CLAY MINERALS IN THE CERAMIC INDUSTRIES

by

THOMAS W. SMOOT

Harbison-Walker Refractories Company, Garber Research Center,
Pittsburgh, Pennsylvania

ABSTRACT

The physical, chemical and mineralogical characteristics of clays used in the ceramics industries are briefly outlined. Clays used include ball clays, fireclays, high-alumina clays of the diaspore and burley types, and three-layer types. The high temperature phases and bonding characteristics are briefly reviewed as are the uses of these various clays in the structural clay products, whitewares and refractories.

The importance of clays in the past for ceramics and, in particular, refractories is reviewed and evaluated for future importance.

INTRODUCTION

The ceramic industries are the major users of clay. These industries used about 70 percent of all clays "marketed in the crude or beneficiated form and those marketed only as finished products" (*Minerals Yearbook*, 1950–1958). For convenience, this discussion will be based on three major divisions of the ceramic industry, namely (1) structural clay products, (2) whitewares, and (3) refractories. These three divisions depend primarily on clay as a major raw material although other ceramic industries do use clays.

It is the purpose of this paper to outline the uses of the various clays employed in these major divisions and briefly to characterize the clays physically, chemically and mineralogically. An overall evaluation of the industry-wide trends, particularly as related to the relative importance of clays, is attempted.

I would like to acknowledge the advice and guidance given by the following members of the Harbison-Walker Staff: J. Spotts McDowell, now retired; H. G. Wilcox, quality control; and D. O. McCreight, Garber Research Center.

STRUCTURAL CLAY PRODUCTS

The structural clay products are in part referred to by the Bureau of Mines as *heavy clay products* and include: (1) building brick, (2) sewer pipe, (3) drain tile, (4) conduits, (5) structural tile, (6) lightweight aggregate, and (7) lightweight clay block, as well as other products. Traditionally, many products such as architectural terracotta and paving brick have been included in such product lists but they now seem to be a part of the history of the industry.

Most of these products are shaped by an extrusion method although relatively few of them are pressed, hand-molded or marketed unshaped to be included in other products.

The clays used in these products cover a wide range of chemical, physical and mineralogical properties. One thing that all must have in common, however, is that they must be easily accessible. In any given area, the accessibility of a deposit may prove almost as important as the basic requirements regarding chemical and physical properties.

Very few restrictions are placed on deposits considered for use in these products. Probably the most important is that the clay be suitable for forming. Briefly listed below, in decreasing order of importance, are the specifications which, ideally, should be met by raw materials used in most structural clay products.

1. Plastic enough for shaping
2. Dry without excessive cracking and warping
3. Have low and wide vitrification range
4. Low carbonate content
5. Have a spread in particle size
6. Contain non-clay constituents

The first two requirements are self-explanatory. The low and wide vitrification range is desirable for favorable unit firing cost and for ease of firing. The low carbonate content is desirable for two reasons: (1) the fluxing action of carbonates tends to shorten the firing range or cause localized flux spots and (2) CaO and MgO resulting from firing of common carbonate-bearing clays will hydrate rather easily with resulting disruption to the fired product.

A spread in particle size tends to widen the vitrification range and also generally promotes a stronger texture than is found in a clay that has a narrow range of particle sizes. This, especially in conjunction with the next point about non-clay minerals such as quartz, is particularly important in extruded shapes. In a mix containing a great predominance of two-dimensional (flaky) particles with nearly the same particle size, a forming pressure might orient the particles so that parallel zones of weakness would result. If a range of particle sizes is available in the clay fraction and a variety of three-dimensional shapes are supplied by non-clay materials, then these parallel patterns are generally disrupted and a close-knit texture is formed which is equally strong in all directions.

If the saleable product is one that depends in part upon fired color, then excessive amounts of iron compounds in the clay are harmful. This is of particular importance in only a few products such as face tile and, to a certain extent, face brick.

From these qualifications, it is apparent that a wide variety of mineral assemblages will suffice. Even shales rich in relatively nonplastic and impure illites and chlorites, if they contain enough non-clay minerals and are sufficiently plastic for shaping, are employed in structural clay products. Surface deposits, even till, which might contain a hodge-podge of clay minerals including montmorillonites, are profitably used (R. E. Grim, personal communication). Such clays commonly have low and comparatively wide vitrification ranges with alkali contents in excess of 5 percent. Such mineral assemblages commonly are plastic enough for forming and are easily fired.

If the clay is characterized by considerable bloating upon firing, it can be used for making lightweight aggregate. Slight bloating can be tolerated in the clays as can appreciable firing shrinkage if these tendencies can be offset by addition of non-clay minerals to the mix.

In rare cases, plasticizers such as ball clay or certain montmorillonite clays or plasticizing chemical additions can be profitably blended with locally available "hard" clays to increase workability. This can only be justified, however, if the cost of purchase, shipping and blending is still less expensive than the cost of importing fired products into an area.

In summary then, a tremendous range of physical and chemical properties can be tolerated in clays used by the structural clay industry.

THE WHITEWARES INDUSTRIES

For this discussion, the whitewares industries are considered to produce such products as dinner ware, sanitary ware, electrical porcelain, floor and wall tile, art pottery, spark plugs, and chemical and refractory porcelain, as well as many other products. This major division contains products formed by a wide variety of methods including slip casting, jiggering, extruding, power pressing and hand molding. Most of the products must be made from white-burning materials. The great variety of products, their variety of forming methods, and service conditions for this division, assure that the raw materials requirements vary greatly, although they are likely to be highly exacting for any given product.

Most of these products are composed of a mixture of kaolin, ball clay and ground non-clay materials including feldspar, quartz, talc and others. Higher alumina materials such as kyanite and specially treated kaolins are being incorporated in some of the whiteware products such as radomes and electrical and refractory porcelains. This industry uses about two-thirds of all domestic and imported ball clays, even though they are used only in proportions necessary to promote plasticity. The impurities, both chemical and mineralogical, which are always present in ball clays discourage their use in excessive quantities (McNamara, 1949, p. 475). Ball clays are necessary in most whitewares that are cast because they are readily dispersed in slips; and in molded products they are necessary for plasticity.

Although a certain amount of montmorillonite is generally found in ball clays, the proportion rarely exceeds 10 percent. In some cases, however, sodium-montmorillonites reportedly have been added up to 15 percent to otherwise low plastic whiteware mixes to increase plasticity (Polucktova, 1960,

p. 114). It must be assumed that these additions proxy for some of the ball clays.

As in other branches of the ceramic industry, the trend is toward the use of treated or beneficiated clays. Some of the new whiteware products use greater proportions of non-clay materials such as sillimanite and alumina. Clays are still needed, however, to promote plasticity necessary for forming and the mullite and glassy bonds needed for fired strength.

THE REFRACTORIES INDUSTRY

The refractories industry in recent years has used a considerable proportion of the annual clay production. In 1944 the refractories industry accounted for about 30 percent of the clays used (*Minerals Yearbook*, 1944). While this proportion decreased to about 10 percent in the late 1950's, it represented only a slight decrease in total tonnage from the 1944 figures (*Minerals Yearbook*, 1957, 1958, 1959).

The number of refractories that are based on clay is long. An abbreviated list would include these major products (*Modern Refractories Practice*, 1950, pp. 20–22): (1) fireclay brick—all classes; (2) high alumina brick—most classes; (3) ladle brick and acid proof brick; (4) a large variety of monolithic refractories including castables, plastic firebrick, ramming and gunning mixes; (5) treated clays sold for special uses; and (6) refractory mortars.

Fireclay brick are shaped in a variety of ways. Most of them are power pressed, many are extruded, a lesser number are slip cast, and some of the special shapes are hand molded. Although typically they are burned, at least experimentally, some high calcine types have been placed in service as unburned products. Naturally, the monolithic products, which may contain calcined grog components, are sold unshaped and unburned. These monolithic linings are emplaced directly in the furnace by air-ramming, gunning or casting and are then fired in place either in the first heat-up or prior to service.

Most of these refractory products are made from clays that are rich in kaolinite and from the high-alumina clays which carry diaspore, gibbsite, boehmite and other aluminum hydrates. They depend upon the formation of siliceous glasses, mullite, or corundum, or combinations of these, for their ceramic bonds.

The American Society for Testing Materials recognizes many classes of fireclay and high-alumina brick, based generally on their melting behavior and alumina contents. The classification of raw materials used in these products, however, is not so well established. For example, Norton (1949, p. 27) recognizes a fireclay as a clay having a PCE of 19 or higher. The ceramic industry has used loose classifications for fireclays which include the following: (1) flint and semi-flint clays, (2) plastic and semi-plastic clays, (3) kaolins, and (4) siliceous clays. High-alumina clays, also broadly classified as fireclays, include diaspore clays, burley clays, and other types commonly found associated with bauxites. Fireclays are also loosely defined as nonwhite-burning clays. The term fireclay, in common usage, has so many connotations that it is almost meaningless.

The refractoriness of ladle brick, which cannot be compared to products made from pure kaolinite, depends, for the desired properties, upon a sizeable proportion of three-layer clay minerals that expand upon heating.

Thus, it can be seen from these various classifications of clays used in refractories, that a variety of mineral assemblages or mixtures are used. The requirements, however, are such that the major clay mineral is kaolinite in association with aluminum hydrates and quartz. In relation to other industries using clays, the clays used in refractories must be relatively free from alkalies and from compounds of iron, titanium or alkaline earths.

In addition to the refractory products that contain clays as their major raw materials, numerous other refractory products incorporate clays as minor or trace constituents. These include some very high-alumina products, many basic refractories based on chrome ore and magnesia, and a number of special refractories. Although refractory clays are employed in many of these applications, the clays are being used for one or more special reasons. Clays of high purity and specially ground or otherwise treated clays are often used to increase plasticity, as pressing aids, to increase green and dried strength or to promote fired bonds.

Clays of high purity and specially treated kaolins are used in some of these applications. Ball clays and bentonites may be employed. The reason for using these clays as plasticizers and pressing aids are obvious. The clays are also used as components to aid dispersion in slips that are not basically clay slips. Their uses as high-temperature bonds, however, are not quite so obvious.

In high-alumina mixes where corundum and mullite are the normal fired phases, clays used as bonding agents may yield cristobalite and glass in addition to mullite. The mullite supplied by the fired clay may be important in that its intergranular position can promote a firmer bond. In basic refractories, clays may be used to form magnesium aluminate spinels, forsterite, or other silicates as fired bonds.

Recently there has been a trend toward greater use of monolithic refractory linings. Monolithic refractories, since they are in essence formed during installation, may require a higher degree of plasticity or greater unfired strength than their comparable fired counterparts. These different requirements are often satisfactorily met by the addition of small amounts of clays some of which would not meet the present definition of refractory clays. A hypothetical example might be the use of a clay of low refractoriness but high plasticity in a gunning castable to permit satisfactory emplacement in a short period of time with a minimum of waste. Many more examples could be cited, but it is hoped that those mentioned here indicate the considerable variety of the uses of clays in the refractories industry and their importance to the industry.

A brief look at some recent statistics on the production and sale is in order. These statistics, when related to those amounts used in the ceramic industries, tend to show the influence of some of the recent trends on the clay market and, further, give some basis for a look into the future importance of clays in ceramics. It should be noted, however, that the statistics reported for the 1940's and early 50's may not have been as comprehensive as those that have been published more recently.

RECENT TRENDS OF CLAY USE IN THE CERAMIC INDUSTRIES

In the past decade, the amount of clays produced and sold in the United States has shown an increase. The dual classification of *produced* and *sold* is necessary, for in many cases, tremendous tonnages of clays are produced

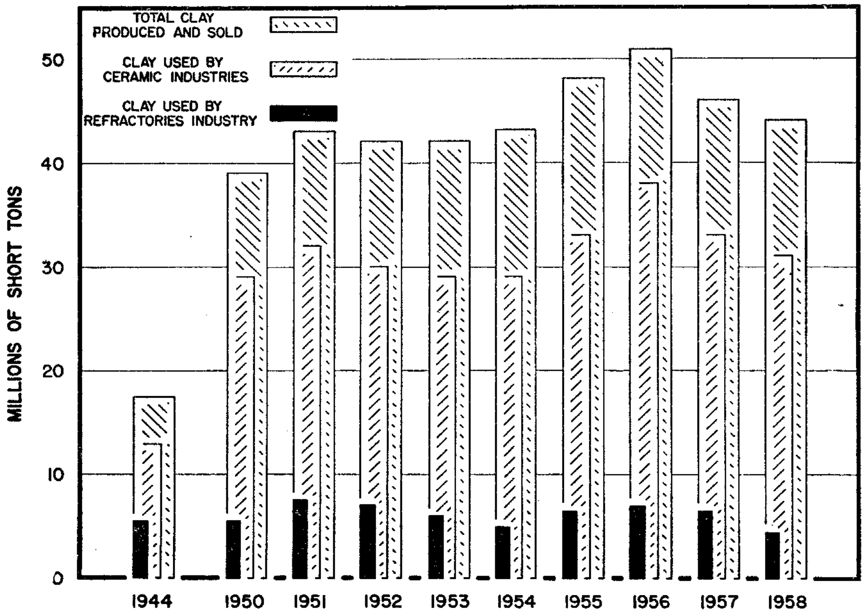

FIGURE 1.—Total clays produced and sold, used by the ceramics industries and by the refractories industry; 1944 through 1958.

which are sold only as finished products. In other cases, crude clays are sold as the finished product.

Figure 1 shows the relationships between annual clay production and the amount of clays used by the ceramics industries as well as the portion used by the refractories industry for the years 1944 and 1950 through 1958. The 1944 production figures were chosen because (1) they are representative of the early 40's and (2) 1944 was the first year in which the data included total amounts of clays used by industry. It was unfortunate that the early 1940

https://doi.org/10.1346/CCMN.1961.0100126 Published online by Cambridge University Press

figures were not broken down so that the data for the ceramic industries could be analyzed. There was, in that period, a tremendous mid-war peak of use by the refractories industry at the same time as a fractional structural clay production. Table 1 has been compiled to show the average tonnages for the years 1944, 1945 and 1946. This table shows the total clays used by industry, the totals used in ceramics and the proportion of the total used in ceramics in general and refractories in particular for the middle 1940's and 1950 through 1958.

Table 1 and Fig. 1 show a tremendous jump in total production from the middle 40's to the 50's. This jump in total is also reflected in the jump in tonnage of clay used by the ceramics industries. It is also evident, however, that the amount of clay used annually by the refractories industry was about the same in the 40's as it was in the 50's. This reflects improved efficiency in the use of refractories.

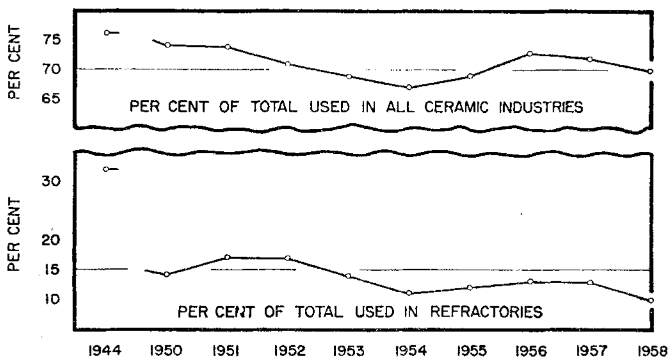

FIGURE 2.—Proportion of clays produced and marketed, used by all ceramic industries and the refractories industry; 1944 and 1950 through 1958.

Figure 2 shows the proportion of the annual clay production used by the ceramic industries as a whole and the refractories industry in particular for the same years. The considerable decrease in percentage of total clays used by the refractories industry while the tonnages remain about the same gives an idea of the general growth of the ceramics industries.

As have all other industries that use clay, the ceramic industries have gone to the use of greater proportions of the more highly refined and specially treated clays. Along with this trend, there has been a clearly discernable increase in the dollar value per unit of clay. This not only reflects added production cost but also added quality. Murray (this Volume) has given some idea of the tremendous differences in kaolins marketed. Many of the clays available for use now bear little resemblance to their parent materials.

In the refractories industries, the trend is toward specialization, with a specific refractory designed for a single and very particular application. Missile launching pads, for instance, must be able to withstand conditions

TABLE 1.—TOTAL CLAYS USED BY INDUSTRY; MIDDLE 1940'S AND 1950 THROUGH 1958*

Year	Av., 1944 through 1946	1950	1951	1952	1953	1954	1955	1956	1957	1958
Total clay used, millions of tons	22	39	43	42	42	43	48	51	46	44
Total clay used by the ceramic industry, millions of tons	17	29	32	30	29	29	33	38	33	31
Percent used by the ceramic industries	77	74	74	71	69	67	69	74	72	70
Percent used by the refractories industry	23	14	17	17	14	11	12	13	13	10

* From *Minerals Yearbook*, 1944–46 and 1950–58.

https://doi.org/10.1346/CCMN.1961.0100126 Published online by Cambridge University Press

that formerly did not exist. In other fields, refractory coatings have been called for to protect metal parts which formerly would have been capable of withstanding the service conditions. In another instance, a small specialty glass producer might want a specially made melting pot. Many of these special items, of course, are developed from refractory clay based materials; others must rely on other refractory materials such as basic or high purity oxide ceramics. Other branches of the industry continue to use large tonnages of clay each year with new clay products being developed to offset discontinued use of outmoded products.

In summary, it now appears that the ceramic industries will continue to use the largest proportion of the annual clay production. Although that proportion may not greatly change, it will represent an increase of total clay production and not a discernable decrease in the use of clays in ceramics.

REFERENCES

McNamara, E. P. (1949) *Ceramics*, v. 3, *Clay Products and Whitewares:* Pennsylvania State College, State College, Pennsylvania.

Minerals Yearbook (1944) U.S. Bureau of Mines, Division of Minerals, U.S. Govt. Printing Office.

Minerals Yearbook (1950–1958) U.S. Bureau of Mines, Division of Minerals, U.S. Govt. Printing Office.

Modern Refractory Practice (1950) 3rd ed., Harbison-Walker Refractories Company, Pittsburgh, Pennsylvania, 439 pp.

Murray, H. H. (1962) Industrial applications of kaolin: This volume.

Norton, F. H. (1949) *Refractories:* 3rd ed., McGraw-Hill, New York, 782 pp.

Polucktova, E. F. (1960) U.S.S.R. Patent No. 86, pp. 111–116, also, *Chem. Abstracts:* v. 55, no. 14, col. 13779 c, 10 July 1961.