

NOTES

PROPERTIES OF FLASH-CALCINED KAOLINITE

Key Words—Density, Dehydroxylation, Flash calcination, Kaolinite, Thermal treatment.

Flash calcination is a process whereby a solid, usually in finely divided form, is heated rapidly, held at temperature for a short time, and then cooled rapidly. Heating and cooling rates on the order of 10^3 – 10^5 degrees per second and times of exposure at temperature of a few tenths of a second to about two seconds are typical. Although the kinetics of many physical and chemical transformations within a solid at high temperature are quite rapid, flash-calcination conditions are such that the transformations may not be complete before the temperature is reduced to the level that further changes are kinetically frozen.

The properties of solids prepared by flash-heating and/or -cooling processes may be quite different from the properties of the material treated at conditions where chemical and physical equilibrium are achieved. For example, the splat cooling of metals can produce at room temperature metastable phases not attainable by conventional quench techniques (Liebermann and Walter, 1982). In ceramics, glassy, water-soluble V_2O_5 has been produced by splat cooling (Livage and Colongues, 1976). There are no comparable results in the literature on the behavior of kaolinite or other clay materials subjected to flash processing.

When kaolinite is heated at normal rates (soak calcined), complete dehydroxylation occurs near 600°C with the resultant solid, known as metakaolin, maintaining a semblance of the kaolinite structure. Further heating to near 1000°C results in the transformation of metakaolin to an aluminum-silicon spinel plus free silica. At about 1200°C, mullite and christobalite are formed (Grim, 1962). The density of the kaolinite starting material also changes during the heating process. Reike and Mauve (1942) and Harmon and Parmelee (1942) found that as soak-calcination temperature increased the density initially decreased, reached a minimum, and then increased, eventually exceeding the density of the starting kaolinite. Specifically, Reike and Mauve (1942), working with a kaolinite having a density of 2.64 g/cm³, found a minimum density of 2.47 g/cm³ at 450°C. By 900°C, the density of the calcined product had increased to that of the raw clay, and, at the maximum calcination temperature (1000°C), the density was 2.79 g/cm³. This latter value is the theoretical density which should exist when a stoichiometric mixture of mullite and christobalite are produced by kaolinite decomposition.

To compare the density of a kaolinite starting material produced by flash calcining with that of the products of soak calcination, the following investigation was

conducted. The relationship between product densities and degree of dehydroxylation was also examined.

EXPERIMENTAL

SPS grade kaolinite supplied by ECLP Ltd., St. Austell, Cornwall, United Kingdom, was used in this study. This clay, which is designed for the paint industry, has a brightness of approximately 89.0. The density and bound water content were measured as 2.60 g/cm³ and 12.4%, respectively.

Flash calcination was carried out in a resistance-heated, laminar-flow furnace in a helium atmosphere. The residence time of the clay in the isothermal zone was controlled by varying the flow rate of the helium carrier gas. The construction and operation of the furnace have been described fully (Davies, 1984). Because of its sticky nature, direct feeding of the kaolinite powder into the furnace proved impossible and required the development of a special feeding technique. The clay powder was therefore consolidated into chalk-like sticks 1 cm in diameter and 9 cm in length by forcing a thick paste of clay and distilled water (2 to 3 parts clay to 1 part of distilled water) through an extruder nozzle of the proper diameter into brass molds. The molds were placed in an oven and dried overnight at 105°C. The sticks were then removed from the molds and stored in the oven at 105°C until used. The clay sticks were fed into a grinding chamber above the calcination furnace using a screw piston. Feed rate was controlled through a variable speed motor driving the piston. The re-ground clay was pneumatically transferred into the calcination furnace using helium. The feed system has been described separately (Davies, 1985).

The kaolinite was flash calcined between 900° and 1250°C with total exposure times, including heating and quenching, of 0.2–2.0 sec. Although these temperatures are sufficient to produce total dehydroxylation at equilibrium, the exposure times were too short for equilibrium to be attained. The extent of dehydroxylation of the product was determined from the additional weight loss when the flash-calcined sample was subsequently soak-calcined at 1000°C for 2 hr. The density of the product was measured using water displacement in a pycnometer with special care taken to remove all air from the sample. Some voids in many of the particles were apparently inaccessible to water, thereby causing a decrease in effective particle density. Based upon multiple measurements using the same sample, the analytical methods for the extent of de-

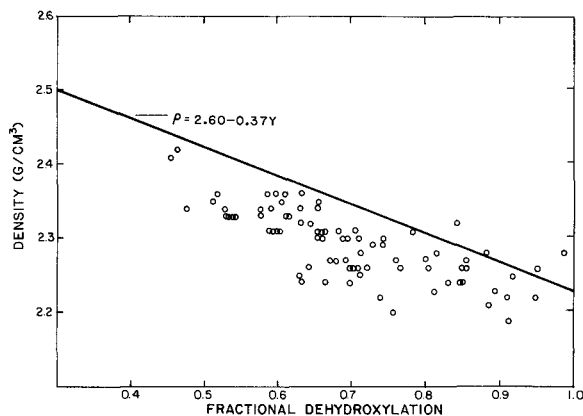


Figure 1. Density of flash-calcined kaolin.

hydroxylation and density were found to be reproducible to $\pm 2\%$. Brightness measurements were conducted on selected samples. Electron photomicrographs were taken to provide visual confirmation of product properties.

RESULTS AND DISCUSSION

Eighty-one samples of kaolinite were flash calcined under the above conditions. Fractional dehydroxylation ranged from 0.45 to 0.99, with the more severe treatment (higher temperature and longer residence time), as expected, producing greater dehydroxylation. The product densities ranged from 2.19 to 2.42 g/cm³. These values are 6.9% to 15.8% less than the density of the raw clay, and as much as 21.5% less than the density of the fully soak-calcined product (Reike and Mauve, 1942).

In general, product density decreased as fractional dehydroxylation increased as shown in Figure 1. The straight line in Figure 1 expresses the density as a function of fractional dehydroxylation by assuming that the particle volume does not change during calcination. Thus,

$$\rho = \rho_0(1 - XY), \quad (1)$$

where

ρ = density of the flash-calcined product,

ρ_0 = density of the original kaolinite,

X = the mass ratio of the bound water to the dehydroxylated kaolinite in the raw material, and

Y = fractional dehydroxylation.

For the kaolinite used in this study $\rho_0 = 2.60$ g/cm³ and X = 0.142; hence

$$\rho = 2.60 - 0.37Y. \quad (2)$$

The significance of this equation is that flash-calcined densities *less* than predicted by Eq. (2) must correspond to an increase in particle volume during flash calci-

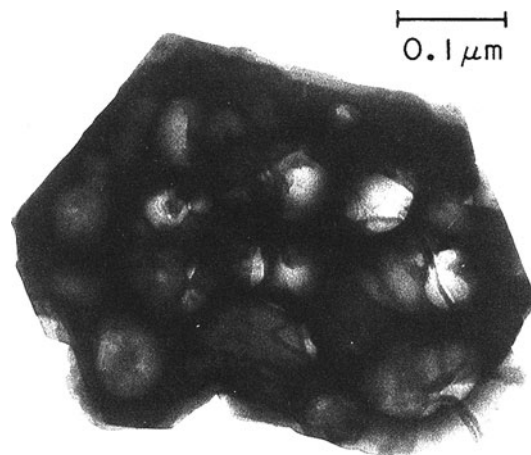


Figure 2. Kaolin particle flash-calcined in helium: top view.

nation; conversely, flash-calcination densities *greater* than those predicted require a decrease in particle volume. All but 4 of the 81 experimental points lie below the line indicating that particle swelling is associated with flash calcination.

What appear to be voids and the bubble- or balloon-like appearance of some of the flash-calcined particles were evident by electron microscopy. Figure 2 shows a top view, and Figure 3 an edge view of the flash-calcined product. Whereas not all of the flash-calcined particles exhibited this appearance, it was reasonably common, particularly in those samples having the lower densities. In one test, three electron microscope observers concluded that slightly more than half of the particles contained voids. The raw clay was completely free of such voids and exhibited the hexagonal lamellar structure commonly associated with kaolinite.

The bubbling may have been the result of the very



Figure 3. Kaolin particle flash-calcined in helium: edge view.

rapid heating rates which caused dehydroxylation to occur faster than product water could diffuse from the particle. The result was a build-up in steam pressure within the particle which, at the proper temperature, became elastic permitting bubble formation. The high quench rates then froze the bubbles into the product.

Wada and Wada (1977) reported an allophane having a similar structure. The allophane was described as hollow spherules or polyhedra with external diameter 35–50 Å and wall thicknesses 10 Å or less. These samples also had low density, with the apparent density being dependent upon the fluid used in the density measurements. This led to the further speculation that the walls contained molecular-size openings which allowed small molecules (water) to penetrate but prevented the entry of large molecules (methanol) into the void space.

Subsequent soak calcination (1000°C for approximately 2 hr) of the flash-calcined kaolinite samples did not destroy the bubble structure and caused only small increases in particle density. Ten flash-calcined samples having densities of 2.26–2.37 g/cm³ experienced an average 2.7% density increase. The densities of these doubly-calcined samples ranged from 2.35 to 2.43 g/cm³, well below the 2.79 g/cm³ value reported by Reike and Mauve (1942).

The flash-calcined product was clearly less bright than the raw kaolinite. The brightness of four flash-calcined samples was 79.3–81.7% compared to the approximate 89% brightness of the raw material. The decreased brightness was presumably due to impurities in the original kaolinite (perhaps Fe) and/or the helium carrier gas. Heat treatment in air at about 500°C restored the original brightness.

CONCLUSIONS

Flash processing of metals and ceramics is known to produce alloys and glasses not previously observed at room temperature. The preliminary results of the present study indicate that clay products having unique properties may also be produced by flash calcination. The degree of dehydroxylation can be controlled over a wide range of values. Densities of flash-calcined prod-

ucts as low as 2.19 g/cm³ can be produced. A correlation between degree of dehydroxylation and product density was shown, and products appeared to contain numerous internal voids. Some had a balloon-like appearance.

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