Calcination of kaolinite clay particles for cement production: A modeling study

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ABSTRACT

Kaolinite rich clay particles calcined under certain conditions can attain favorable pozzolanic properties and can be used to substitute part of the CO_2 intensive clinker in cement production. To better guide calcination of a clay material, a transient one-dimensional single particle model is developed, which fully addresses the conversion process of raw kaolinite particles suspended in hot gas. Particles are discretized into a number of spherical cells, on each of which mass, momentum, energy and species conservation equations are numerically solved by using the finite volume method. Reactions considered in the model include dehydration, dehydroxylation and various phase transformations. Thermogravimetric analysis is used to determine reaction kinetic data required as inputs in the model and to validate the model. Finally, model-based sensitivity analysis is performed, from which quantitative guidelines for calcination condition optimization are derived.

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1. Introduction

Use of supplementary cementitious materials (SCM) to substitute part of the CO_2-intensive cement clinker is an attractive way to mitigate CO_2 emissions from cement industries. Calcined clays are one of the potential candidates for SCMs to produce green cements [1,2]. Thermal treatment of kaolinitic clays to a temperature at or beyond dehydroxylation activates their pozzolanic properties, and results in the best performance in cement. Optimally calcined kaolinite has pozzolanic activity equal to or higher than the well-known artificial pozzolans (e.g., fly ash and silica fume) [3–6]. Calcination at inappropriately high temperature (>1000 °C) or long retention time may decrease the reactivity of clay particles due to possible recrystallization of the reactive phase into a stable crystalline phase [7].

There are different calcination modes, e.g., flash calcination and soak calcination. Flash calcination is characterized by rapid heating and cooling of the pulverized material suspended in gas; whereas soak calcination is characterized by slow heating for relatively long periods. As such, the products of soak calcination are harder and might need further grinding after heat treatment [8]. Unlike soak calcination products, flash calcination products may not need further grinding [8]. The properties of flash-calcined and soak-calcined kaolinite have been studied [9–12]. Comparing to soak calcines, flash calcines are characterized by low density and high void fraction in their structure. This is due to the high vapor pressure developed inside the flash-calcined particles which

later disrupts the structure by creating additional channels allowing faster water diffusion out of the crystal.

Experiments have been commonly used to study kaolinite dehydroxylation. However, little effort was made to understand the phenomena through modeling, particularly modeling at particle scale. Reliable mathematical modeling can provide very useful details for in-depth understanding of the fundamentals of clay calcination and serve as a powerful tool for design, operation and optimization of industrial clay calcination processes. Salvador and Davies [11] investigated heating and dehydroxylation of kaolinite particles during flash calcination (particle diameters up to 500 μm, hot gas temperatures in the range of 550–1000 °C) by proposing a thermo-chemical model. The model was basically a simple lumped system method, without addressing any intra-particle processes (e.g., heat transfer, mass transfer or reactions inside clay particle) for particles as large as 500 μm in diameter. It was found that smaller particles dehydroxylated faster than larger particles. Gas temperatures were also found to greatly affect dehydroxylation: the higher the temperature, the shorter it took for clay particles to get dehydroxylated. Thus, when gases were heated to 1000 °C, the dehydroxylation time for large particles of 500 μm in diameter was found to be 1 s.

As the very first effort in literature, a transient one-dimensional (1D) particle model which fully addresses not only the particle-ambient flow interaction but intra-particle processes is developed in this paper to investigate calcination of clay particles. The particle is discretized into a number of spherical cells (or control volumes), on each of which mass, momentum, energy and species conservation equations are numerically solved by using the finite volume method [13]. The external heat and mass transfer between the particle surface and the ambient

flow serve as boundary condition in the model. Beside dehydroxylation which is widely studied in literature, all other potential reactions (e.g., dehydration and various phase transformations) are also included in the model. Thermogravimetric analysis (TGA) is used to determine reaction kinetic data inputs in the model, and TGA recorded mass loss is used to validate the model prediction. Finally, a model-based sensitivity study is carried out to derive quantitative guidelines for calcination of the clay in order to obtain optimum pozzolanic properties.
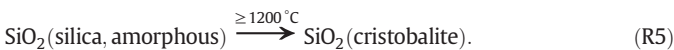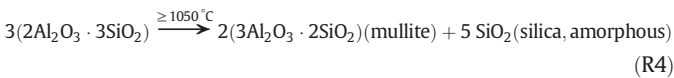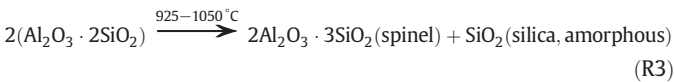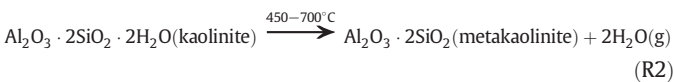
2. Methodological approach

2.1. Mathematical modeling

When a raw clay particle is suddenly exposed to the hot environment in a calciner, it will heat up under external convective and radiative heat transfer and then undergoes a series of conversion processes. If the raw clay particle contains free or bound water, the following reaction will occur first during clay calcination,

$$H_2O(l, bound) \xrightarrow{100 °C} H_2O(g). \tag{R1}$$
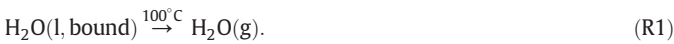
With further increase in clay particle temperature, a number of reactions will occur subsequently, including dehydroxylation and various phase transformations, which may be simplified by the following reaction scheme [14–16],

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O(kaolinite) \xrightarrow{450-700°C} Al_2O_3 \cdot 2SiO_2(metakaolinite) + 2H_2O(g) \tag{R2}$$

$$2(Al_2O_3 \cdot 2SiO_2) \xrightarrow{925-1050°C} 2Al_2O_3 \cdot 3SiO_2(spinel) + SiO_2(silica, amorphous) \tag{R3}$$

$$3(2Al_2O_3 \cdot 3SiO_2) \xrightarrow{\geq 1050°C} 2(3Al_2O_3 \cdot 2SiO_2)(mullite) + 5 SiO_2(silica, amorphous) \tag{R4}$$

$$SiO_2(silica, amorphous) \xrightarrow{\geq 1200°C} SiO_2(cristobalite). \tag{R5}$$

The reactions are influenced by many factors, e.g., degree of disorder of kaolinite structure [17], partial water vapor pressure [18], heating rate [19], and particle size [20].
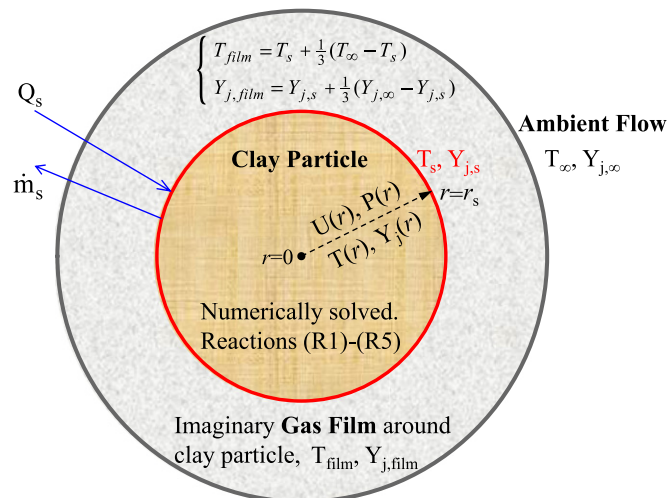
To develop a transient 1D particle calcination model (as sketched in Fig. 1), a number of assumptions are used: (1) spherical clay particles with homogeneous composition, (2) negligible change in particle volume and particle porosity during calcination, (3) symmetrical heat and mass transfer condition at the particle surface, (4) ideal gas for individual gas species and gas mixture, and (5) local thermal equilibrium among different phases within the particle. The clay particles prepared for calcination are tiny in size (about 14 μm in average diameter) and near-sphere in shape. When water is being expelled from the clay particles, the particle volume is likely to swell slightly, e.g., [21], which is also confirmed by our flash calcination tests. Flash calcination of the clay is performed in an industrial gas suspension calciner under different conditions and the clay samples before and after calcination are fully characterized. In the measured particle size distribution (PSD) for the raw clay sample (as shown in Fig. 2), there is only one major peak, at about 3 μm. In the PSD for all the calcined samples, two major peaks are observed: one is slightly over 3 μm and the other (i.e., the new peak) is at about 40–50 μm. The common peak at about 3 μm before and after calcination could imply there is only a slight increase in volume of the clay particles after calcination, which can be attributed to the relatively small loss of ignition (about 13–14%). However, quite significant particle agglomeration effect may occur during the calcination tests, resulting in the new peak at about 40–50 μm. The experimental results from the gas suspension calciner will be presented in detail in a separate paper. As for particle porosity, porosity of kaolinite is usually in the range of 0.3–0.6 [22]. During the thermal treatment of kaolinite, the porosity is found to slightly decrease from 0.4 at 700 °C, to 0.38 at 1050 °C and 0.27 at 1250 °C and dramatically decreases to 0.084 at 1300 °C and 0.04 at 1400 °C, as a result of the formation of an amorphous phase and crystals of mullite and cristobalite which replace the layered structure [23]. In this paper, a constant particle porosity of 0.3 is used, which may be acceptable for the range of temperatures used in our calcination tests. Moreover, the effect of the particle porosity is studied numerically, which is found to make a remarkable difference in the results for large particles (100 μm in diameter or above) while only make a slight difference in the results for small particles as used in this project (< 20 μm in average diameter), as shown later.

The governing equations, i.e., the mass, momentum, energy and species conservation equations are summarized in Eq. (1). They are rather general transport equations for flow, temperature and species mass fraction within a solid particle or liquid droplet during thermochemical conversion process. For instance, based on the similar governing equations a 1D model for solid fuel particle combustion has been successfully developed, validated and applied to CFD simulation of biomass/coal co-firing in a burner flow reactor [24]; a 3D model for liquid droplet heating and evaporation has also been successfully developed and validated in which the flow, heat and mass transfer within the droplet are numerically solved [25]. Clay particle conversion does not make a difference on the general conservation equations, the numerical method, or the modeling framework. The major difference in clay particle calcination
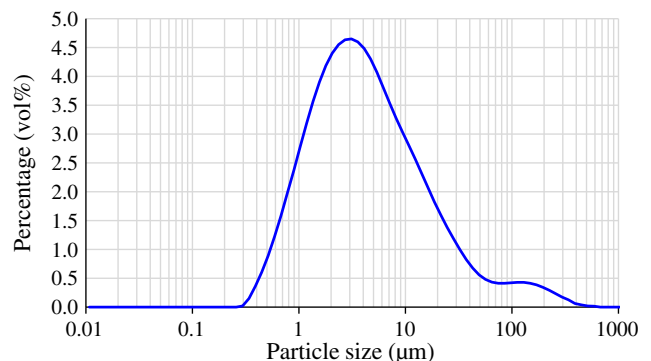

Fig. 1. Sketch of the 1D clay particle calcination model.

Fig. 2. Particle size distribution of the raw clay sample.