

## Calcined Clay for Paper and Paperboard

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### WHAT IS CALCINED CLAY?

ONE has learned from Chapter 4 and Chapter 5 that pigment particle size as well as coating pore size are important for light scattering. There are optimum sizes, generally about one half of the wavelengths of light, for these parameters at which light scattering is maximized. Ultrafine particles do not scatter light as efficiently as larger but optimally sized particles and hence give lower opacity. Kaolin, even the coarser particle grades, contains a significant quantity of ultrafine particles. However, these particles can be “structured” or aggregated with a large “preformed” pore or void volume and optimum pore size. A significant portion of pore size and pore volume carries through into the paper coating and primarily contributes to increases in opacity and, to some extent, brightness. The porosity also increases bulk, coverage, and smoothness of the coating. Pore size and pore volume depend on the type of structuring. There are three ways kaolin particles can be structured:

1. Thermal treatment (thermally structured): Kaolin is treated at high temperatures to cause structural changes, followed by partial fusion or aggregation of the fine particles [1–3].
2. Chemical treatment (chemically structured): Both inorganic additives and precipitates [4–6] or organic polymers such as polyamines [7] are used to bond or selectively flocculate ultrafine particles.
3. Hydrothermal treatment (chemically structured): Kaolin is sub-

jected to elevated temperatures and pressures in the presence of caustic or alkali metal silicate solution to facilitate a higher degree of particle aggregation than the chemical treatment [8–10].

Thermally treated clay dominates the structured clay market. It was introduced in the early 1940s and improved whiteness and opacity of sheets when used in coatings and as a filler. Initially, the product was more abrasive than the unstructured clay. However, further improvements in the calcining technique in addition to the proper selection and processing of the calciner feed starting in the 1960s led to calcined products with reduced abrasion and increased light scattering [1,2]. These improvements in the properties of calcined clay spurred its growth in the paper industry. The important properties of calcined clay as a paper coating and filler are presented in **Table 6.1**. About 500,000 tons of thermally structured clay are currently used in the paper industry. The chemically structured clays that once commanded a fair market share have largely been discontinued due to unfavorable performance-to-cost ratio, rheological issues, and manufacturing complexities. The chemically structured clays have been discussed in more details elsewhere [11]. Henceforth in this chapter, thermally structured clay is described and referred to as calcined clay.

## CALCINATION TYPE

Heat treatment of hydrous kaolin at a temperature in excess of 550°C (1,022°F) causes dehydroxylation (loss of structural hydroxyl groups) and converts it to an amorphous (noncrystalline) aluminosilicate phase. Generally, calcined clays are produced using two methods: (1) soak calcination (conventional) and (2) flash calcination. Soak calcination involves heating the kaolin to a high temperature for an extended time, usually 30–60 minutes, to ensure the required degree of calcination. The temperature of calcination depends on the type of product required, and it ranges from about 700°C to 1,200°C (1,292°F–2,192°F). In flash calcination, a sample is heated at high temperature (800°C–1,200°C or 1,472°–2,192°F) for only a few tenths of a second to about 2 seconds at an extremely high heating and cooling rate on the order of 1,000°C–500,000°C (1,832–900,032°F) per second [12,13]. The soak calcination ensures that the product is fully dehydroxylated whereas the products of the flash calcination is only partially dehydroxylated and leads to materials with differing physical properties.

**TABLE 6.1. Typical Characteristics of Standard Calcined Clay.**

Characteristic	Value
Brightness	92.5–93.5
Particle Size, % <2 $\mu\text{m}$	83–92
Median Particle Size (Sedimentation), $\mu\text{m}$	0.6–0.8
Surface Area, $\text{m}^2/\text{g}$	14–17
Refractive Index	1.56
Einlehener Abrasion, $\text{mg}/100\text{K rev}$	16–22
Specific Gravity	2.72
Mercury Intrusion	
Pore Volume, $\text{mL/g}$	0.8–1.2
Pore Size, $\mu\text{m}$	0.2–0.4
Oil Absorption, $\text{g}/100\text{ g}$	80–120
Typical Solids, %	50
Viscosity @ 50% Solids	
<sup>1</sup> Brookfield, cP @ 20 rpm	30–60
<sup>2</sup> Brookfield, cP @ 20 rpm	100–400
Hercules, rpm @ 18 Dynes	400–1100
pH	
Dry (as Manufactured) @ 20% Solids	4.0–5.0
Dispersed Slurry	6.5–8.0
Zeta Potential	
As Manufactured, mV	–50
Optimally Dispersed Slurry, mV	–60

<sup>1</sup>Without suspending agent.<sup>2</sup>With suspending agent.

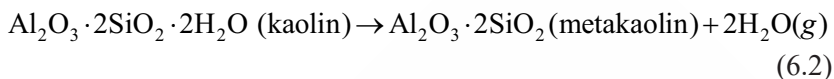
## CALCINATION REACTION

When kaolin is heated, it goes through a series of reactions such as loss of adsorbed water, dehydroxylation, loss of crystallinity, and recrystallization to new phases [13–20]. These thermal reactions can generally be represented as follows Equations. (6.1, 6.2, 6.3, 6.4, and 6.5):

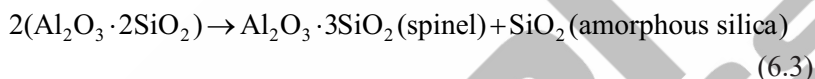
A. Dehydration of absorbed water ( $T \leq 150^\circ\text{C}$  or  $320^\circ\text{F}$ )



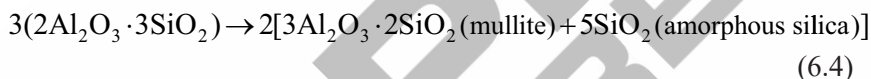
- B. Dehydroxylation in the temperature range of 400°C–700°C (752°F–1,292°F) (peaks at approximately 550°C or 1,022°F) with a loss of about 14% structural water and formation of metakaolin



- C. Formation of spinel phase at around 980°C (925°C–1,050°C) or 1,796°F (1,769°F–1,922°F)



- D. Nucleation of the spinel phase and transformation to mullite (>1050°C or >1,922°F)



- E. Formation of cristobalite ( $\geq 1,200^\circ\text{C}$  or  $\geq 2,192^\circ\text{F}$ )



Temperatures of these reactions can vary greatly depending on the time of exposure, kaolin type, heating rate, mixing, fluxing agent, and other environmental conditions in the calciner or furnace.

Formation of mullite from kaolinite, whether preceded by either a spinel phase [Eq. (6.3)] or gamma alumina ( $\gamma\text{-Al}_2\text{O}_3$ ), has been a subject of debate for over 60 years since its first report by Brindley and Nakahira in 1959 [20]. This reaction has been investigated by a multitude of analytical techniques ranging from infrared, neutron, and x-ray diffraction; transmission electron microscopy; and  $^{27}\text{Al}$  and  $^{29}\text{Si}$  nuclear magnetic resonance spectroscopy. Although a typical spinel structure is represented by magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ ) (or  $\text{AB}_2\text{X}_4$ ),  $\gamma\text{-Al}_2\text{O}_3$  also fits the spinel structural model [21]. Thus, it is also likely that the formation of mullite from kaolinite is preceded by spinel-like  $\gamma\text{-Al}_2\text{O}_3$  containing a small amount of silicon in tetrahedral position.

**Figure 6.1** presents the thermogravimetric (TGA) and differential thermal analysis (DTA) curves for a hydrous kaolin [22]. The TGA

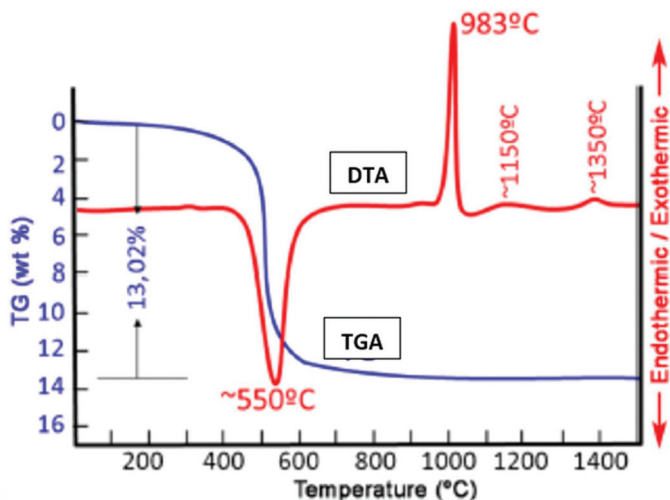


FIGURE 6.1. Thermogravimetric (TGA) and differential thermal analysis (DTA) curves of kaolin as a function of temperature.

curve shows that the weight loss begins at about 400°C (752°F) and is nearly completed by 700°C (1,292°F) with the loss of almost all of the structural water (hydroxyl groups). The structural water for an ideal kaolinite is 13.9%, although the weight loss (loss on ignition) in most hydrous kaolins varies depending on the amount and type of impurities present. The DTA curve shows an endothermic peak at around 550°C (1,022°F), which results from the loss of structural hydroxyl groups from kaolin. The exothermic peak at 983°C (1803°F) represents crystallization of the spinel/ $\gamma$ - $\text{Al}_2\text{O}_3$  phase. Calcination at  $\geq 1,050^\circ\text{C}$  (1,922°F) would begin to convert the spinel phase to mullite. Further calcination to  $\geq 1,200^\circ\text{C}$  (2,192°F) would convert spinel and amorphous silica to mullite and cristobalite. The product calcined at a temperature higher than the exotherm is considered fully calcined clay, whereas the product manufactured at a temperature lower than the exotherm is considered metakaolin. Because of its high reactivity, metakaolin, especially produced at 700°C–800°C (1292°F–1,472°F), is primarily used in nonpaper applications such as high-strength cement, concrete, and geopolymer [23]. However, a fully calcined clay is preferred in paper coating applications because of its relative inertness.

The alteration from a crystalline to an amorphous phase upon calcination can be monitored by an X-ray diffraction (XRD). The XRD

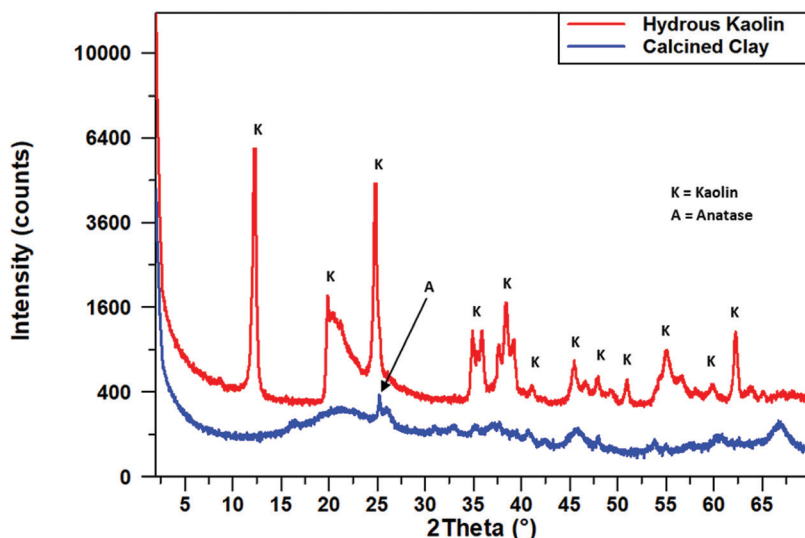


FIGURE 6.2. X-ray diffraction patterns of hydrous kaolin (top) and fully calcined clay (bottom).

patterns in **Figure 6.2** show that all sharp diffraction peaks associated with the crystalline hydrous kaolin mineral have been destroyed upon calcination; the figure shows only the broad humps and diffused peaks associated with the amorphous phases and early crystallization stages of aluminosilicates such as  $\gamma$ - $\text{Al}_2\text{O}_3$  and mullite. A small sharp peak observed at  $25.3^\circ$  2-theta in the calcined clay is due to the presence of a small amount of anatase titanium dioxide ( $\text{TiO}_2$ ) that exists as an impurity phase.

## MANUFACTURE OF CALCINED CLAY

Calcined clay for paper is manufactured in a large indirectly heated Herreschoff-type multiple-hearth calciner (vertical) or a rotary (horizontal) kiln by using ultrafine kaolin and heating it above  $1,000^\circ\text{C}$  ( $1,832^\circ\text{F}$ ). A general flowsheet for the manufacture is presented in **Figure 6.3**. Selected crude kaolin is first refined following the wet processing steps as described in Chapter 4 and spray dried. Pulverization (milling) before heat treatment is an essential processing step. Processing of feed and calcination conditions are optimized to maximize brightness, whiteness, and light scattering while controlling particle size distribu-

tion and keeping the abrasion and 325-mesh residue (grit) to a minimum. The product is cooled, pulverized again, and shipped dry in bags, sparger cars, or tank cars as an optimally dispersed slurry. Traditionally, the product is shipped as 50% slurry, although rheologically improved grades can be shipped at 59% solids. Similar microbiological prevention and control measures, including good housekeeping protocols as described in Chapter 4, need to be followed to prevent slurry spoilage.

A small amount of suspending agent (carboxymethyl cellulose or xanthan gum) is added to the slurry to prevent calcined clay particles from settling.

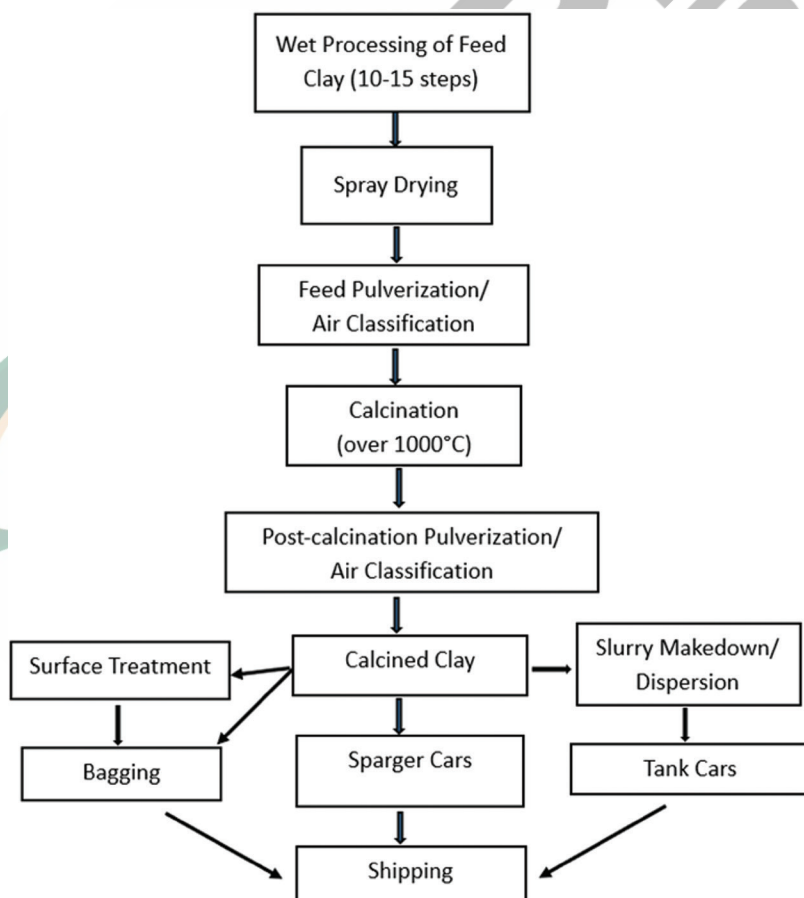


FIGURE 6.3. A general flowsheet for the manufacture of calcined clay (soak calcination).