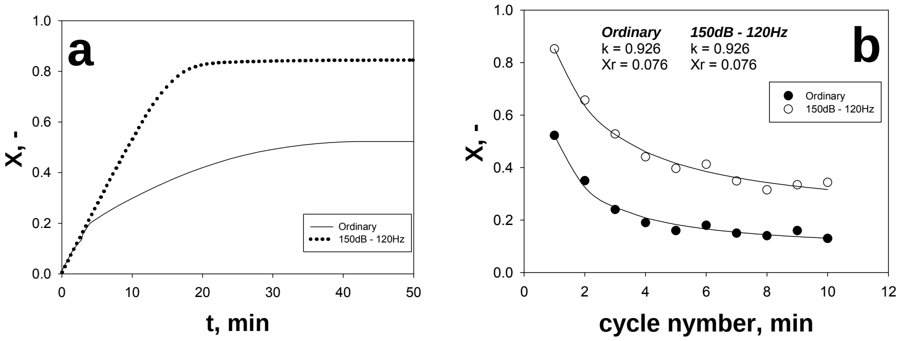

Figure 3: a) Carbonation conversion vs time under ordinary and sound-assisted conditions; b) Carbonation conversion vs cycle number and deactivation fit curve under ordinary and sound assisted-fluidization conditions. Inlet flow rate: 115 NL/h; Carbonation: T = 800 °C; 70%vol. of CO_2 in N_2. Calcination: T = 800 °C; 100%vol. N_2.

As a further confirmation of these considerations on the positive effect yielded by the sound on the CaL performances, a specific test has been carried out, in which the sound was switched on at a certain time. In particular, the test has been started under ordinary conditions and only at a time t* the sound as been turned on (Figure 2). This test emphasizes, even more significantly, how the sound can affect the extent and evolution of the carbonation reaction. Indeed, for time lower than t*, namely before sound was switched on, the CO_2 outlet profile is the same as that obtained under ordinary conditions. Then, when the sound was switched on at t*, the CO_2 concentration suddenly drops down before rising up again following now the typical trend of the sound assisted test. This result confirms is the clear proof of the actual ability of the sound to provide a better exploitation of the sorbent surface. Indeed, as soon as the sound was switched on, that specific surface, precluded to the fluid under ordinary conditions and, therefore, remained unreacted, suddenly becomes available causing CO_2 concentration to drop down because of the renewed sorbent reactivity.

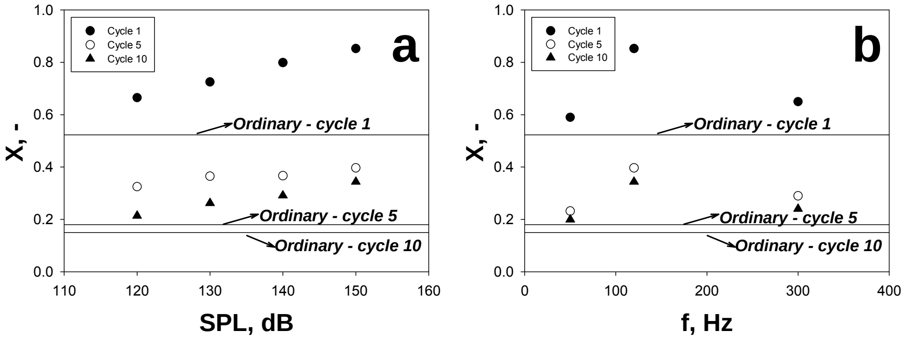

Figure 4: Carbonation conversion as a function of (a) SPL, at a fixed sound frequency of 120 Hz, and (b) frequency, at a fixed SPL of 150dB.

In analogy to what done for the preliminary fluid-dynamic characterization, the effect of the acoustic parameters on the CaL performances has been investigated. With reference to the SPL, the monotonic effect obtained on the fluidization quality is reflected on the Carbonation performances (Figure 4a), which is consistent with the enhanced disaggregation mechanism due to the increased strength of the acoustic wave. Likewise, also the non-monotonic effect of the sound frequency on the fluidization quality is confirmed for the carbonation performances (Figure 4b), according to the observed optimal range of frequencies, at which the propagation of the sound wave inside the bed and, therefore, the disaggregation mechanism is optimized.

4. Conclusions

In this work a preliminary study on sound assisted Calcium looping for TCES in CSP applications has been carried out in order to evaluate the agglomeration phenomena. The application of the acoustic perturbation remarkably enhances the carbonation performances. Indeed, it can hinder the agglomeration phenomena, which negatively affect carbonation from both the gaseous (CO_2) and solid ($CaCO_3$) sides of the reaction, thus enhancing the fluidization quality and providing better gas–solid contact and mass transfer coefficients. Most interestingly, besides increasing the carbonation conversion, the application of the sound results in a remarkable decrease of the deactivation rate. Indeed when such fine sorbent particles are employed under ordinary conditions their strong agglomeration causes a supplementary decrease of sorbent surface in addition to the intrinsic decline over repeated cycles caused by sintering. Therefore, this additional cause of sorbent surface reduction can be avoided when sound is applied, thus resulting in a remarkable limitation of the deactivation rate (which, as in the case of coarser particles, is only due to natural sintering occurring during calcination). The effect of SPL and frequency has also been investigated, showing even further the tight link existing between the gas-solid contact efficiency, i.e. fluidization quality, and the CaL performances. Indeed, both SPL and frequency exhibit on the CaL performances the same effect as that obtained from the fluidization experiments, i.e. increasing SPL are advantageous and the same optimum range of frequency has been found.

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