



Research paper

Structural and chemical changes in kaolinite caused by flash calcination: Formation of spherical particles



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ABSTRACT

To understand the morphological changes of three commercial kaolins during flash calcination and to compare them with those obtained during traditional heat treatments in the laboratory (an electric furnace at 700 °C for 5 h), this paper presents the physical and chemical characteristics of metakaolins obtained from an industrial flash calciner. In the metakaolin products, kaolinite was not completely dehydroxylated during calcination, and the proportion of untransformed kaolinite was greater in flashed metakaolins than in traditional rotary-calcined metakaolins. Several particle morphologies were discernible in the metakaolins, including spherical particles that were formed in flash calcinations. These spherical particles were cut with a focused ion beam (FIB) and were revealed to contain a vitrified aluminum silicate phase with traces of mullite and various gases. These spherical particles were produced from the direct calcination of several submicron kaolinites near the flame of the calciner.

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1. Introduction

The calcination of clay minerals has attracted much interest due to their widespread use in a diverse range of applications (paints, rubber, render, plastics etc.) (Harvey et al., 2013). The calcination of kaolins (K) (including kaolinite, quartz and subsidiary materials) produces materials having pozzolanic activity, i.e., metakaolins (MK).

Thermal decomposition of kaolinite (Kaol) has been the subject of many studies over the years (Insley and Ewell, 1935; Brindley and Nakahira, 1958). The calcination of Kaol at temperatures between 700 °C and 850 °C generates metakaolinite (MKaol) (Brindley et al., 1967; White et al., 2010; Heller-Kallai, 2013). This heating causes the dehydroxylation of Kaol and leads to the production of MKaol, a material that appears amorphous under X-ray diffraction. Typically, two independent processes occur during calcination: (1) the continuous loss of physisorbed water (dehydration) according to the reaction $\text{H}_2\text{O} (\text{l, free}) \rightarrow \text{H}_2\text{O} (\text{g})$ at 100 °C (Teklay et al., 2015); and (2) the discontinuous loss of structural hydroxyls (dehydroxylation) according to the reaction $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaol}) \rightarrow \text{Al}_2\text{Si}_2\text{O}_7 (\text{MKaol}) + 2\text{H}_2\text{O}$ between 450 and 750 °C (Salvador, 1995; Sperinck, 2010; Teklay et al., 2015). MKaol has good properties as a mineral additive in applications such as in cement-based materials (Garcia-Diaz, 1995; He et al., 1995; Barbosa

et al., 2000; Cyr, 2000). MK (i.e., a trade name referring to a mixture of MKaol, quartz and other minerals) possess a huge reactive potential in basic environments (San Nicolas et al., 2013) and have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio between 1.5 and 2.5, depending on the purity of the raw K material used in their production. On an industrial scale, MK is obtained from calcination in a rotary kiln for several hours between 650 °C and 700 °C.

Another industrial process was introduced in MK production: flash calcination (Davies, 1984; Salvador, 1992; Meinhold et al., 1994). Flash calcination enables the dehydroxylation of powdered Kaol within several tenths of a second, while traditional soak-calcination requires minutes at least. In this process, a solid, usually in a finely divided form, is rapidly heated, held at an elevated temperature (>700 °C) for a short time, and subsequently, swiftly cooled (San Nicolas et al., 2013).

The aim of this paper is to highlight the physical and chemical transformations between three commercial K after traditional calcination with a laboratory-scale electric furnace at 700 °C for 5 h and after flash calcination.

2. Background of flash calcination

In this study, a flash calcination process used by one of the two French producers of MK was employed. After grinding and drying the clay, the raw material is preheated at 500 °C, allowing its dehydration, in a system of cyclonic separators using gases released from the

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calcination chamber. Clay is then taken to a 200 μm sieve, then brought to a temperature of approximately 700 °C in a calcination chamber, i.e., a cyclonic oven. In this calciner (Fig. 1), the product swirls around the flame, which has a temperature of 1100 °C. Clay spends only a few tenths of a second in the calciner, just enough time for the transformation into MK (San Nicolas et al., 2013). Once this transformation has taken place, the MK is then separated from the hot gases in a cyclonic separator and then cooled in a system of successive cyclonic separators. Finally, the finished product is collected and packed in silos.

3. Materials and methods

3.1. Samples

Three commercial K (with different origins, compositions and levels of purity) were studied in this paper. The crystallinity of Kaol in each clay was evaluated by different indices obtained by X-ray diffraction (XRD) (Aparicio and Galan, 1999).

- K1 is a K from sedimentary deposits located at Fumel (South of France). The Kaol in this sample has a disordered structure.
- K2 is a K from sedimentary deposits located at Fumel (South of France). The Kaol in this sample has a disordered structure. B2 is even less phase pure than K1.
- K3 is a K collected at a quarry located in primary deposits developed in the North of France. This sample contains ordered Kaol.

Samples were named MKx for the metakaolins with x being the number of the K.

3.2. Characterization

Bulk elemental composition (Table 1) was determined with inductively coupled plasma-optical emission spectrometry (fusion glass prepared with Pt crucibles along with LiBO_2 at 980 °C in an automatic tunnel oven, dissolved in a HNO_3 – H_2O_2 mixture and analyzed with ICP-OES, Thermo Fischer Icap 6500, SARM Laboratory of Nancy).

XRD analysis was performed on dried K. The XRD patterns were recorded on G3000 INEL equipment (GET laboratory, University of Toulouse) using $\text{Cu-K}\alpha$ radiation. Through these methods, including a Rietveld analysis (Rietveld, 1967, 1969) of the XRD data using the MAUD program (Lutterotti et al., 1999), the amounts of Kaol and other minerals in the K and MK were estimated (Bish and von Dreele,

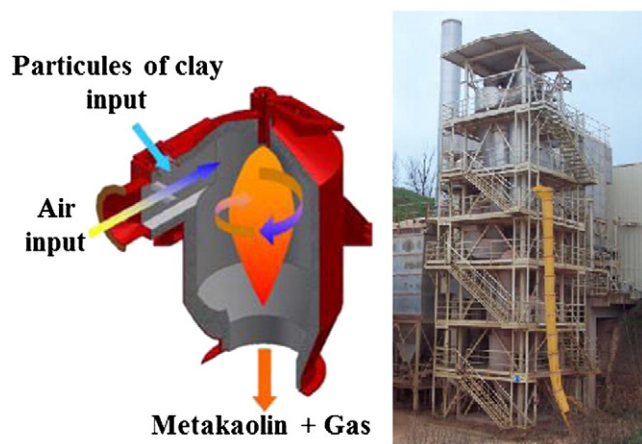


Fig. 1. Schematic representation of a flash calciner used in MK production (San Nicolas, 2011) and photography of the flash process tower.

Table 1

Chemical composition (dry basis, wt.%) of the K samples.
L.O.I.: Loss on ignition (measured by thermogravimetry)

Chemical analysis (%)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	MgO	CaO	$\text{H}_2\text{O total}^*$	L.O.I.	Total
K1	51.62	32.01	1.31	1.48	0.06	0.13	0.45	12.62	12.71	99.76
K2	66.24	20.81	2.29	1.04	0.21	0.15	0.62	8.53	8.81	100.17
K3	67.67	21.79	0.77	0.35	1.26	0.14	0.06	7.31	7.48	99.52

* Analytical method: Titration Karl Fisher.

1989). However, this quantification by Rietveld refinement is a semi-quantitative estimate involving some uncertainties. The amount of mineral phases by Rietveld analysis was compared with the corresponding amount estimated by stoichiometry based on the results of the chemical analysis (Bich, 2005).

Fourier transformed infrared spectra in the near-infrared region (NIR-FTIR) spectra were recorded at a resolution of 4 cm^{-1} between 4000 and 11,000 cm^{-1} using a Nicolet 6700 FTIR spectrometer (HydrASA, IC2MP, University of Poitiers) with a smart NIR integrating sphere (CaF_2 beam splitter and InGaAs detector).

Particle size distributions were measured in ethanol dispersions using a laser analyzer CILAS 1090 (LMDC, University of Toulouse) under ultrasound polydispersion. The sizes determined from these measurements were likely too large due to the incorrect assumption of spherical particles (rather than plates) in the data analysis.

An environmental scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDX FEG JEOL 6700F, Centre de Microcaractérisation, Toulouse) was used for the morphological analysis of the surface structure and to determine the Al, Si, Fe, Ti, Ca and O elemental compositions of the particles. An accelerating voltage of 20 keV was used for the EDX microanalysis.

Focused ion beam (FIB) thin section was extracted from spherical particle, using a dual beam SEM/FIB FEI Helios NanoLab 600 (septum; CP2M, Marseille). The FIB sectioning consisted of the following steps:

- a protective platinum sheet of about 1.5 μm thickness was deposited upon the surface in the region of interest;
- trenches were then milled at 30 kV on both sides of this sheet to create a 300–500 nm thick foil (reducing current from 6 nA to 80 pA, while thinning);
- using a micromanipulator, in situ lift-out was performed by sputtering a platinum sheet to connect the micromanipulator tip with the TEM foil;
- the TEM foil was attached to a Cu TEM grid and a final FIB thinning and cleaning at 5 kV–40 pA were carried out in order to obtain a foil of less than 100 nm thick.

FIB section was then observed on a transmission electron microscope (TEM) JEOL 3010 at 300 kV (CINaM, Marseille) for bright-field and dark-field imaging and recording selected area electron diffraction (SAED) patterns.

Energy-dispersive X-ray spectroscopy (EDX) analysis was achieved on both FIB section with a JEOL 2011 at 200 kV (CINaM, Marseille).

4. Results and discussion

4.1. Mineralogical characteristics

Through chemical analyses (Table 1) and XRD (Fig. 2), including the Rietveld analysis of the XRD data (Table 2), the amounts of Kaol, quartz and muscovite in the K samples were estimated. The K1 has a high Kaol content at 89%, and the K2 and K3 have moderate Kaol contents of 56%

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