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A discrete-continuous approach to describe $CaCO_3$ decarbonation in non-steady thermal conditions

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ABSTRACT

In cement production, direct measurements of thermal and chemical variables are often unfeasible as a consequence of aggressive environments, moving parts and physical inaccessibility, and therefore prediction models are essential tools in these types of industrial applications. This article addresses the problem of the numerical prediction of the $CaCO_3$ calcination process, which is the first and the most energy expensive process in clinker production.
This study was conducted using the Extended Discrete Element Method (XDEM), a framework which allows a Eulerian approach for the gas phase to be combined with a Lagrange one for the powder phase.
A detailed validation of the numerical model was performed by comparison to non-isothermal TG curves for mass loss during the $CaCO_3$ decarbonation process. The complex three-dimensional predictions for solid and gas phases are believed to represent a first step towards a new insight into the cement production process.
Thus, the high accuracy and detailed description of the problem addressed, serve as a basis to assess the uncertainty of more simplified models such as those used in soft sensors.

1. Introduction

Calcium carbonate ($CaCO_3$) is a chemical compound commonly found in nature. Calcite is its most common crystalline form, and can be found in nature as the major constituent of limestone, a sedimentary rock.

Among all the applications that its production is addressed to, the most important is the cement industry; on its own this sector represents about 25% of the global demand. The Portland Cement Association expects cement consumption to reach nearly 86 Mt in 2014 [1].

Portland cement, which is the most common type of cement, is obtained by grinding a mixture of gypsum and clinker. The latter is produced by a pyroprocessing treatment, performed in precalciner kilns, and consists of heating up to a sintering temperature of about 1500°C a pre-grinded raw mix, of which limestone constitutes the major component.

Several chemical reactions occur during the heating of this material. The first is calcination, which starts around 840 °C and is almost completed inside the calciner:

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 178\ \frac{kJ}{mol}. \tag{1}$$

Calcination is a high endothermic reaction and, as a consequence, it requires a remarkable quantity of energy in order to be completed. For that reason up to 70% or more of the total fuel used for clinker production is burned in the calciner. Moreover, calcination has a strong impact on plant emissions because it represents the main source of CO_2 together with fuel burning.

The clinker production process is very complex. Currently, there is no complete description of all the factors involved in this process, owing to the complex thermal and chemical phenomena which take place. The lack of direct measurements on many process variables, as a result of several technical difficulties (e.g. moving parts, aggressive environment) also has a role in making this process difficult to understand. These factors have contributed to this process being considered as a black box, where success is entrusted to the experience of the operator and to fuzzy control strategies [2]. There is great interest in optimizing the clinker production process, because of its high-energy demand, its low efficiency and the high emissions it is characterized by. A constant

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price increase for fossil fuels, as well as increasingly severe environmental regulations, is therefore inducing world cement producers to optimize their processes and to verify that they are continuously run in optimized conditions [3].

Within this context the development of advanced and accurate numerical models, able to predict all the complex thermal and chemical phenomena involved, is gaining relevance. The complexity of these models is also increased by materials that are in different states, i.e. gaseous, liquid and solid, as well as powder. Besides providing predictions, these models could also furnish theoretical support for new measurement strategies based on soft-sensors. Soft sensors — also known as software sensors or neural-network-inferential calculators — are mathematical models, which provide a correlation of non-measured variables with others that are measured. In the last two decades soft sensors have become recognized as a valid alternative to traditional methods for the acquisition of critical process variables [4]. They appear particularly suited for processes like cement production, where difficulties in the measurement of particular variables (temperature profile of the material inside the kiln, evolution of the chemical species inside the kiln, etc.) are counterbalanced by a relevant number of measurements on other variables (temperature on the external shell, temperature at the inlet and the outlet, chemical composition at the inlet and the outlet, etc.).

$CaCO_3$ calcining has been extensively studied [5]. According to the results obtained by different authors the apparent magnitude of the Arrhenius parameters range from 110 to 3800 kJ/mol for the activation energy, and from 10^2 to 10^{157} S^{-1} for the frequency factor. Gieorgieva [5] concludes that wide variations in the values can be ascribed to the shape of the crystalline phase, the mean size of the particles, the sample mass, isothermal or non-isothermal heating, the heating rate, the static or dynamic atmosphere around the sample, the furnace atmosphere, the partial pressure of carbon dioxide, and the particular calculation procedure adopted.

Mikulcic [6] presented a numerical modeling of the calcination reaction mechanism for cement production using a CFD code to simulate turbulent flow, temperature, concentration fields of the reactants and products, as well as the interaction of particles with the gas phase. In his review he found that the first mathematical model for calcination mechanisms was developed by Borgwart [7], who concluded that the reaction rate is determined by heat and mass transfer inside a particle. Bes [8] proposed a 3-stage model for $CaCO_3$ calcination in cement calciners. A study by Mohr [9] describes the mathematical model of the calcination process, showing the impact of various parameters in the rate of calcination. Several CFD models have been developed, in order to describe heat and mass transport inside cyclone heat exchangers. According to Slack [10], almost all CFD models for cyclone heat exchangers are based on the Reynolds Stress Turbulence Model or Large Eddy Simulation. Hillers investigated the influence of several turbulence models on the calcination results using the same calcination model. Hu [11] provided a combined Eulerian Lagrangian approach for numerical modeling of a cement calciner, where the gas phase was modeled according to a $k-\epsilon$ model, particle dynamics were accounted for by a stochastic trajectories model, and a shrink core model surface controlling reaction was used for raw meal calcination.

This paper presents an Extended Discrete Element Method (XDEM) approach to predict $CaCO_3$ decomposition.

The Extended Discrete Element Method has successfully been used to study different thermochemical processes that appear during industrial processes. Estupinan [12] successfully applied XDEM in the prediction of heterogeneous reactions in packed beds. Estupinan et al. [13] applied XDEM techniques to model heat transfer in packed beds. XDEM simulations for water removal in packed beds were reported by Peters [14] and Mahmoudi et al. [15]. Peters [16–18] predicted the complex thermochemical processes of pyrolysis by the XDEM concept. Hoffman et al. [19,20] reviewed iron oxide reduction by using the same XDEM approach. Similarly, a CFD–DEM numerical investigation on heat and mass transfer related to the chemical conversion of limestone into quicklime in shaft kilns was proposed by Bluhm-Drenhaus [21]. However, in the latter, conductive and radiative heat transfer between the particles and the walls was not taken into account. This certainly affects heat transfer and may be worthwhile for certain cases. Nevertheless, Bluhm-Drenhaus [21] presents a setup that provides results in good agreement with experimental data.

Consequently, this paper describes the application of XDEM to the calcination process of a $CaCO_3$ sample in the powder state. The proposed numerical model accounts for gas flow via an open source CFD code, heat and mass transfer with particles and a 1D conductive–diffusive model for heat and mass transport inside each single particle. Predictions are validated with the experimental data documented by Gieorgieva et al. [5], where conduction with the solid walls plays a major role in the process.

This model should represent a first step towards the development of a soft sensor for the prediction of thermal and chemical variables inside a cement kiln. To that end, a complex CFD–DEM model will estimate the accuracy of simplified 1D models, which are suited for online implementations (rapid calculation times, etc.).

2. Extended Discrete Element Method (XDEM)

The Extended Discrete Element Method (XDEM) is an advanced multi-physics and numerical simulation framework in which the dynamics of granular material or particles described by the classical discrete element method (DEM) (Cundall [22] and Allen [23]) are extended by additional properties such as the thermodynamic state, and the stress/strain for each particle (Peters [14] and Mahmoudi [15]). In addition, the XDEM concept covers the coupling between discrete and continuous phases simultaneously. Thus, within this framework, continuous numerical approaches such as CFD (Computational Fluid Dynamics) and/or Finite Element Analysis (FEA) are coupled to discrete approaches in order to address numerous challenges in engineering e.g. drug production, agriculture and food processing industries, mining, construction and agricultural machinery, metal manufacturing, energy production and systems biology. Hence XDEM is considered as a Euler–Lagrange model, where the fluid phase is continuous, but each solid particle is tracked with a Lagrangian approach.

For a better understanding of the symbols used in the following subsections the reader is invited to review Section 5 of this paper.

2.1. Modeling fluid flow in porous media

The gas phase is solved according to a CFD model for porous media. One important quantity which characterizes a porous medium is its porosity ϵ_f. Porosity can be computed as the ratio between the void space and total volume of the packed bed, ranging between 0 and 1:

$$\epsilon_f = \frac{V_{void}}{V_{total}}. \tag{2}$$

The fluid model is based on a description of the flow as a continuous flow with averaging of the relevant variables on a coarser level, with respect to the sizes of the individual channels of the tortuous void space. This is done through the introduction of a Representative Elementary Volume (REV), which respects the following condition:

$$L_g << L_{REV} << L \tag{3}$$

with L being the characteristic length of the problem, L_{REV} the linear dimension of the REV, and L_g the microscopic length scale, i.e. the one associated with void dimension.

State variables, velocity and chemical concentrations inside the gas phase are averaged over the REV ($\langle\rangle$ symbol in the following equations).