Solar calcination of minerals

By

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Intro

The use of renewable energy not only for electricity production but also for process heat is a theme which is gaining more and more attention. Few renewable sources can produce heat efficiently at high temperature and among them, concentrated solar thermal (CST) energy has a huge potential.

As an example, solar calcination of minerals is a point of study since the 1980ies (Flamant et al. 1980) and projects on this topic have never stopped turning up since then. The most used calcination process takes place in the cement industry, responsible for 7 % of the total global emission (Marmier 2023). About half of this emission are due to the process itself (unavoidable emission) while the other half is due to the fuel combustion. This shows the huge potential of substituting fossil fuels with greener energy sources. Several reactors were proposed and studied to this scope. The material can be directly heated by the solar radiation (directly heated reactors), or the heat can be transferred through an intermediate material which can be an opaque wall or another heat transfer medium (indirect reactor concept). The first group allows to have the highest temperature on the reactants itself, while the second group requires a further temperature gradient in order to transfer the heat to the reactant. Also, the reactor can operate in a closed configuration, or open to ambient atmosphere. The first concept has the big advantage of potentially collecting the CO_2 produced by the reaction, but when operating at high CO_2 concentration, the temperatures required are much higher and problems related to material reconversion can take place. On the other hand, an open reactor has the potential of irradiating directly the reactant, thus allowing lower temperature inside the reactor and therefore using cheaper construction materials.

Limestone and Dolomite

The calcination of limestone ($CaCO_3$), which is the main component of cement raw meal, takes place over 900 °C under atmospheric conditions. Already in 1980, the first experimental studies on solar calcination of limestone were carried out (Flamant et al. 1980, Badie et al. 1980). Two directly heated reactor concepts were tested and compared: a fluidized bed operated in batch mode and a rotary kiln operated in a continuous mode, both treating limestone particles of 200–315 µm diameter. The fluidized bed operated in closed configuration, *i.e.* the particles were confined inside a transparent silica tube and were not in contact with the ambient air. About 10 g of material was treated with an incident power of 1.7 kW. The rotary kiln was open to ambient air and treated 0.28 kg/h with a power of 1.5 kW. The material calcination could reach respectively 100 % and 60 %.

Few years later, Salman and Khraishi (Salman and Khraishi 1988) proposed to press 0.8 g of limestone in the shape of pellets, which were introduced into a graphite rod. The fixed bed of pellets was heated by 1.5 kW. Temperatures much higher than the equilibrium temperature were required to reach a degree of calcination beyond 60 %. The pellet was directly heated and the reactor worked in closed configuration.

As another approach, a vortex concept reactor was proposed by Steinfeld et al. for this application. Fine particles of limestone (1–5 µm) were directly irradiated and could achieve complete calcination in an open reactor concept based on a cyclone gas separator (Steinfeld et al. 1992, Imhof 1991). The reactor operated with a continuous flow of 0.3 kg/h of particles and with an incident power of 3 kW and it could reach calcination degree between 53 % and 94 %.

A different vortex reactor concept was developed by Nikulshina et al. (Nikulshina et al. 2009) combining the two objectives of limestone calcination and syngas production through methane reforming. In this innovative concept, limestone particles were entrained by a flow of methane, and the CO_2 produced by calcination reacted with the methane to produce CO and hydrogen. The particles flow of 0.18 kg/h was directly irradiated by 3.7 kW incident power and the reactor was closed by a window. High calcination rates up to 83 % were achieved.

Of all the proposed concepts, the most used and studied are rotary kilns. After the first concept, proposed by Flamant, Meier et al. tested an open rotary kiln with a flow of 2.3 kg/h of 2-3 mm limestone particles. Calcination above 95 % could be reached. In order to ensure a good particle mixing, high rotational speeds were required. This led to the formation of a dust cloud at the reactor entrance which increased the heat losses. The design was then modified towards a closed indirectly heated reactor concept (Meier et al. 2006). In this reactor, 16 SiC tubes were placed concentrically inside the rotating cavity. Higher flowrates (7 kg/h) of the same particles were applied. In this case, high calcination rates were achieved with peaks above 98 %.

A smaller rotating reactor indirectly irradiated was proposed by Abanades et al. several years later (Abanades and André 2018). At first a simple rotating alumina tube was used which was later on introduced inside a cavity to reduce heat losses. The particles flow of 0.16 kg/h moved in counterflow to the gas, in a closed reactor concept, and was indirectly irradiated by 0.75 kW incident power. Complete calcination could be reached when using argon as flushing gas.

An open rotary kiln, directly irradiated was built and proven for the treatment of cement raw meal (Fig. 1) and is described in the next paragraph. Based on the promising results, the same concept was scaled up and will be tested with limestone particles. This second reactor will be powered by 50–100 kW of incident power and will be able to treat 40–95 kg/h of limestone. The system is at present under construction and will be tested in the beginning of 2025.

Furthermore, the fluidized bed reactor played an important role in the development of solar calcination. Tregambi et al. tested a directly irradiated closed fluidized bed. Here the objective was calcium looping, i.e. the cyclic calcination (from left to right in Eq. 1) and carbonation (from right to left in Eq. 1) of a mixture of sand and limestone (Tregambi et al. 2018a, Tregambi et al. 2018b).

$$CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g) \quad \text{Eq. 1}$$

A batch of about 1 kg particles (400-1000 µm) was irradiated through a glass window by a power of 3.2 kW, obtaining calcination degree of 88 %.

A large fluidized bed reactor was proposed, designed and tested by Esence et al. The closed reactor was irradiated by 33 kW incident power. A flow of 9.4 kg/h limestone and dolomite with particles size between 8 and 375 µm was calcined obtaining a complete conversion of the dolomite but no conversion of limestone, due to lower temperature and a non-uniform flux distribution on the irradiated wall (Esence et al. 2020a). An innovative aiming strategy allowed to reduce hotspots on the irradiated wall and obtaining uniform flux distribution, which allowed to increase the incident power to 45-65 kW and the temperature in the particles bed. With this strategy and the same reactor, a flow of 15-25 kg/h pure limestone particles (1-500 µm) were calcined, with a maximum conversion over 95 % (Esence et al. 2020a, Esence et al. 2020b).

Cement raw meal

Cement raw meal is mainly composed of limestone (about 80 %), with addition of clay and eventually iron ore and quartz sand (Kohlhaas and Labahn 1983, Sprung 2008). Taking this material as feedstock represents a further step to approach cement industry, with its pros and cons. The advantage is the tackling one of the most energy intensive industries, the disadvantage is that the particles size and composition is given by a commercial provider, and can therefore not be modified in the experiment.

The first experiments treating real cement raw meal (CRM) were shown by Imhof et al. A vortex reactor based on the concept proposed by Steinfeld was scaled up (Imhof 1997, 2000). The incident power of 54 kW was entering the rector from the bottom and directly irradiated 25 kg/h of particles (<10 µm) entrained by the gas flowing on a vertical vortex shape. The gas flow was 7 times higher than the particle flow. Calcination degree up to 85 % was achieved.

A second scaled-up concept for the solar treatment of CRM was recently proven by Moumin et al. (Moumin et al. 2019, Tescari et al. 2018). In this study, the rotary kiln shown in Fig. 1 could continuously calcine 4-12 kg/h of CRM particles (1-175 µm). An incident power of 14 kW irradiated the particles flow in an open reactor concept, reaching calcination degree over 95 %. Several hours of reliable operation lead to pursuit this way and propose a bigger improved reactor based on the same concept, presented in the previous paragraph.

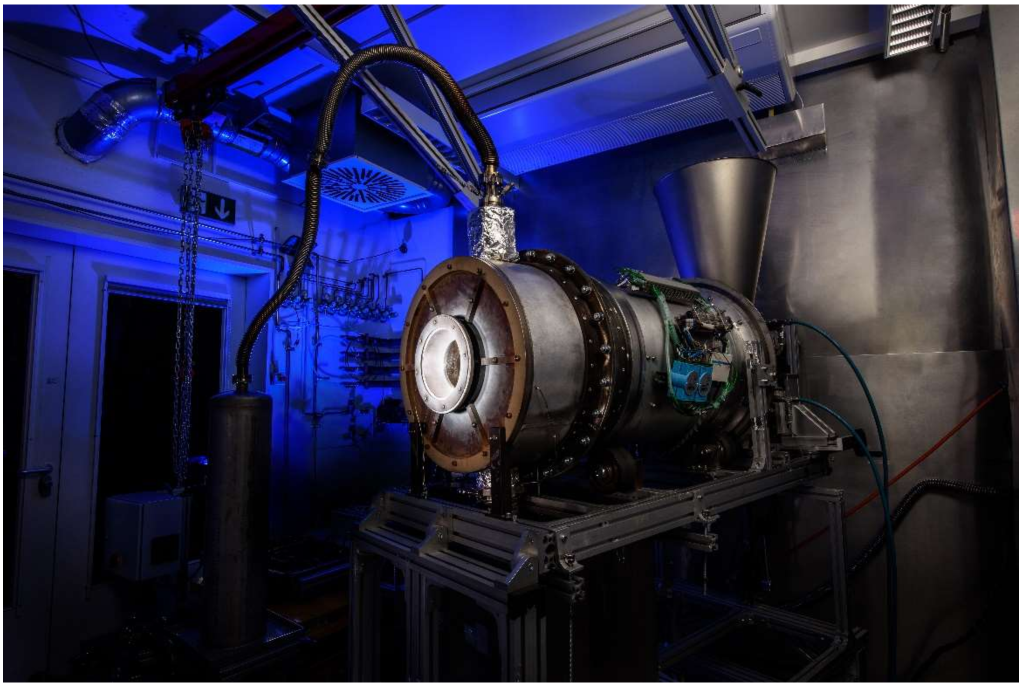

Fig. 1: Directly irradiated rotary kiln, tested in DLR solar simulator. The CRM was introduced by a screw feeder below the conical hopper at the back, then flew through the reactor where it was calcined, and then extracted from the bottom at the front. The gas was extracted from the pipe on the top front. The incident radiation entered the cavity through the aperture in the front.

Due to the small particle size, and due to the advantages of operating in directly irradiated and close configuration in order to enable direct CO_2 sequestration, the window is one of the key points to further improve solar calcination. Several concepts to avoid particles deposition on the window for solar reactors have been proposed but for different solar processes, e.g. gas curtain system to prevent carbon deposition in a fluidized bed gasifier (Kodama et al. 2017), vortex flow systems to avoid carbon deposition (Kogan and Kogan 2002), and Zn condensation (Schunk et al. 2008), or expanding-vortex systems to mitigate particle deposition onto receiver-reactor windows (Chinnici et al. 2016). These systems which are based on aerodynamic protection methods required either inert gases or gases involved in the thermochemical process for its functioning. In the case of solar calciners, CO_2 could be a feasible option to operate the window protection system. With such operation mode, the obtention of a rich-CO_2 gas for further utilization or sequestration processes can be possible. An interesting recent study showed the potential of applying Electrostatic Separation Processes (ESP) to protect the window of a solar calciner from particle deposition. ESP are already very well known in the cement industry for the off-gas cleaning process. The challenge of reproducing this concept and extend its operation to high temperature was studied by Rincon-Duarte (Rincon Duarte et al. 2020, Moumin and Roeb 2023). The study showed that at high temperatures (360 – 660 °C) the electrical resistivity of cement raw meal and calcium oxide particles (10^4 to 10^{11} Ω·cm) enable optimal collection using ESP. The electrostatic precipitator included a window to evaluate the system protection performance. At temperature of 660°C[1], the best results were obtained using positive corona discharge and applying a voltage of 20 kV for the ESP system. The reported reduction of the transmittance of window samples were very low: 0.10% and 0.25% for experiments with CaO and CRM particles, respectively.

Other materials

Though representing a smaller share in the global CO_2 emission balance, several other energy intensive processes show high environmental potential in the implementation of solar energy sources. Examples are the production of kaolin or alumina.

Solar calcination of alumina was shown in a first-of-a-kind experiment in 2017. An entrained vortex reactor operating in closed configuration was proposed and tested (Davis et al. 2017). The reactant aluminium hydroxide particles (15.5 µm mean diameter) was processed with a flow of 0.5-2.5 g/min and irradiated by 2-4.3 kW incident power to reach calcination temperature (~880 °C). It was also noticed that using CST as energy source allowed a higher purity and quality of the product compared to conventional production methods.

Another application case is the calcination of kaolin. The mineral is an essential component for nanofilters, zeolites, but also a promising candidate to replace the emission-intensive limestone in cement mixtures. In a first proof-of-concept, Pasabeyoglu et al. performed the calcination of kaolin to metakaolin in a solar simulator (Pasabeyoglu et al. 2023). 1 kg of material was treated batch-wise, reaching temperatures in the reactor of 600–1000 °C with an input power of up to 5.6 kW. Depending on the applied temperature, very high crystallinities were found for the produced zeolites 4A or 13X. These results indicate a promising option to decarbonize the metakaolin production and to expand the application of CST to the treatment of minerals.

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[1] Particle injection during 90 s, with particle concentration in the gas flow of 9 g/Nm³.

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