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Simulation of flash dehydroxylation of clay particle using gPROMS: A move towards green concrete

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Abstract

The use of SCMs (supplementary cementitious materials) to replace part of the clinker in cement industry is gaining an increasing interest in order to reduce the CO₂ footprint. The abundantly available clay minerals are potential sources of SCMs. Thermal treatment of kaolinite clay under moderate temperatures (700-1000K) yields an amorphous phase called metakaolinite, a material that has great promise as a mineral admixture for cement and concrete. However, the optimum properties of metakaolinite are highly dependent on operating temperature and residence time during thermal treatment. This article presents the development of a numerical model for the simulation of dehydroxylation of kaolinite clay using gPROMS (general PROcess Modeling System). Accordingly, a 1D dehydroxylation model is used to examine the thermal transformation of kaolinite into different phases. This model is used to predict the temperature and residence time at which the kaolinite particle attains optimum pozzolanic reactivity. The usefulness and validity of the method is evaluated by comparing the predicted variables with experimental values collected from a gas suspension calciner (GSC).

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1. Introduction

A drive towards environmental sustainability in construction industry is shaping our attitude towards alternative admixtures that can be applied in cement and concrete industry. Kaolinite, being one of the most abundant clay mineral on earth's crust, has got an increasing interest from cement and concrete manufacturing industry as clinker replacement. This allows a reduced emission of CO₂ from cement industry that is associated with the manufacture of clinker.

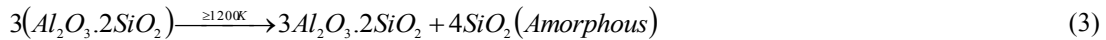
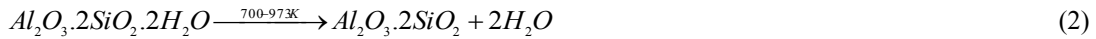
The use of metakaolinite as partial cement constituent in mortar and concrete has been studied widely [1-3]. The work demonstrated that metakaolinite is an effective pozzolan and partial substitution of clinker with metakaolinite enhances the strength and pore structure of the cement paste. The key to producing high-quality metakaolinite is to achieve a near-complete dehydroxylation, without overheating.

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Thermal treatment beyond dehydroxylation may result in the formation of crystalline products such as mullite, which is not pozzolanic.

A complete structural transformation of kaolinite mineral during thermal treatment may pass through a sequence of reactions [4,5]. For the sake of convenience and ease of getting kinetic parameters, the transformation is summarized into the following reactions, where direct transformation of metakaolinite to mullite is assumed.



From the perspective of modelling, a complete work on the thermal transformation of kaolinite appears to be limited. Some attempts has been reported on flash calcination of kaolinite by Salvador et al. [6], where a spherical kaolinite particle is plunged into a hot gas atmosphere at 1273 K. Consequently, a particle of 100µm in diameter was observed to be dehydroxylated approximately in 0.083 seconds. The fast heating rate during flash calcination was suggested for the particle decrepitation [7].

The purpose of this paper is to develop 1D distributed model for the thermal transformation of kaolinite using gPROMS [8], where the governing equations of energy and transport has been solved by built-in solvers in gPROMS. The spatial variables are discretized using centred finite difference method of second order over a uniform grid of 20 elements. Several variables including the variations in particle density, temperature and conversion are exploited as a function of particle radius and time. A sensitivity analysis on the impact particle size and gas temperature on the conversion of kaolinite is investigated and discussed.

Nomenclature

		Subscripts	
D_p	Particle diameter, [m]		
T_{rad}	Radiation temperature, [K]	kk	Kaolinite
ρ	Density [kg/m ³]	mu	Mullite
T_{gas}	Gas temperature, [K]	mo	Moisture
ε	Porosity	Sil	Silica

2. Experimental study

The kaolinite rich clay sample under investigation has initial composition of 90-95% kaolinite and 5-10% quartz. The calcination test is performed in a gas suspension calciner located in FLSmidth R&D Centre, Dania (Denmark). The dried and crushed clay is used as a feed to the GSC. Calcination experiments are accomplished at set temperatures of 1073, 1173, 1273 and 1373 K. During this test a drop in temperature was noticed along the calciner, as indicated in Table 1 in brackets. In all the tests, the clay particles are expected to have about 0.5 s residence time inside the calciner. The calcined clay particles are quenched with fresh air and then collected in a bag filter. The true density of the calcines is measured using the standard test method by gas pycnometer.

The above conditions of the GSC are implemented in the model by considering two cases as shown in Table 1. The first case addresses the calciner set temperatures, while the second case addresses the temperature drop along the calciner.

Table 1. Summary of calcination conditions used for operating GSC and model inputs. The calcination temperatures in brackets are the measured average temperatures of the calciner during which it experiences a drop in temperature.

Method		Calcination T[K]				Particle size	Initial composition	T_{rad} [K]
Experimental		1073	1173	1273	1373	Mean=14 μ m	$\rho_{kk} = 2420\text{kg/m}^3$; $\rho_{sil} = 210\text{kg/m}^3$ $\rho_{mo} = 99\text{kg/m}^3$	--
		(964)	(1058)	(1126)	(1214)			
Model	Case-I	1073	1173	1273	1373	14 μ m	$\rho_{kk} = 2420\text{kg/m}^3$; $\rho_{sil} = 210\text{kg/m}^3$ $\rho_{mo} = 99\text{kg/m}^3$	Not Consid.
	Case-II	964	1058	1126	1214			

3. Result and discussion

3.1 Comparison between Experimental data and model prediction

Figure 1 shows the true density of calcined clays as a function of calcination temperature, from which a good agreement can be observed between the experimental data (GSC) and model prediction. At temperatures 1073K (964K) only reactions (1) and (2) occur and major product is metakaolinite ($\rho=2550\text{ kg/m}^3$). As temperature increase to 1373K, reaction (3) starts to be part of the reaction where mullite ($\rho=3100\text{ Kg/m}^3$) formation becomes significant; causing a slight increase in the density of calcined clays.

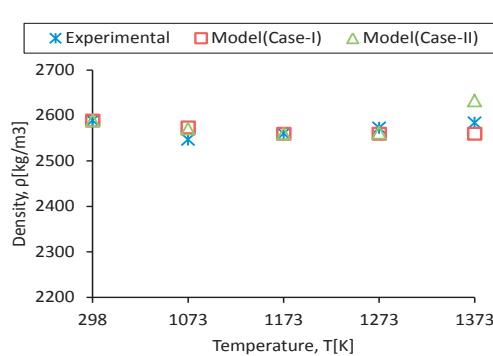


Figure 1. comparison of modelling and experimental results of the GSC.

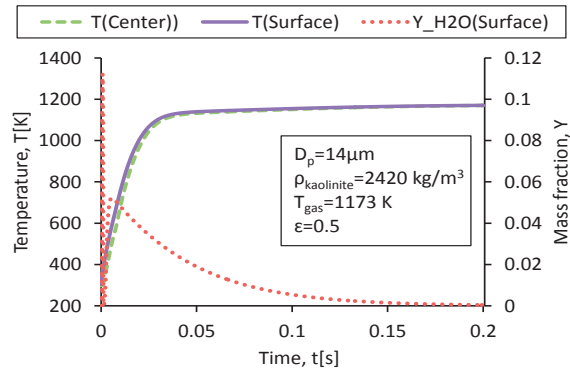


Figure 2. Model predicted temperature and mass fraction of water vapour in 14 μ m clay particle.

3.2 Detailed model results

Dehydroxylation of a reacting kaolinite particle with mean particle size 14 μ m under GSC conditions at gas temperature of 1173K is picked. The predicted temporal and spatial temperature distributions are shown in Figure 2. The particle experiences a temperature gradient between the centre and the surface due to transfer of heat by convection and later by conduction to the particle centre. It is also realized that the particle gets fully dehydroxylated before it gets similar temperature as the surrounding gas. This observation is consistent with literature [6]. In the same figure, as the temperature increases water vapour begins to generate from the particle and eventually diffused out of the particle in 0.15s, signifying full dehydroxylation. The two peaks shown represent the evaporation and dehydroxylation reactions.

Sensitivity analysis on particle size show larger kaolinite particles display longer time to attain complete conversion to metakaolinite, as shown in figure 3(A). As the conduction/diffusion is the dominant heat and mass transfer mechanism inside the particle, the larger the particle the longer time for the transfer process to the center or to the surface. In Figure 3(B), the temperature-time correlations are established based on model results. Temperatures below 1273K allow flexible residence time management during operation. In other words, at lower calcination temperatures the depletion of metakaolinite happens slowly, as a result the residence time could be fairly relaxed inside the calciner. However, for high calcination temperatures (>1273 K) control over residence time is difficult, as the generation and depletion of metakaolinite happens quickly.

The applicability of this model is to monitor the behaviour of calcined kaolinite clay material inside the calciner based on the prediction of optimum pozzolanic reactivity of the material which is revealed by the optimum amount of metakaolinite attained. Thus, the optimum calcination temperature and calcination time predicted by the model are crucial inputs in designing the calciner and its operating conditions.

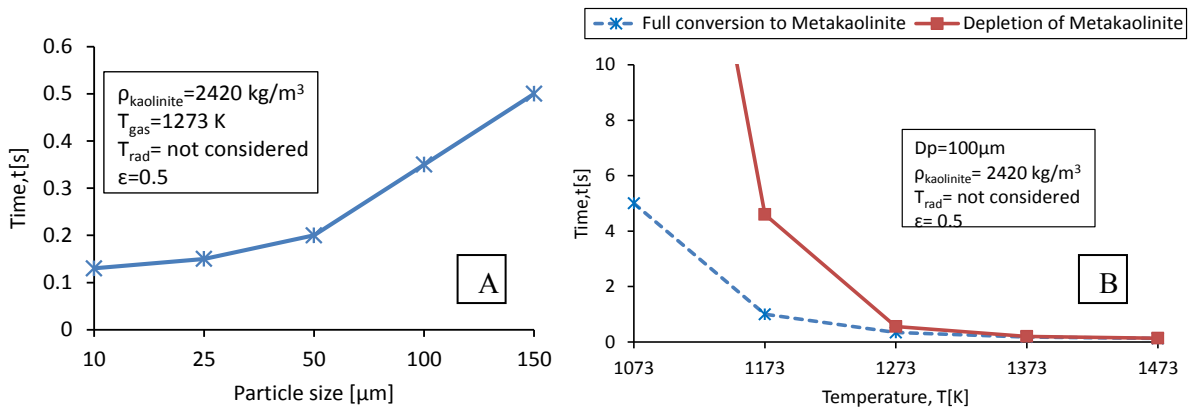


Figure 3. The impact of particle size on the time where maximum mass fraction of metakaolinite is obtained (A). The Temperature-Time correlation on full conversion and depletion of metakaolinite (B).

4. Conclusion

The conversion of kaolinite particles during flash calcination is achieved in a very short time due to fast heating rate. Based on the kinetic data, physical and thermodynamic data used in this work, a kaolinite particle of $100 \mu\text{m}$ in diameter plunged in to a hot gas at 1273 K , gets fully dehydroxylated in 0.35 seconds. Temperatures 1173 K to 1273 K are recommended for operation of a calciner, as it compromises both the residence time and optimum mass fraction of metakaolinite. However, lower temperatures ($\leq 1073 \text{ K}$) might need longer dehydroxylation time (>5 seconds).

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Biography



Abraham Teklay obtained his MSc in Materials Science in 2008 through a joint study at the university of Aveiro (Portugal), Technical university of Hamburg (Germany) and Aalborg university (Denmark). He is currently a PhD student at Aalborg university, Denmark.