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Research paper

# Experimental and modeling study of flash calcination of kaolinite rich clay particles in a gas suspension calciner

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ABSTRACT

Calcination of kaolinite particles under appropriate conditions to produce materials that can replace part of the $CO_2$ intensive clinker is gaining an increasing interest in cement industry worldwide. This paper presents a study of flash calcination of kaolinite rich clay particles in a pilot scale gas suspension calciner, with the aim to derive useful guidelines on smart calcination for obtaining products of the best pozzolanic properties. Calcination tests are performed in the calciner under six different operation conditions. The raw feed and the calcined clay samples are all characterized experimentally and a mathematical model is also developed to predict the conversion of the clay particles. The model properly accounts for the particle–ambient flow interaction and numerically solves all the processes occurring within the clay particles. The model predictions are compared against the experimental results. A good agreement is achieved. Finally, a model-based sensitivity analysis is conducted.

## 1. Introduction

Kaolinite, one of the most abundant clay minerals on earth's crust, is a promising replacement of the $CO_2$ intensive clinker after proper calcination. Thermal decomposition of kaolinite has been studied over the years (Insley and Ewell, 1935; Brindley and Nakahira, 1958; Rashad, 2013). Calcination of kaolinite at moderate temperatures (450–800 °C) causes a release of water from the structure and yields amorphous metakaolinite, which is an effective pozzolan. Partial substitution of clinker with metakaolinite can enhance the strength and pore structure of the cement paste (He et al., 1994; Sabir et al., 2001; Shvarzman et al., 2003; Cassagnabère et al., 2010). Calcination at higher temperatures tends to promote the formation of a spinel-type phase along with amorphous silica, after which crystalline phases of mullite and cristobalite form. The appearance of these crystalline phases causes a decline in the material reactivity (Sabir et al., 2001). So, smart calcination is the key to produce high-quality metakaolinite.

During calcination, the moisture in the kaolinite rich clay, if existing, will be released first, which is the case in this study.

$$H_2O\ (\mathrm{l, free}) \xrightarrow{100^\circ C} H_2O\ (\mathrm{g}) \tag{R1}$$

Then, the structural transformation of kaolinite occurs as a sequence of reactions (Brindley and Nakahira, 1958; Ptáček et al., 2011). Due to lack of kinetic data of some reactions, especially the transformation of metakaolinite into spinel-type phase, a direct transformation of metakaolinite to mullite is assumed here and the reactions are summarized as follows:

$$Al_2Si_2O_5(OH)_4\ (\mathrm{kaolinite}) \xrightarrow{450-750^\circ C} Al_2Si_2O_7\ (\mathrm{metakaolinite}) + 2H_2O\ (\mathrm{g}) \tag{R2}$$

$$3(Al_2Si_2O_7) \xrightarrow{\geq 950\,^\circ C} Al_6Si_2O_{13}\ (\mathrm{mullite}) + 4SiO_2\ (\mathrm{Amorphous}) \tag{R3}$$

$$SiO_2\ (\mathrm{Amorphous}) \xrightarrow{\geq 1200^\circ C} SiO_2\ (\mathrm{Cristobalite}). \tag{R4}$$

In flash and soak calcination of kaolinite, the metastable phase is shown to have higher pozzolanic reactivity than the starting material and flash calcination is found to yield metakaolinite with lime reactivity similar or better than the reactivity of standard metakaolinites obtained by soak-calcination (Salvador, 1995). The products from flash and soak calcination also have different structural properties (Bridson et al., 1985): flash calcined products being characterized by internal voids due to rapid heating rate and buildup of vapor pressure.

In industrial scale, thermal activation of kaolinite may be carried out through conventional calcination using rotary kilns or through flash calcination using pneumatic suspended feed. The conventional type of calcination requires several minutes of residence time to produce metakaolinite during which the product may experience agglomeration (Bapat, 2012). While in flash calcination, a kaolinite, usually in powder form, is heated rapidly (≈$10^4$ °C/s), held at high temperature for a short period of time (0.1 to 1 s), and quenched rapidly with counter

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flow of cold gas. Flash calcination enables the dehydroxylation of powdered kaolinite within several tenths of seconds (Bridson et al., 1985; Slade et al., 1991; Slade et al., 1992). Flash calcined products are characterized by lower density (Slade et al., 1991) and spherically shaped particles (San Nicolas et al., 2013).

From modeling perspective, the works on thermal transformation of kaolinite particles are very limited. A modeling attempt is reported on flash calcination of kaolinite where a spherical kaolinite particle is plunged into a hot gas (Salvador and Davies, 1994). The model is greatly simplified by the assumption that the particle body remains isothermal during the entire heating and conversion process. The kaolinite particle conversion is found to be governed by the transformation kinetics at low temperatures (550–600 °C) and by the external heat transfer at higher temperatures (greater than 700 °C). The impact of particle diameter (0–500 μm) on its transformation rapidity is also discussed. With the gas heated to 1000 °C, the duration required for 90% dehydroxylation of a 500 μm diameter particle is ten times longer than the duration required for a 100 μm diameter particle, and the maximum duration is 1.2 s for the biggest particles (Salvador and Davies, 1994). One has to bear in mind that all these are derived by neglecting intra-particle processes. Inclusion of temperature gradients within the particle is expected to slow down the overall dehydroxylation to some extent.

This paper presents a study on flash calcination of kaolinite rich clay particles in a gas suspension calciner (GSC). Calcination tests are done for a given clay material under six different calcination conditions. The raw feed and the calcines are all characterized to determine particle size distribution, composition, degree of dehydroxylation, density and specific surface area. A cross-check of the results is made to assure their reliability. A transient one-dimensional (1D) particle model, numerically solving the intra-particle processes and properly addressing particle–ambient flow interaction, is also developed in C++ to reproduce the transformation of the clay particles in the GSC. The model predictions show a good agreement with the experimental data. Finally, based on the model, the conversion of a given clay particle subjected to a given calcination condition is shown in details. The impacts of key factors in clay calcination (e.g., particle size, gas temperature and reaction kinetics) are also examined and discussed via a model-based sensitivity analysis.

## 2. Experimental study

### 2.1. Thermogravimetric study

The objective of the thermogravimetric study is to quickly estimate the kinetic parameters such as, the activation energy (E) and frequency factor (A) for the dehydroxylation of kaolinite rich clays which are important inputs to the model. The thermogravimetry tests are carried out by using STA 409 PC, which simultaneously measures both the heat flows (DSC) and weight changes (TGA) associated with transitions in a material as a function of temperature and time in a controlled nitrogen atmosphere. In each test, approximately 20(±2) mg of the clay sample is placed in a platinum crucible with a flat base, which ensures optimum heat transfer with lowest possible temperature gradient between the sample and sample holder. The sample is heated up to 1200 °C at different heating rates, i.e., 5, 10, 20, 30, 40 and 50 °C/min, respectively. The relevant data are collected from the plots of weight loss (TGA) and its derivative DTG.

### 2.2. Flash calcination tests in the GSC

The flash calcination tests are performed in a GSC in FLSmidth R&D Centre, Dania (Denmark). The schematic sketch of the GSC is shown in Fig. 1, in which SB1, SB2 and SB3 are secondary burners along the gas/particle flow path and TC-I–TC-IV denote the four thermocouples in the calciner for temperature measurement and monitoring. The three secondary burners may be put into operation to obtain a uniform temperature profile along the calciner tube. In the tests, kaolinite rich clay particles are fed into the calciner from the bottom, near the downstream of the main propane burner. The composition of the clay feed is given in Table 1. It has to be mentioned that the numbers in Table 1 do not sum up to 100% because it is tedious to determine the remaining traces or they are beyond the experimental facilities at hand. The mineralogical composition of the clay is 90–95% kaolinite and 5–10% quartz impurities. The clay material contains 13.65% crystal water (loss of ignition). The particle size distribution (PSD) of the feed is shown in Fig. 2. The hot gas generated in the main burner is drawn into the GSC from the bottom and pulled through the reactor tube together with the suspended particles by an extraction fan. The hot gas/particle flow is mixed with a stream of quenching air at the exit of the GSC, and finally enters the filter in which the product material is separated from the gas flow.

Two sets of calcination tests are performed in the GSC, as listed in Table 2. The first set of tests, Exp-I, is conducted without putting the secondary burners into operation. The gas temperatures at the GSC inlet (i.e., the reading of the thermocouple TC-I) are 800, 900, 1000 and 1100 °C, respectively. In these tests, remarkable temperature drops along the calciner tube are observed. To better present the four tests, the average gas temperatures within the calciner are used. The four tests, as well as their product materials, are denoted by $\text{MK691}_{\text{NB}}$, $\text{MK785}_{\text{NB}}$, $\text{MK853}_{\text{NB}}$ and $\text{MK941}_{\text{NB}}$, in which MK, the number and the subscript NB represent the product metakaolinite, the average gas temperature in the GSC in the unit of °C, and "no secondary burner in operation", respectively. The second set of tests, Exp-II, is performed with the secondary burners in operation to maintain a uniform gas temperature profile throughout the GSC, at 800 and 1000 °C, respectively. The two tests in Exp-II are denoted by $\text{MK800}_{\text{WB}}$ and $\text{MK1000}_{\text{WB}}$, respectively, where the subscript WB stands for "with secondary burner in operation". In all the 6 calcination tests, the raw clay particles are fed at a rate of 6 kg/h and have a residence time of 0.5 s in the GSC.

### 2.3. Experimental characterization of the clay samples

To study the effects of calcination conditions, all the clay samples collected in the six calcination tests are characterized to obtain their water content (or degree of dehydroxylation), composition, density, particle size distribution, and specific surface area.

The water content is measured using LECO RC612 multiphase carbon and hydrogen/moisture analyzer. 250 mg clay sample is placed into the system where nitrogen is purged to ensure an inert atmosphere. The equipment features a state-of-the-art furnace control system, allowing the temperature of the furnace to be programmed from near-ambient to 1100 °C. The raw feed clay sample is held at 150 °C for 15 min to make sure that the free water is removed. Then, the clay sample is exposed to a heating rate of 120 °C /min until 1000 °C and held at 1000 °C for about 7 min to secure a complete dehydroxylation (i.e., a complete removal of the crystal water). Infrared detection is used to quantify the amount of vapor in a weight percentage. For the calcined clay samples, the same procedure is repeated except that a heating rate of 20 °C/min is used until 900 °C and then the sample is held at this temperature for 5 min. By comparing the crystal water left in each calcined sample ($m_{\text{CW\_CS}}$) to the initial amount of crystal water in the raw feed ($m_{\text{CW\_RF}}$), the degree of dehydroxylation $\alpha$ for each calcination test can be determined as,

$$\alpha = 1 - \frac{m_{\text{CW\_CS}}}{m_{\text{CW\_RF}}}. \tag{1}$$

X-ray diffraction (XRD) of the raw feed and calcined samples is carried out using PANalytical CubiX PRO X-ray diffractometer. Rietveld analysis of randomly oriented clay powders is used to quantify the composition of the calcined clay materials. Quantification of phases is