Sustainable use of natural materials as Calcium Looping sorbents for CO_2 capture in the cement industry

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The cement industry is the second largest CO_2 emitting industry accounting for over 5% of anthropogenic global CO_2 emissions[1]. About 50% of CO_2 emissions come from the process of converting limestone ($CaCO_3$) into calcium oxide (CaO), 40 % from the combustion of fuel into kiln and around 10 % from electricity consumption and transport.

The Cement Sustainability Initiative of the World Business Council for Sustainable Development and the International Energy Agency developed a cement technology roadmap which gives a clear message that besides further improvement in energy efficiency, use of alternative fuels and reduced clinker to cement ratio, a breakthrough is also required by CO_2 capture and sequestration (CCS) for achieving the long term reduction target.[1] In November of 2017, the European Parliament and Council has reached a provisional agreement to revise the EU Emissions Trading System (EU ETS)[2] for the period after 2020, and the sectors covered by the ETS, as cement industry, should reduce their emissions by 43% compared to 2005. The development of low-carbon technologies in cement industry is essential to reach this goal.

The "CaReCI - Carbon Emissions Reduction in the Cement Industry" project, funded by *Fundação para a Ciência e Tecnologia*, started in 2016 focusing the use of natural CaO-based sorbents to capture CO_2 through the Calcium-Looping Cycle (Ca-looping) and the incorporation of the exhausted sorbents in the cement industry as raw matter, fulfilling the circular economy concept.

Ca-looping is one of the most promising processes for CO_2 capture based on the reversible chemical reaction between CaO-based sorbents and CO_2 to form $CaCO_3$. During the calcination step CO_2 is selectively released from $CaCO_3$, and if this step is carried out under a higher CO_2 partial pressure, a pure stream of CO_2 can be generated suitable for storage or for conversion processes (e.g. fuel, chemicals).

Currently, the main Ca-looping challenge for CO_2 capture is related with the decay of the sorbent reactivity with increasing number of CO_2 capture cycles. To minimize this limitation, the CaReCI project is currently studying the CO_2 carrying capacity of several CaO-based sorbents: calcite, dolomite and waste marble powder[3]. The flue gases concentration of 25% of CO_2 has been used to mimic the real flue gases CO_2 concentration in the cement industry. Carbonation temperatures between 600 ºC and 700 ºC were evaluated, as well as the effect of using different pre-calcination atmospheres. Depending on the sorbents used, a CaO conversion

between 20 and 40% has been observed after 20 cycles, which means that for achieving a high CO_2 capture efficiency the ratio CaO/ CO_2 (ton/ton) should be maintained between 6.5 – 3.3 respectively, and a make-up of CaO should be considered to reach this ratio along the carbonation-calcination cycles. A unique and relevant advantage of the Ca-looping technology application in the cement industry is the use of cement raw matter (limestone) to capture CO_2 before its incorporation in the clinker, reducing costs and avoiding the production of wastes associated to the CCS.

References

[1] Cement Technology Roadmap 2009, Carbon emissions reductions up to 2050, International Energy Agency.

[2] EU Emissions Trading System: landmark agreement between Parliament and Council delivers on EU's commitment to turn Paris Agreement into reality, https://ec.europa.eu/clima/news/eu-emissions-trading-system-landmark-agreement-between-parliament-and-council-delivers-eus_en, acceded 21 November 2017

[3] Pinheiro, C.I.C., Fernandes, A., Freitas, C., Santos, E.T., Ribeiro, M.F. Waste Marble Powders as Promising Inexpensive Natural CaO-Based Sorbents for Post-Combustion CO2 Capture. Ind. Eng. Chem. Res., 2016, 55 (29) 7860– 787.