

BULK DENSITIES OF SELECTED DRIED NATURAL AND FIRED KAOLIN CLAYS

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Abstract—Bulk (lump) densities of 31 kaolins were measured on the clay in the natural or raw state after drying at 100°C and after firing to 1510°C (2700°F). The kaolins were selected from such diverse origins as surface-weathered and sedimentary accumulations, hydrothermally altered bodies and flint-clay deposits. The sedimentary group ranged in density from 0.82 to 1.85 in the dried raw clay, and 1.93 to 2.63 when fired. The hydrothermally altered clays ranged from 1.83 to 2.50 in the dried raw state, and 2.02 to 2.66 when fired. Flint clays ranged from 2.20 to 2.60 in the dried raw state (a “toasted clay” from Russia, 1.75), and 1.99 to 2.70 when fired. The effect of the genetic process on bulk density values is discussed and related.

INTRODUCTION

Bulk density, i.e. the density measured on a small or hand-specimen size fragment, is an important property of rocks. It is a direct measurement that reflects the density of the constituent minerals or materials plus the included open pores. Indirectly, it may yield significant information on the environment under which the rock originated and on the packing, cementation, or crystallization of its components. Kaolins (defined as rocks which are characterized by a significant content of kaolin minerals) may vary widely in bulk density with their origin—e.g. whether *in situ* surface-weathered products, sedimentary clays, hydrothermally altered within or under a heavy, tight rock cover, or as sedimentary deposits comprised of flint clays.

The bulk density of clay (kaolin) commonly plays also an important role in its economic value when fired (as a refractory, filler, coater, absorbent, etc.). High-density is commonly desired, or demanded for clay refractories because high fired-density usually confers high physical strength at high service temperatures and high resistance to service corrosion, slag penetration, and abrasion. High-density clays in the natural, lump state which also are high in P.C.E. (Pyrometric Cone Equivalent, a measurement of fusion) typically yield refractory material in the high-density range, but not necessarily so.

During the firing process, clays flux over a wide range in temperature, wherein the most active fluxing begins at loci of alkali and alkaline-earth elements. As the clay particles flux, their surfaces become wet, whereby they cohere with adjacent particles, shrinking the mass and reducing its porosity. Depending upon the composition of the clay, a higher rise in temperature eventually will overfire the clay, developing many initially microscopic, gas-filled, closed pores. These pores may enlarge upon further heating, due to expansion of the gas and melting of clay,

thereby greatly expanding the mass and decreasing the bulk density. Such porous fired material may be useful for insulation and light-weight adaptations.

Literature on the bulk densities of kaolins is not abundant and is typically appended to other observations on clays. Klinefelter *et al.* (1943) however, reported that the dry bulk specific gravities of Georgia kaolins ran from 1.32 to 1.55 in soft kaolins, 1.57 to 1.66 in semi-hard varieties, 1.61 to 1.79 for hard, and one sample of very hard kaolin ran 2.00. Patterson and Hostermann (1962), published bulk densities on 38 samples of refractory clay from the Olive Hill District of Kentucky. These air-dried clays ranged from 2.10 to 2.52 in bulk density, 11 being in the 2.30–2.39 group, and 21 from 2.40 to 2.49 inclusive. When heated to 1400°C, bulk densities ranged from 1 at 1.06, to 1 at 2.60, with the modal group (12) in 2.40–2.49. Some samples exhibited overfiring at 1600°C.

LABORATORY MEASUREMENTS

Thirty-one kaolins from diverse origins and localities were selected for study. Single fragments of kaolin, ranging in weight from about 5–25 g, were broken from field samples and dried at 100°C. These were thinly coated with melted paraffin (to prevent penetration by water), reweighed to correct for the volume of paraffin and their volumes measured in a volumeter displacing water.

After the dried natural (raw) clays were measured, the samples were fired in individual crucibles in a large industrial laboratory test furnace to 2750°F (1510°C), and soaked at that temperature for 1.5 hr. The heating schedule generally used for measuring fired-densities was followed, although our samples were larger (adopted to geologic samples of raw clays) than in the industrial procedure. Density results are listed in Table 1.

DISCUSSION

Bulk densities of dried natural, unfired kaolins

The bulk densities of kaolins in the dried natural (raw, or unfired) state reflect their mode of genesis. Those which originated as surficial weathered deposits, or as deposits of either sedimentary kaolin or water-laid materials which were later kaolinized, possess relatively low bulk densities. All are under 2.0—indeed, the highest found in this study was 1.85, in endellite from Gardner Ridge, Indiana. This clay is actually not a clastic kaolin and perhaps should be placed in a separate category. The lowest density, 0.82, is of endellite (4) collected from a “concretionary” deposit (definitely non-clastic) currently neoforming within a residual, Paleozoic paleosol, over Silurian Brassfield limestone. It was solution-soaked and very soft when dug out of the bed cropping out in a road cut. Very high porosity was developed upon drying.

Note that Georgia (2, 14, 16), Murfreesboro, Arkansas (10), and Jacal, Mexico (17) sedimentary kaolins, and North Carolina “primary kaolins” (halloysite) (3, 6) possess low bulk densities. Near-surface kaolinization of these clays with relatively little overburden generated high porosity and low bulk density, a mean value 1.45 for 11 samples. This order of magnitude is believed to be genetically significant for sedimentary kaolins.

Hydrothermally formed kaolins (all from Mexico) have distinctively higher bulk densities. Four of them which were altered from lava, schist, or a calcareous sandstone (1, 18, 11, 19) run over 2.0, a mean of 2.36. No. 15 is a vein deposit, hence more like No. 4 in

Table 1.

A. Surface-Weathered and Sedimentary Kaolins

Sample Number	Natural-Raw (Dried at 110°C) Clay Density	Fired (1510°C) Clay Density
2	1.28	1.93
3	1.46	2.54
4	0.82	2.52
5	1.52	2.52
6	1.39	2.39
10	1.78	2.67
12	1.85	2.57
13	1.40	2.39
14	1.57	2.63
16	1.67	2.42
17	1.27	---

Characteristically: ≤ 2

B. Hydrothermally Altered Kaolins

1	2.50	2.32
11	2.26	2.02
15	1.89	2.66
18	2.20	2.38
19	2.47	2.53
22	1.83	2.57

Characteristically: 1.83-2.50

C. Flint Clays

7	2.36	2.67
8	2.34	2.70
9	2.45	2.63
19	2.47	2.53
20	2.40	---
21	2.20	2.60
23	1.75*	2.18
24	2.56	2.32
25	2.53	2.54
26	2.57	1.97
27	2.60	?
28	2.44	2.25
29	2.51	1.99
30	2.24	2.58
31	2.25	2.48

Characteristically: 2.2-2.6

*“Toasted” Clay, flint(?)

Legend:

- Hydrothermally altered felsite (rhyolite?) near Tepic, Nayarit, Mexico.
- Georgia Kaolin Co., Wrens-area Mine.
- Halloysite, Spruce Pine, NC, weathered pegmatite.
- Endellite, Stanford, Kentucky. Literature reference Keller *et al.*, 1966.
- Kaolin from Hungary, Collector, G. Bardossy.
- Halloysite, Spruce Pine, NC.
- Flint clay, Permian, Dunedoo, Australia, Collector, F. Loughnan.
- Flint clay, Bueker pit, MO. Literature reference Keller *et al.*, 1954.
- Flint clay, Triassic, Putty, Australia, Collector, F. Loughnan.
- Kaolin, Murfreesboro, AR.
- Hydrothermally altered schist, Guanajuato, Mexico, Literature reference Hanson and Keller, 1966.
- Endellite, Gardner Ridge, IN.
- Kaolin, Hungary, Collector, G. Bardossy.
- Georgia Kaolin Co., Dry Branch Mine.
- Hydrothermal halloysite and kaolinite, Sombrerete, Zacatecas, Mexico. Literature reference Keller and Hanson, 1969.
- Georgia Kaolin Co., Dry Branch Mine.
- Kaolin, Jacal, Mexico. Literature reference Keller and Hanson, 1975.
- Hydrothermal kaolin, Sombrerete, Zacatecas. Literature reference Keller and Hanson, 1969.
- Hydrothermal “flint” clay, Estola, Guerrero, Mexico. Literature reference Keller and Hanson, 1971.
- Flint clay, near Goodpasture, CO.
- Flint clay, Forbes pit, Rolla, MO.
- Hydrothermal kaolin, San Luis Potosi, Mexico. Literature reference Keller and Hanson, 1968.
- “Toasted” clay, USSR, Collector, F. Chukhrov.
- Flint clay, Hammarskrall deposit, Vereeniging, South Africa.
- Flint clay (“block”), Olive Hill type, Clearfield, KY.
- Flint clay, (black), Fort Hill, PA.
- Flint clay, Chase mine, Clearfield Co. PA.
- Flint clay, Lansing pit, Minford, OH.
- Flint clay, Big Savage Mountain, Frostburg, MD.
- Flint clay, Branson pit, Owensville, MO.
- Flint clay, Terzain pit, Rosebud, MO.

origin; No. 22 is from a flow breccia, an originally porous rock which retained its openness throughout alteration.

High bulk-density of hydrothermal kaolins probably derives, in part at least, from (a) dense parent rock which has been altered under (b) heavy overburden, or (c) being formed within confined space. The space which clay occupies when it is hydrothermally formed or deposited within solid parent rock must be developed by the dissolution and removal of silica and certain metal cations from the parent rock. Hydrogen and H_2O , especially where the clay is endellite, are added, thereby increasing the volume of the argillized product and necessitating it be tightly packed in its restricted site of formation. Secondary vein filling by kaolin (endellite) within the hydrothermal environment may or may not be restrained by space depending upon the origin of the vein space.

Flint clays, although sedimentary in origin, have notably high bulk densities, a mean value 2.38 for the 15 studied. Only No. 23 from the U.S.S.R. runs under 2.0. This type of clay was referred to by Chukhrov (1970), in terms used by the Russians, as "toasted clays". He reported the bulk density of this "Borovichy Toasted Clay" as 1.701 (1970, p. 3) which accords closely with the determination 1.75, made on a lump of "toasted clay" sent us (to W.D.K.) in 1970. Chukhrov noted (1970, p. 1) that U.S.S.R. "toasted clays" differ from typical flint clays by possessing lower bulk density and higher porosity. Flint clays from Australia (7, 9), Africa (24) and hydrothermal flint clay from Mexico (19) run 2.3 or higher, resembling those from the U.S.A. in that respect.

Flint clays consist of tightly interlocked small crystals and tiny packets of plates of kaolin minerals. Some are well-ordered kaolinite whereas others, especially if intermixed with illite, may be less well ordered. Flint clays typically form in an environment allied to deposition of coal (commonly, but not necessarily, in the Carboniferous or Cretaceous). The origin of sedimentary flint clay has been interpreted (Keller, 1968) as crystallization of kaolin mineral from colloidal parent material, characteristically a second-generation kaolinitic and/or illitic paleo-soil that was transported and refined in a marsh or swamp compatible with coal deposition. The parent "gel" presumably was heavy (pasty) from which tight, compact, low-porosity, finely-crystalline, high-density kaolinitic flint clay was crystallized. An exception to this environment is a hydrothermal flint clay No. 19 in this study which was derived from a sedimentary parent rock (Hanson and Keller, 1971).

Bulk densities of kaolins fired to 1510°C

Upon firing to 1510°C, kaolins lose hydroxyls and water, and then tend to be converted to mullite ($3Al_2O_3 \cdot 2SiO_2$) and a siliceous glass. Excess silica is released upon mullitization of the kaolin composition ($Al_2O_3 \cdot 2SiO_2$) and this silica combines with the alkali, alkaline earth, iron and other metal cations to form a siliceous glass in which the newly-formed mullite needles are embedded. Mullite density varies slightly upward, depending upon composition, from

3.2 and silicate glass will run 2.4 or higher as the iron content increases. Because of these chemical and mineral changes, kaolin shrinks significantly upon firing; the lumps of the lower bulk-density varieties may even become cracked. Before using such kaolins, the refractory industry precalcines them to "remove the shrinkage" in order to manufacture ware the service-size of which must be closely controlled. Shrinkage of ceramic ware during firing is one of the leading causes for problems in manufacturing in the ceramic industry. Certain flint clays (and also some hydrothermal kaolins) which possess high densities in both dried natural and fired states—hence change volume least upon firing—can be used industrially in the raw state where other kaolins must be calcined. Conversely to shrinkage, where a clay becomes less dense upon calcining, it is suspect of some degree of overfiring at the temperature of calcination indicating inferior refractoriness.

For many other large volume and very important uses, e.g. in the paper industry, kaolins are preferred which are open in texture, occur in expanded books or loosely coherent crystals and have high porosity—hence low bulk density. The bulk density of kaolins is one of the important physical properties relative to both geologic origin and industrial application.

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