Modelling and simulation of the calcium looping cycle sorbent performance for CO₂ capture

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Objectives and Project Scope

With increasing ambitious targets set forth by the European Commission concerning the reduction of CO₂ emissions, there is a pressing need for the development and implementation of carbon capture and utilisation or storage (CSS) technologies, instrumental in achieving such directives. This need is becoming considerably more urgent if the trend shown on Fig. 1 is considered, where it can be observed that the global CO₂ emissions have been steadily rising since 1960 and more sharply so since the beginning of the 21st century.

Out of the five main sources in Fig. 1, the cement industry – in green – has in the last 10 years been responsible for approx. 5% of the global CO₂ emissions. The CaReci - Carbon Emissions Reduction in the Cement Industry research project aims to tackle this issue by performing a techno-economic evaluation of the implementation of a Calcium looping (CaL) cycle reactor for CO₂ capture in a Portuguese cement producer’s industrial plant. The CaL technology is a CO₂ capture regenerative cyclic process based on the reversible gas-solid reaction between CO₂ and CaO(is) to form CaCO₃(is), aiming to produce a concentrated stream of CO₂. Great potential lies in the integration with cement plants due to the synergy brought by the use of deactivated sorbent in the process – exemplified in Fig. 2. The creation of a validated multi-scale model for a fluidised bed reactor is envisioned as the final goal of this project, where the gPROMS ModelBuilder® is used as a platform for model development and parameter estimation.

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Figure 2 – Process integration between the calcium looping process and a cement plant

Figure 3 – Experimental CaO molar conversion as a function of time for the 1st cycle for different sorbents® and their estimation using the OGM.

Reaction Modeling

Despite various models having been proposed in the literature, one which explicitly dictates the relation between sorbent deactivation with increasing cycle number and the structural properties of the sorbent does not exist. In this work, two different models are used to describe the carbonation reaction and its cyclic behavior, with a third which relates to the structural properties of the sorbent currently being studied in order to be used to predict the cyclic behavior of the sorbent.

Overlapping Grain Model®

The Overlapping Grain Model (OGM) uses the grain model, which tries to describe a gas-solid reaction by modeling a particle as a composition of many grains of different size, and builds upon it, allowing for the overlapping of grains during the grain growth associated with the reaction. The OGM allows for the simulation of a single carbonation reaction, being able to accurately replicate the two characteristic regimes observed: the first one where the kinetics control the reaction and the second where diffusion is the limiting mechanism – seen on Fig. 3 for different sorbents. Fixed bed reactor experiments are used in conjunction with the parameter estimation tool in gPROMS ModelBuilder® to determine the first order rate constant k, the product layer diffusivity Dp, and a, the fraction of solid occupied by grains of the ith size fraction. As for the decreasing CO₂ carrying capacity of the sorbent observed when it is subjected to continuous carbonation and calcination cycles – present in Fig. 4 – it is calculated using Valverde’s equation®, which relates maximum conversion with the cycle number using a sintering factor a, and a regeneration factor b, obtained by fitting of experimental results.

Further work - Rate equation theory for pore size distribution during calcination®

Since the aim is to link sorbent deactivation to structural parameters, a rate equation is essential to simulate the pore network evolution during the calcination reaction. In its essence a shrinking core model – it describes the porous network as being the result of the collision and coalescence of vacancies via a combination of two distinct mechanisms, as can be seen on Fig. 5:

- The decomposition of CaCO₃ in which the outwards diffusing CO₂ produces a releasing force which promotes the coalescence of vacancies;
- The CaO sintering itself, described by the collision and coagulation theory of vacancies;

Therefore a rate equation is developed for the distribution of vacancies along the particle radius as a function of time, from which a pore size distribution (PSD) curve can be calculated for different calcination times, allowing the estimation of structural properties like total pore volume, total specific area and average pore diameter. Parameter estimation will also be used together with experimental Hg porosimetry data – such as the present on Fig. 6 – for different sorbents to adjust critical model parameters.

Final remarks

The carbonation reaction was modelled using the OGM model. The model was validated with Ca-Lopping experimental results obtained with different sorbents. While the sorbent’s deactivation with increasing cycle number is currently estimated using an equation developed by Valverde, further work includes the incorporation of a rate equation describing the evolution of the porous network during the calcination reaction in the OGM in order to predict cyclic behaviour has a function of sorbent structural parameters.

References