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Efficient CO_2 Capture from Lime Production by an Indirectly Heated Carbonate Looping Process

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Abstract

Lime is used in a wide range of products and applications in agriculture as well as in different sectors of the industry. Today, main lime applications are as fluxing agent in iron & steel production, as a binder in building and construction and in a variety of environmental applications such as for the neutralization of waste water and for the removal of acidic gas compounds in flue gas treatment. Lime (CaO) is produced by burning of limestone ($CaCO_3$) at 900 – 1200 ºC in vertical shaft or horizontal rotary kilns fired mainly by gas, oil, coal, coke and some types of secondary fuels (e.g. used oil, plastics, paper). CO_2 emissions from combustion can be reduced by replacing fossil fuels by renewable fuels, such as biomass. Process CO_2 emissions resulting from the decomposition of $CaCO_3$ amount to around 65 % of total CO_2 emissions and can only be omitted by CCS technology.

Several CO_2 capture processes are currently being developed, but most of them have the consequence of high energy consumption leading to lower plant efficiencies and increased costs. Pre-combustion capture is not suitable for lime processes since process CO_2 emissions cannot be captured. Oxyfuel combustion has the potential to capture CO_2 from both process emissions and combustion emissions, but requires an air separation unit for supply of pure oxygen. Post-combustion capture technologies generally have the possibility to capture the major part of CO_2 emissions. Solvent based technologies are highly developed, but require huge amounts of heat for sorbent regeneration.

The carbonate looping (CaL) process has the potential to significantly reduce the efficiency loss compared to solvent based technologies, since the process operates at high temperatures, which allows the utilization of heat for power production in a highly efficient steam cycle. Furthermore, the CaL process offers synergies with the lime industry since the sorbent is the raw material of the process. The CO_2 contained in the flue gas is absorbed by CaO in the carbonator at around 650 °C. The $CaCO_3$ formed hereby is transferred to the calciner, where the CO_2 is released at around 900 °C. As the calcination reaction is endothermic, the calciner needs to be supplied with heat. The most straightforward heat supply is the direct combustion of fuel with oxygen in the calciner. This oxy-fired CaL process has been successfully tested in in several pilot plants of to MW_{th} scale.

The efficiency penalty of the CaL process can be further decreased when the need for technical oxygen in the plant can be avoided. This can be achieved by indirect heating of the calciner, e.g. through metallic walls, by solids circulation, or via heat pipes. The flue gas of the external combustion chamber is directed to the carbonator, where most of the CO_2 contained in this flue gas is absorbed by CaO. The main advantages of this indirectly heated carbonate looping process (IHCaL) compared to the standard CaL process are summarized as follows:

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- No air separation unit is needed to produce technical pure oxygen, which leads to lower investment costs and to a lower energy consumption.
- Fewer impurities (sulphur, ash) from a supplementary firing are brought into the Ca-loop, so that spent sorbent will be of higher purity and therefore be better suited for further utilization.
- Lower CaO deactivation rates are expected due to “mild” calcination around the heat pipe surfaces compared to rather harsh conditions in an oxy-fired calciner, so that sorbent remains more reactive.
- Lower attrition rates are expected due to a low fluidization velocity in the calciner, which improves the operability of the fluidized bed system.
- An almost pure CO_2 stream leaves the calciner, which allows for technically easy and cost-effective CO_2 purification process for compression and storage/utilization of CO_2.

The IHCaL concept with heat pipes was previously evaluated with respect to CO_2 capture from coal-fired power plants. Heat pipes offer an excellent heat transfer performance based on evaporation and condensation of a liquid (i.e. sodium for temperatures >800 °C) inside a closed pipe. CO_2 avoidance costs have been calculated to 22.6 €/t CO_2 excluding CO_2 storage. A 300 kW_{th} pilot plant for investigation of indirect calcination via heat pipes was successfully operated for more than 300 hours with stable CO_2 capture at a temperature difference between combustor and calciner of around 100 K.

This study presents two novel concepts for integrating the IHCaL process into a lime production plant. One is a tail-end solution in an existing lime plant placed after the kiln and capturing the CO_2 of the flue gas. The other is an integrated solution, as illustrated in Figure 1. Raw material (limestone) is used as sorbent for the IHCaL process, and the purge from the IHCaL process consists of CaO, which is the main product. The heat of the flue gas leaving the carbonator or calciner is used to pre-heat the raw material. The heat of the remaining flue gases is extracted in heat recovery steam generators for power generation using a highly efficient steam cycle as well as for pre-heating the combustion air. The produced electricity is partially used on site for various consumers and partially sent to the grid generating additional income for the plant operator. This integrated concept results in a completely new lime production process that has various advantages compared to conventional lime kilns:

- The fuel is no longer in direct contact with the lime, which improves the purity of the lime and allows the utilization of a wider range of secondary fuels
- The temperature in the calciner is uniform and well controlled, which enables the production of well-designed products.
- A smaller particle size is used (0.1 – 0.5 mm) compared to shaft furnaces, which reduces the calcination time, intensifying production and minimizing inhomogeneities within the particle mixture.

The heat & mass balances for the IHCaL processes integrated into the lime plant are elaborated and optimized by means of process simulations using the ASPEN PLUS™ process simulation software combined with used defined blocks for the main reactors.

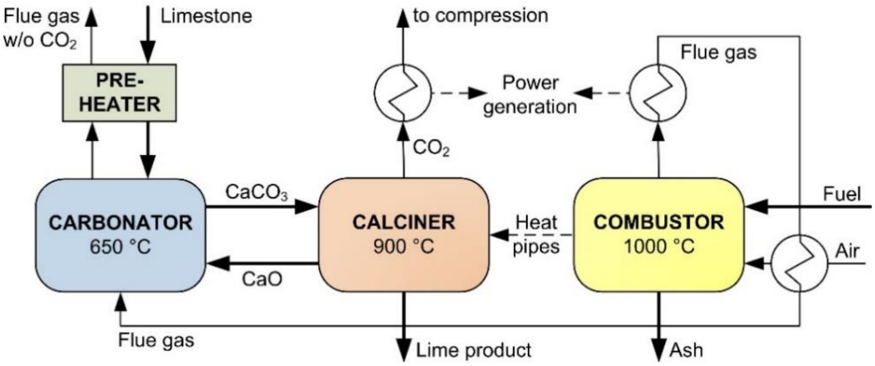

Figure 1: Concept of an IHCaL process integrated into a lime plant

Keywords: Lime production ; CO2 capture ; calcium looping ; indirect heating ; heat pipe ; process simulation