CLAYS AND SHALES OF MICHIGAN

AND

THEIR USES

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CLAYS AND SHALES OF MICHIGAN

AND

THEIR USES

BY

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PREPARED UNDER THE DIRECTION OF

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LETTER OF TRANSMITTAL

To the Director, and the Board of Commissioners of the Department of Conservation of the State of Michigan:

John Baird, Director.
W. H. Wallace, Chairman.
Howard B. Bloomer.
Chas. E. Lawrence.
Herman Lunden.
T. F. Marston.
Geo. W. Millen.
Fred Z. Pantlind.
Edgar Cochrun, Secretary.

Gentlemen: I have the honor to submit herewith a monographic report entitled The Clays and Shales of Michigan and Their Uses, and recommend that it be published and bound as Publication 36, Geological Series 30, of the Geological Survey Division, Department of Conservation.

This monograph represents the results of nearly four years of field study and laboratory work by Dr. George G. Brown of the University of Michigan.

The object was first to make an inventory of the clay and shale resources, second to determine so far as possible their character and distribution and the uses for which they appear most adapted, and third to direct attention to, and arouse interest in their economic possibilities, that would result in commercial development and the creation of taxable values.

Michigan produces only a small part of the high grade brick, building tile, and conduit used in the State, the supply being imported from Ohio and other neighboring states. This is due chiefly to the few known deposits of suitable raw material advantageously located for the manufacture of the high grade ceramic products, and in part to a general lack of knowledge concerning the possibilities of the clays and shales of Michigan.

As a consequence it costs the people of Michigan not only large sums annually for their supply of higher grade brick and tile materials, but also a large amount for freight charges. Moreover a considerable part of the State is so far from a source of supply that the freight charges make the general use of such materials practically prohibitive.

The field and laboratory studies showed that while Michigan is relatively poor in good clay and shale resources, as compared with Ohio, they are sufficient when developed to provide a large part of the ceramic

products now imported from other states. It is hoped and expected that this report will result in a more rapid and intelligent development of the clay products industry in Michigan. Already a number of developments are under way or projected and presumably when the results of the field and the laboratory investigations are available in printed form development will be accelerated.

Special attention has been given in the report to the factors which must be considered in the development of the clays and shales of this State. The large decline in the number of brick and tile plants during the past fifteen years has been due largely to a lack of appreciation of the relative importance of the various factors which influence or control the success or failure of a ceramic enterprise. Special chapters are devoted to the origin, character, and occurrence of clays and shales, methods of prospecting, physical and chemical properties, and methods of mining, preparation, and burning for the efficient production of commercial ceramic products.

The investigation of the clays and shales of Michigan has been carried on in cooperation with the Department of Chemical Engineering of the University of Michigan. Through this cooperation a more complete and comprehensive survey and report was made possible. More than 300 deposits of clay and shale were visited, some 240 sampled, and 177 burning tests and 50 analyses were made. These were supplemented by 37 burning tests and 88 analyses made previously in university, college, and commercial laboratories. Much credit must be given Dr. Brown for his painstaking work, not only in the field and laboratory but in the preparation of this report, which it is believed will meet a pressing need for information as to the character, occurrence, and economic possibilities of the clays and shales of the State.

Very truly yours,

R. A. SMITH,

State Geologist.

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PREFACE

This report is prepared primarily for the residents of Michigan who are interested in clay and shale or the products made therefrom. The field work was done largely during the summer of 1922 and finished in 1923. Testing and burning of the samples were completed by 1924. The actual writing of the report has been done whenever possible in the intervals of University work.

Part One is a general survey of the properties of clays and the methods used in manufacturing clay ware, particularly the heavy clay products used as building material. This part will aid in answering the many questions raised by those persons interested, but unfamiliar with the clay and the clay industry. It may also be of value to many producers in outlining the fundamental factors and in suggesting other and better methods of operating. Throughout the report references have been given so that persons seeking more detailed information may know where it may be found.

Part Two is a detailed description of the clay areas and deposits throughout the State, and is believed to be a complete record of all the available data. The information was obtained by field work, laboratory testing, and from past records which have been carefully reviewed. These areas are described by counties for the Southern and Northern Peninsulas respectively. So far as possible the probable economic use of each clay deposit has been indicated. This has been done even in those cases where the information is so incomplete that the indicated economic use may be very questionable because even incomplete data was considered more valuable than none. The economic uses have been considered almost entirely from the standpoint of building material or heavy clay products. This was done for two reasons—there exists at present a good demand for high grade brick and tile, which is partially supplied by shipments from Ohio and other states as far south as Missouri, and there is evidence that this demand will increase particularly as a local supply is developed. The types of clay suitable for building material are available in Michigan and are rather well defined.

Many of the clays classed as good brick or tile clays may be used for some pottery purposes such as flower pots, earthenware, and glazed tile. Some clays suitable for special uses have been indicated, such as the slip clay from Ontonagon County and the Fuller's earth from Harrietta and Petoskey. It is very probable that other special uses will be noted as the clays are more carefully tested. This report simply indicates some of the possible uses and deposits of Michigan clays.

Without exception every one throughout the State cooperated fully in supplying information that is essential to a report of this kind. I

wish to acknowledge this courteous aid received from many persons throughout the State. Mr. J. C. Malone of Burt and Mr. C. C. Cushman of Otsego have kindly given permission to include the results of tests made for them through the Department of Engineering Research of the University of Michigan. Mr. James Evans of Cleveland, Ohio, and Cadillac, Michigan, and Mr. L. Shay of Ann Arbor have kindly permitted the use of the results of tests made on Michigan Fuller's earth.

My brother, Donald L. Brown, of Brooklyn, New York, recorded all the field notes and samples during the most intensive part of the field campaign of 1922. In the summer of 1923 the field work was practically completed with the help of Dr. A. R. Carr, Professor of Chemistry in the College of the City of Detroit. Most of the burning tests and many of the analyses were made by H. W. Jackman, M. S. E., in the Ceramic Laboratories of the Department of Chemical Engineering.

Cuts and photographs illustrating the methods and equipment used in manufacturing clay products have been generously loaned by the following organizations:

The Hadfield-Penfield Steel Co. of Bucyrus, Ohio.

The Lancaster Iron Works of Lancaster, Pa.

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The American Ceramic Society Journal, Ross C. Purdy, Editor, Columbus, Ohio.

Brick and Clay Record, Industrial Publications, Inc., Chicago, Ill.

Fuels and Furnaces, F. C. Andresen and Associates, Pittsburg, Pa.

Ohio Geological Survey.

The work was originally conceived, promoted, and finally carefully reviewed and edited by Mr. R. A. Smith, State Geologist. Without his patient efforts this work would never have been started.

GEORGE G. BROWN,
Ann Arbor, Michigan.

June 5, 1925.

Chapter I

ORIGIN OF CLAY

DEFINITION

Clay is the term applied to natural earthy materials that are plastic when wet, and can then be molded into almost any desired shape that is retained when dry. Physically, clay is composed of small particles, mostly of mineral character ranging from coarse grains of sand to particles of microscopic size, or under one thousandth (0.001) of a millimeter in diameter. When heated to redness or to higher temperatures, some of these particles begin to soften or melt, so that when cooled the entire mass of clay is hard or vitrified much like rock. The economic value of clay lies largely in its plasticity when wet, (so that it can be formed into desired shapes) and in its burning properties.

ORIGIN

Clays are always of secondary origin, being formed by the decomposition of rocks that very frequently contain feldspar. As some of the most plastic clays known have been formed from rocks such as serpentine which contain no feldspar,[1] it cannot be said that clay is always derived from feldspathic rocks. The process of weathering may be divided into physical decomposition of the rock mass and chemical decomposition of the minerals contained therein.[2]

When a mass of rock, such as granite, is exposed to the weather minute cracks are formed in it, due to the rock expanding when heated by the sun and contracting at night, or as joint planes formed by the contraction of the rock as it cooled from the molten state. Water percolates into these cracks, and freezing in cold weather expands, opening the fissures, or may even wedge off some rock fragments. Plant roots force their way into these cracks and supplement the action of frost. If continued, this process alone may reduce the rock to a mass of small angular fragments, or even sand.

[1] G. Hickling, Trans. Inst. Min. Eng. (Eng.). XXXVI p. 10, 1908-9. V. Selle, Sprechsaal XL, p. 463, 1907.

[2] See H. O. Buckman, T. A. Cer. Soc. XIII p. 336 (1911) for discussion and bibliography.

During the physical decay of the rock solution of some of the minerals by the surface waters proceeds more or less slowly, but continuously. This process of solution is aided by the physical disintegration of the rock as more surface is exposed to the water. In 1835, Forschammer[1] advanced the idea that the solution of the minerals was largely due to the carbon dioxide dissolved in the water. This view has been supported by a number of writers[2] since that time. But as many of the minerals found in rocks are known to be soluble in pure water, although their solution may take place slowly, the importance of carbon dioxide is very doubtful as has been indicated by Cameron and Bell[3] and others[4]. In addition to simple solution, hydrolosis of the minerals takes place. This is shown by the fact that solutions obtained by treating powdered minerals[5] with pure water have an alkaline reaction with phenolphthalein. Oxidation and other reactions also occur during weathering of the rock.

The following equation is assumed to represent approximately the action of water on orthoclase feldspar.[6]

$$K\,Al\,Si_3O_8 + H_2O = KOH + H\,Al\,Si_3O_8$$

The Potassium hydroxide (KOH) may unite with carbon dioxide to form potassium carbonate or bicarbonate, or it may react with other acids if present. The aluminum silicate ($HAl\,Si_3O_8$) so formed is apparently unstable, and may lose some silica (SiO_2) forming kaolinite ($Al_2O_3 . 2SiO_2 . 2H_2O$) as follows:

$$2H\,Al\,Si_3O_8 + H_2O = 4SiO_2 + Al_2O_3 . 2SiO_2 . 2H_2O$$

or possibly pyrophyllite ($Al_2O_3.4SiO_2 . H_2O$) as

$$2H\,Al\,Si_3O_8 = 2SiO_2 + Al_2O_3 . 4SiO_2 . H_2O$$

Such decomposition of aluminum silicates forming hydrated aluminum silicate, and usually setting free silica, is termed *kaolinization*. The mineral kaolinite is always of such secondary origin. The changes occurring in the feldspars may be given as in Table I.[7]

[1]Pogg. Ann. XXXV p. 331, 1835.

[2]Rogers, Am. J. Sci. V, p. 404, 1848.
Bischof. Naturhist. Ver. Bonn, XII, p. 308, 1855.
Daubrée, Compt. rend. LXIV, p. 339, 1867.
Miller, Tscherm. Mitth., p. 31, 1877.

[3]Bur. of Soils, Bull. 30, p. 16, 1905.

[4]Cushman and Hubbard, Bull. 28, Office of Pubic Roads, Washington.
Ries, Clays Occurrence, Properties and Uses, 1908, Wiley & Sons.

[5]F. W. Clarke, U. S. Geol. Survey Bull. 167, p. 156, 1900.
H. Stremme, Zeitschr. prak. Geol. XVI, p. 122.
Merrill, Rocks, Rock-weathering and soils, p. 234, 1897. Bur. Soils, Bull. 30.

[6]Cameron and Bell, Bur. of Soils Bull. 30, p. 18, 1905.

[7]H. Ries, Clays, l. c. page 3.

TABLE I.

Changes during Kaolinization of the Feldspars.

	SiO_2	Al_2O_3	K_2O	H_2O	%
Orthoclase	64.86	18.29	16.85	.....	100
Lost	43.24	.....	16.85	.....	60.09
Taken up	.....	.....	.....	6.45	6.45
Kaolinite	21.62	18.29	.....	6.45	46.36
	SiO_2	Al_2O_3	Na_2O	H_2O	%
Albite	68.81	19.40	11.79	.....	100
Lost	45.87	.....	11.79	.....	57.66
Taken up	.....	.....	.....	6.85	6.85
Kaolinite	22.94	19.40	.....	6.85	49.10
	SiO_2	Al_2O_3	CaO	H_2O	%
Anorthite	43.30	36.63	20.07	.....	100.00
Lost	.....	.....	20.07	.....	20.07
Taken up	.....	.....	.....	12.92	12.92
Kaolinite	43.30	36.63	.....	12.92	92.85

The kaolinite may be formed from orthoclase or plagioclase varieties. The latter decompose more easily.[1]

A deposit of kaolin near Jösingfjord at Ekersund, Soggendal, Norway, that has been formed from labradorite, is reported by Vogt.[2] He states that hornblende, augite, beryl, topaz, etc., are known to be occasionally converted into kaolinite, but gives no evidence. It is very probable that such silicates yield a hydrous aluminum silicate that is not known to be kaolinite.[3]

The silica accumulates in relatively large proportions and may be present as quartz. There is a tendency for it to be gradually changed over into other forms through solution and redeposition.[4]

There is no absolute proof that the mineral kaolinite is formed from silicates other than the feldspars. All clays apparently contain some hydrated aluminum silicate in variable amounts, which may or may not be kaolinite.

[1]Ries—Kaolins of Europe. U. S. Geol. Surv. 19th An. Rept. part VI, p. 377, 1898.
Leimberg, Zeitsch, d. d. Geol. Ges., Vol. 35, 1883.
Rösler, Neues Jahr. Beil. Bd., XV 2nd. Heft, p. 231.

[2]Am. Inst. Min. Eng. Trans. XXXI, p. 151, 1902.

[3]Merrill, Rocks, Rock-weathering and Soils, p. 21, 1897.

[4]Hayes, Jour. Geol. V, p. 319, 1897, and Bull. Geol. Soc. Am. VIII, p. 213, 1897.

Other methods of feldspar decomposition to kaolinite[1] than ordinary weathering processes seem possible. At Cornwall, England, the feldspar of the granite on both sides of the tin veins has been kaolinized, apparently by the action of fluorin vapors the presence of which is rather clearly indicated by the finding of tourmaline and topaz. Collins[1] claims to have carried out such a reaction in the laboratory by exposing feldspar to hydrofluoric acid, obtaining a hydrated aluminum silicate mixed with potassium fluoride. Pure silica was deposited on the sides of the tube. If this theory be correct, the kaolin deposits should extend to great depths, but if the kaolinization be due to weathering, undecomposed feldspar should be encountered at the limit reached by the weathering. In Cornwall the kaolin mines run over 400 feet deep, likewise at Zettlitz in Bohemia, without any signs of the kaolin giving out. In many localities, however, the kaolin decreases with the depth, running to undecomposed feldspar at 60 to 120 feet.[2]

CLASSIFICATION OF CLAYS

On the basis of origin clays are of two general classes, residual, or transported or sedimentary.

Residual Clays. Clay found overlying the rock from which it was formed is called residual clay because it represents the more or less insoluble residue of rock decay. In such a deposit there is usually a gradual transition from the fully formed clay at the top, through zones containing clay and partially decomposed rock fragments to the solid parent rock beneath; except in the clay derived from limestone where the passage from clay to rock is abrupt. Limestone consists of carbonates of calcium and frequently of magnesium, with variable quantities of clay impurities. The carbonates are dissolved by the surface waters during the process of weathering and the insoluble clay residue remains as a mantle covering the undissolved rock, the change from rock to clay being sudden and not due to a gradual decomposition of the rock minerals as in the case of granite.

Kaolin is the name given to white residual clays derived from rock composed entirely of feldspar, or to clays containing little or no iron oxide and usually a high percentage of kaolinite or other similar alumi-

[1]J. H. Collins Mining Magazine, VII p. 213, 1887.
Von Birch, Min. Tasch., 1824.
Von Birch & Daubrée, Ann. des mines, XX, 1841.
Daubrée, Etudes synthetique de Geologie Experimentale, 1879.
B. von Inkey and Semper, Nagyag u. seine Experimentale, Lagerstätten, Budapest, 1885.
Cross and Penrose, U. S. Geol. Survey, 16th Ann. Report, Pt. II, p. 160.
Ransome and Lindgren, U. S. Geol. Surv. Bull. 254, p. 21, 1904.
H. Rösler, Beiträge zur kenntniss der Kaolinlagerstätten, Neues Jahrb. f. Min., Geol. u. Pal., XV Beilage Band 2d Heft, pp. 231-393.
G. P. Merrill, What Constitutes a Clay. Am. Geol., XXX, Nov., 1902.
H. Ries, Origin of Kaolin, Trans. Am. Cer. Soc. II, p. 93, 1900.
E. Zalinski, Econ. Geol. II, p. 479, 1907.
Stütze, Zeit, prak. Geol. XIII, p. 23, 1905.

[2]H. Ries, Clays, loc. cit.

num silicates. Kaolin is the term applied to the clay or rock mass and must not be confused with the term kaolinite referring to the mineral of definite chemical composition. The name kaolin is a corruption of the Chinese Kauling, meaning high ridge, the name of a hill near Jaucha Fu where the material was obtained.[1]

TABLE II.
Analysis of Kaolins

	I.	II.	III.	IV.	V.
SiO_2	73.55	73.55	73.56	48.68	48.73
Al_2O_3	21.09	18.98	16.47	36.92	37.02
Fe_2O_3	.....	.....	.27	.....	.79
CaO	2.55	1.58	1.17	.....	.16
MgO	.15	1.08	.21	.52	.11
K_2O	.....	.46	5.84	.58	.41
Na_2O	.....	2.09	.....	.....	.04
H_2O	2.62	1.96	2.45	13.13	12.83
Total	99.62	99.70	99.98	99.83	100.00

I Natural original kaolin from King-te-chin as used in finest Chinese porcelain.
II from same locality used for blue Canton ware.
III English Cornwall stone.
IV Washed kaolin from St. Yrieux, France.
V Washed kaolin from Hockessin, Del.[2]

The form of a deposit of residual clay depends upon the shape of the parent rock. If the rock occurs in great mass, the deposit may form a mantle covering a large area. If the clay-yielding rock is present in veins the outcrop of residual clay along the surface will form a narrow belt.

Residual clays vary widely in color. If derived from rock containing much iron oxide they will be yellow, red, or brown depending on the iron compounds present.

The depth of a residual clay deposit depends on climatic conditions, the character of the parent rock, topography, and location. Generally rock decay proceeds more rapidly in moist climates, but even then the rate of decay must be measured in centuries except for soft rocks such as shale which change to clay in an easily measurable time.

If located on a flat surface or gentle slope the clay will remain where formed. In some cases the residual material is washed a short distance and accumulates at the foot of the steep slope, forming a deposit similar to the original residual clay in physical and chemical properties. Such deposits have been called colluvial deposits,[2] to distinguish them from the strictly original residual clays.

[1]Dana, System of Min., p. 687, 1892.
Richthofen, Am. J. Sci. 1871, p. 180.

[2]G. P. Merrill, Non-metallic Minerals, p. 224, 1904.

Residual clays are formed in many parts of the United States, particularly in that portion east of the Mississippi and south of the southern limit reached by the ice sheet of the glacial period. North of the terminal moraine they are found only in protected (fig. 1)[1] situations or non-glaciated areas.

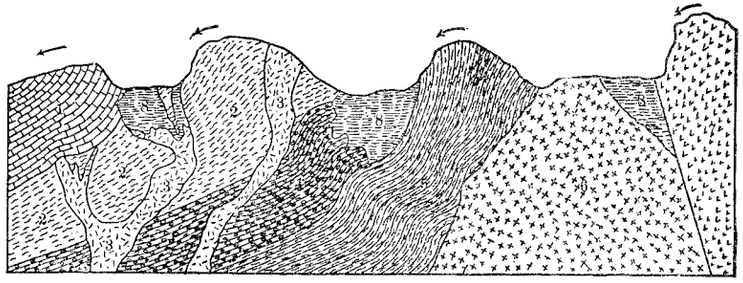

Figure 1.—Generalized section showing three possible occurrences of kaolin in a glaciated country. 1, limestone; 2, mica schist; 3, pegmatite; 4, feldspathic quartzite; 5, dark gneiss; 6, light granite; 7, dark granite; 8, kaolin, protected from glacial erosion. Arrow indicates direction of ice-movement. (After Laughlin, Conn. Geol. and Nat. Hist. Surv., Bull. 4, p. 70, 1905.)

As Michigan is largely covered by glacial drift, and the entire state was covered by the glaciers, there is slight chance of finding any residual clay in Michigan even in the limited areas where the bed rock outcrops and might have protected the residual clay from the glacier.

Transported or Sedimentary Clays. Residual clays rarely remain on steep slopes, but are washed away by the rain into streams and carried off to lower and distant areas. This process may be seen in any abandoned clay bank where the clay on the slopes is washed down and spread over the bottom of the pit. Clays of different character may be washed into the same stream, mixed and deposited together. So long as the stream maintains its velocity, the clay will be carried in suspension. If the water becomes quiet the particles of clay begin to settle on the bottom forming a layer of clay that may be added to continuously, or at intervals. Such a deposit is called sedimentary.

If the material deposited is absolutely uniform, one thick homogeneous bed would be formed. Usually there is some variation in the material deposited so that the bed is stratified or made up of layers of varying thickness, and as there is less cohesion between unlike particles, the layers tend to separate along the line of contact.

As the fine material can be deposited in quiet water only, and the

[1]Laughlin, Com. Geol. and Nat. Hist. Surv. Bull. 4, p. 70 (1905).
Chamberlain and Salisbury, 6 Ann. Rep. U. S. Geol. Survey, p. 240 (1885).
G. P. Merrill, Rocks, etc., pp. 301, 306.
I. C. Russell, U. S. Geol. Surv. Bull. 52.
H. Ries, U. S. Geol. Survey, Prof. Paper 11.
H. Ries, J. Am. Cer. Soc. I, p. 446 (1908).
M. Whitney, Maryland Agricult. Exp. Sta. Bull. 21 (1893).

coarser material in disturbed water, the character of the deposit enables us to determine fairly well the conditions under which it was formed. Sedimentary clays can be distinguished from residual clays by the fact that they bear no direct relation to the underlying rock, and by their stratified nature.

Because of the nature of deposition, one bed of sedimentary clay may show variations in thickness and composition from point to point. Occasionally a bed of clay may be worn away by currents after deposition. Such a bed has a very uneven upper surface which may be covered by an entirely different kind of material.

Sedimentary clays may be divided into the following six classes:

Marine Clays are those sedimentary clays that are deposited on the ocean bottom where the water is quiet. The water is shallower and more disturbed near shore where only coarser materials may be deposited. Marine clays may be of vast extent and thickness, but will show variation because the different rivers flowing into the sea usually bring down different classes of material. The areas of deposition may overlap, thus forming an intermediate zone, which may be of wide extent showing a gradual change, or only a few feet wide.

The most extensive marine clays are found in the rocks of the Silurian, Devonian, and Carboniferous systems and some in Mesozoic formations (the so-called Red Clay[1] covering many square miles of the deeper parts of the ocean floor).

Estuarine Clays are sedimentary clays deposited in shallow arms of the sea, and are found in comparatively long and narrow deposits tending toward basin shapes. The fine clays will be found at a point most distant from the mouth of the river supplying the estuary, or in areas of quiet water in recesses of the bay shore. Estuarine clays often show sandy laminations, and may be associated with the shore marshes as the estuary becomes gradually filled up and covered with plant growth.

The clays of the Hudson Valley of New York and of the Hackensack region of New Jersey are examples of the more important estuarine deposits formed at the close of the glacial period when this region was lower than at present.[2]

Lacustrine or Lake Clays are sedimentary clays formed in the basin shaped depressions of present or former lakes. They are a common type and are variable in extent, frequently showing alternating beds of clay and sand, the latter in such thin layers as to be easily overlooked although causing the clay layers to split apart readily. Many of the lake

[1]The composite analysis of a number of samples, less absorbed sea-salts, calcium carbonate, and some gypsum is given by Clarke, (J. Geol. XV., p. 787) as follows:
SiO_2, 54.58; Al_2O_3, 15.94; TiO_2, 0.98; Cr_2O_3, 0.012; Fe_2O_3, 8.66; FeO, 0.84; NiO.CoO, 0.039; MnO_2, 1.21; MgO, 3.31; CaO, 1.96; SrO, 0.056; BaO, 0.20; K_2O, 2.85; Na_2O, 2.05; V_2O_3, 0.035; As_2O_3, 0.0011; MoO_3tr.; P_2O_5, 0.30; CuO, 0.024; PbO, 0.008; ZnO, 0.005; H_2O, 7.04.

[2]N. J. Geol. Survey, Vol. V., p. 196.
N. Y. State Museum, Bull. 35, p. 576.

clays are of glacial origin, some being laid down in basins or hollows along the margin of the ice sheet, others in valleys dammed up by an accumulation of drift which obstructed the drainage of the valley giving rise to a lake. Clay beds of this type are abundant in all glaciated regions, and compose a large part of Michigan's usable clay. They are generally surface deposits,* often highly plastic, and rarely refractory. Their chief use is for brick and earthenware.

Fluvial or Flood-plain Clays are sedimentary clays deposited upon the flood plain of a stream when the water overflows the regular banks. As there is usually some current over the plain at these times, the finest sediments settle only in protected spots. Most flood-plain clays are sandy with occasional pockets of fine, plastic clay. Where several terraces are found due to the river cutting a deeper bed, each terrace represents a former flood-plain. Clays of the different terraces even along the same stream may differ greatly.

Glacial Clays often called till or boulder clays, are clays deposited directly by the glaciers. They consist of a mixture of rock flour with more or less residual and transported clays, eroded and carried along by glacial ice. They are usually tough, dense, gritty clays, in many places containing numerous pebbles and stones. They are generally too strong and sandy to be of economic value. Locally the boulder or till clay may be plastic enough and sufficiently free from stones to be usable, but such deposits are generally of limited extent, of little value, and frequently require special treatment in preparation. Boulder clays are abundantly distributed throughout Michigan and all that portion of the United States formerly covered by the continental ice-sheet.

Morainic Clays are boulder clays deposited in the moraines or hilly tracts. When the rate of ice advance was equal to the rate of melting much of the material carried by the glacier was dumped at the front of the ice sheet to form a moraine. These morainic clays are very similar to the till clays deposited under the ice sheet but are found in the hills and knolls making up the moraines instead of the till plains.

Clays deposited in lakes, or along flood plains, or in outwash aprons by the streams issuing from the glacier are properly classed as lacustrine (lake), estuarine, or flood-plain clays of glacial age and should not be confused with the boulder clay which is deposited directly by glacial ice.

Coal Measure Clays. The origin of the clay partings found in coal seams has been a doubtful question for some time. The common explanation has been that the organic debris was covered by sedimentary clay and that this clay composing the soil was later purified by vegetable growth. This theory supposes a break in plant life and is unable to account for the uniform composition of the different clays.

*Lake clays formed in earlier geologic periods may be subsequently covered by other deposits, as is the case with many of the clays found under the carboniferous coal measures. Sometimes these clays show the upright stumps of trees that grew in the swamp where the clay was deposited.

The modern conception of the origin of these clays is entirely different. These "pure clays" found in, under, or over the coal seams are considered as a plant residue formed under oxidizing conditions that destroyed the carbonaceous matter, leaving only the mineral residue.[1] The ash of the coal occurring with the clays has the same chemical composition as the clay, with the addition of sodium, potassium, iron, lime, and other fluxing agents that form rather soluble salts and are readily leached out of the clay. When the conditions favored preservation of the carbonaceous matter, as during high water levels, the carbon was preserved as coal. Under oxidizing conditions, as during low water, the carbonaceous material was destroyed, leaving the colloidal mineral matter as a clay of uniform composition and physically homogeneous.

This conception calls for no break in plant life during coal formation, and easily explains the existence of clay partings in the coal strata. The clays account for a larger part of the plant life than can be accounted for satisfactorily in any other way.

Shale. Shale is the firm or rock mass formed when clay is consolidated by pressure or cementation. Sedimentary clays, particularly those of marine origin where covered by many hundred feet of other sediments, are compacted to form shale. If shale is ground and mixed with water it will develop as much plasticity as many surface clays. This fact is evidence that the cohesion of the particles is due mostly to pressure alone. In certain regions the shale may have been subjected to mountain building forces,—pressure and heat, and metamorphosed into slate or even mica-schist, both of which are devoid of any plasticity when ground. Sometimes the shale is hardened by the deposition of mineral matter around the grains which acts as a cement.

The Coal Measures shales must not be confused with the more refractory clays. The shales are true sedimentary deposits of material brought in by the water. In many places the clay may grade into the shale.

Shales vary widely in plasticity. The carbonaceous shales as found in the Michigan Coal Measures and the older Michigan shales are frequently very plastic, while the red Triassic shales of New Jersey are sandy, having poor plasticity and low fusibility.

SECONDARY CHANGES IN CLAYS.

Secondary changes in clays are the changes occurring in clays after their deposition. Such changes may be local or wide-spread, as in the formation of shale, and may greatly improve the deposit or render it worthless. These changes may be simply mechanical in nature or they may involve chemical changes which entirely alter the properties of the clay.

[1]W. Stout, Trans. Am. Cer. Soc. 17, p. 557 (1915).

Mechanical Changes. These involve tilting, folding, faulting, and erosion. Tilting is caused by the uneven elevation of beds after their deposition and is evidenced in the dip of clay or shale beds. Beds of clay and shale sometimes show folds or undulations which in the case of hard beds may be due to lateral pressure caused by movements in the earth's crust, while in soft beds the cause may be local such as shoving by the ice sheet.[1] If the bed is not sufficiently plastic to bend under pressure it breaks, and if the beds on opposite sides of the break slip past each other, a fault results. If the breaking surface or fault-plane is at a low angle one portion of the bed may be thrust over the other for some distance.

Erosion. All land areas are being constantly attacked by weathering agents (frost, rain, etc.) which combine to disintegrate the surface rocks and wash away the loose fragments and grains. This process results in forming hills and valleys; the valleys being cut out leaving the relatively unworn formations as hills. The results of this action are sometimes puzzling if the cause is not understood. Figure 2 indicates the results of this action on horizontal beds. If the beds have a uniform dip the result (figure 3) might mislead one into believing that bed (b) ran into bed (c) because they are at the same level. This dipping of layers

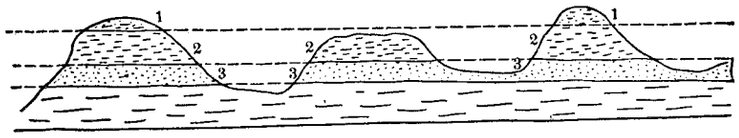

Figure 2.—Horizontal beds with several layers exposed by wearing down of the land surface.

sometimes accounts for the great differences in beds at the same level in adjoining pits. Beds of clay outcropping at the same level on opposite sides of a hill may or may not be the same bed, depending upon whether or not the beds are horizontal or inclined. Beds of clay or shale may thin out or grade into other kinds of rock.

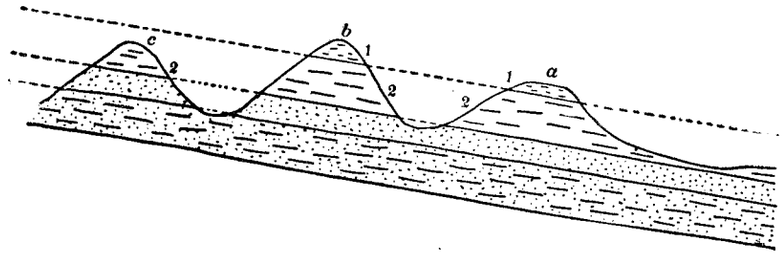

Figure 3.—Inclined strata, showing rise of the bed above sea-level, when followed up the slope or dip. (After Ries, N. J. Geol. Surv., Fin, Rept., VI, p. 19, 1904).

[1]Hollick, Trans. N. Y. Acad. Sci, XIV, p. 8, 1894.
Clapp. Bull. Geol. Soc. Am., XVIII p. 505, 1908.
Prussian Geol. Survey, 1906.

Chemical Changes. These changes due mainly to weathering agents, such as percolating surface waters, take place in nearly all deposits of clay.

These changes may be grouped under the four heads:

Change of color
Leaching
Softening
Consolidation

Change of color is frequently due to oxidation or rusting of the iron compounds contained in the clay. The depth to which weathering of the clay has proceeded can often be told by the depth of the yellow, red, or brown color. The lower limit of this is usually irregular and depends upon the nature of the deposit, sandy open clays being affected to a greater depth than dense ones. Frequently the water seeping into the clay may bring in the iron oxide and distribute it irregularly thru the clay. Changes in color noticed in clay beds are not always to be taken as evidence of weathering, for in many cases the difference in color is due to differences in chemical composition of the clay as deposited. Discoloration caused by weathering can usually be distinguished from differences in primary color in that the former begins at the surface and works into the clay, penetrating to greater depths along planes of stratification and joints, or following roots.

The overburden often has a great influence in the weathering of clay, the thicker the overburden the less the weathering of the clay. This factor is frequently overlooked. Some unweathered clays crack badly in drying and burning. Weathering apparently mellows them and increases their plasticity so that the tendency to crack is in many cases diminished or destroyed. If clay is being worked the fact should be kept in mind that the most weathered clay will be usually under the thinnest stripping or overburden.

Sometimes clay may be reduced rather than oxidized. Red glacial clay may be converted to dense blue clay ("hardpan") containing iron in ferrous condition by the reducing action of organic matter and pyrite contained therein, when the clay is deep and protected from the oxidizing action described above.[1]

Leaching occurs when the surface water seeping into the clay drains off at lower levels. The water contains small quantities of carbon dioxide and readily dissolves some minerals, particularly calcium carbonate (lime) in the form of bicarbonates. In many cases where calcareous clays occur, the upper layers of the deposit contain less lime than the lower layers, due to this solvent action of the surface water.

[1]E. Orton Jr. Am. Cer. Soc. Trans. V., p. 378, 1903.

For the same reason residual clays from limestone may contain little or no lime.

Softening of the clay occurs as the weathering process either disintegrates the deposit or leaches out some of the soluble constituents that may have served as bonding or cementing material. This is usually a beneficial action recognized by many maufacturers who spread the clay on the ground and allow it to weather for months or even years before using it.

Consolidation or the reverse of the softening effect just described, takes place in the formation of shale,[1] and in the formation of limonite crusts in the clay. These crusts may form only at a few points or along certain layers, or in all parts of the mass permeating the clay deposit with a network of rusty sandy chunks and strips which seriously interfere with digging the clay.

Concretions are formed in some deposits when limonite, or siderite (iron carbonate), collects around nuclei such as pebbles or grains of sand and grows into somewhat symmetrical lumps. If large, these concretions can be discarded in mining. Such concretions are most abundant in the weathered parts of the deposit and must not be confused with the lumps of pyrite of yellow color and metallic lustre found in some clay beds. Many calcareous clays are abundant in lime concretions. Drift clays also frequently contain lime concretions for the same reason. The lime pebbles found at random in many boulder clays of Michigan are frequently pieces of limestone rather than concretions. The lime pebbles found in a layer at the lower limit of weathering of a lake clay, as in the Detroit district, are good examples of lime concretions.

Dehydration occurs when clay or shale is transformed into slate or schist,[2] or by burning of adjacent coal seams,[3] or by igneous intrusions. The clay loses its combined water, and forms other minerals containing aluminum silicate (Al_2SiO_5) and silica (SiO_2) or is baked to a brick-like condition or to viscosity forming a slag-like mass.

[1] See "Shale" on page 23.

[2] F. W. Clarke, U. S. Geol. Surv. Bull. 330, p. 527, 1908.

[3] E. S. Bastin, Jour. Geology XIII, p. 408, 1905.
J. A. Allen, Proc. Bos. Soc. Nat. Hist., XVI, p. 246, 1874.
A. G. Leonard, N. Dak. Geol. Surv., 4th Bien. Rep., p. 79 1906.
Zirkel, Lehrbuch der Petrographie, III, p. 775, 1894.

Chapter II

PROSPECTING FOR CLAY

SURFACE INDICATION

The facts outlined in the first chapter concerning the occurrence of clay should be of much aid to the clay worker prospecting for clays, but the following more definite suggestions should be considered in locating and determining clay deposits.

Outcrops. These are the most frequent and important indication of clay beds. These exposures are found on inclined surfaces or where natural or artificial cuts have been made, such as washouts, stream or river valleys, road or railroad cuts. The newer the cut the better the exposure as the sides of such excavations wash down rapidly, the surface loam or sand frequently covering the clay so as to completely hide it from view.

Wells and Excavations. These are frequently sources of much valuable information, not only of the surface deposits but of the lower strata in the case of deep wells. In prospecting for clay over a rather large area or when the time does not permit for thorough work, outcrops along roads, rivers, and the information given by well diggers and local "old timers" are the most fruitful sources of information concerning the probable location of clay beds.

Springs. Springs issuing from the same level may indicate the upper surface of clay strata. Water seeps down from the surface until it reaches an impervious layer, such as clay, which is followed to the face of the bank, or hillside. However, the impervious layer may not be clay as cemented sand or dense silt may produce the same effect.

Ponds or Swamps. These may indicate a bed of clay for the same reason. And to a limited extent the character of vegetation may be used as a guide to the subsoil.

EXPLORATION OF DEPOSITS

Methods. If a deposit of clay has been located, its thickness, extent and character may be determined by a *thorough field examination.* The deposit should be carefully *sampled* for the *chemical* and *burning tests* to determine the possible uses and economic value of the clay. The thickness and extent of a deposit may be largely determined by a careful examination of all outcrops in gullies or cuts on the clay property. As most clay slopes wash down easily, it is generally necessary to dig ditches from top to bottom of the cut to uncover the undisturbed clay

beds. In most cases the cuts or gullies are not sufficiently close or deep, and additional means must be taken to determine the thickness at intermediate points. The only satisfactory method available is to make borings well into or through the deposit. A very satisfactory auger for this purpose may be readily and cheaply made by welding a 2 inch carpenters auger to a short length of ¾ inch pipe. By using a number of three or four foot sections of pipe which are screwed in as the depth of the hole increases, and a T joint to make a handle, the auger may be run down thirty feet or more by one man and to 100 feet by two men. If the clay is tough and plastic the auger must be pulled up and cleaned every few inches or it may become firmly imbedded in the clay. When working at depths of over 25 feet, it is advisable to employ some form of lever to aid in pulling the auger. A post-hole auger or digger may be satisfactory for limited depths.

If the clay is sandy and wet the hole washes in and fills up as soon as the auger is withdrawn. This may be checked by driving a pipe down the hole behind the auger.

From comparison of the data obtained from the bore-holes and outcrops, any vertical or horizontal variations in the deposit may be traced. Limonite concretions, weathering and dryness of the beds may be ascertained, as well as variations in thickness of the bed and overburden. Small samples for laboratory testing may be taken from the borings and the bottom of trenches on the outcrops.

For larger samples where boring is impractical, pits may be dug. The pits should be small, about 3 feet or less in diameter, and sunk as rapidly as possible to avoid caving in of the side walls. Such work must be done when the ground is dry, with sharp tools and by an expert, otherwise it is expensive, uncertain and dangerous.

The gross samples including all the material removed from such a pit should be crushed to lumps not over one and one-half inches in diameter, mixed on a heavy sail cloth about eight feet square, and reduced to 75 or 100 pounds by quartering.

If the deposit shows distinct differences in structure, color, or texture, each bed showing individual differences should be sampled separately if the beds are sufficiently thick to be mined separately.* In such cases the thickness of each bed shold be carefully noted and recorded on the sample tags as well as on the field report sheet to enable the laboratory to prepare a representative composite sample if necessary.

Usually a sample of at least 50 lbs. should be sent to the laboratory for testing, where it is further reduced by careful quartering. In some cases it may be necessary to reduce the sample to 10 or 20 pounds in the field, but such practice is not recommended.

*Bulletin 116 U. S. Bur. of Mines, Methods of Sampling Coal.
Report of Sub-Committee on Field Sampling of Clays—Comm. on Cer. Chem. Nat. Res. Council
Bull. No. 43 Iowa Eng. Exp. Sta. Practical Handling Iowa Clays.

The tentative method of the American Ceramic Society for sampling clay deposits recommends the following treatment to reduce the gross sample:

"After the gross sample has been collected in the case of unground material, it shall be systematically crushed, mixed, and reduced in quantity by quartering to convenient size for testing. The largest sizes of pieces allowable with various weights of samples are shown in the following table:

100 pounds plus	2.0	inches
100 pounds to 50 pounds	1.0	inches
50 pounds to 25 pounds	0.25	inches
25 pounds to 10 pounds	No. 4	sieve
10 pounds to 5 pounds	No. 10	sieve
5 pounds and under	No. 20	sieve

Quartering. The sample crushed to the required size shall be thoroughly mixed by coning and reconing on a clean surface. The cone shall be flattened and then marked into quarters by two lines which intersect at right angles directly under a point corresponding to the apex of the original cone. The diagonally opposite quarters shall then be removed and the space that they occupied brushed clean. The material remaining shall be successively crushed, mixed, coned, and quartered until the two opposite quarters equal the size necessary for testing."

The final samples should be placed in clean tightly woven strong sacks, and carefully and completely labeled by two tags, one placed within the sack and the other securely fastened to the outside. These labels should give the exact location, extent and depth of the deposit, the method of sampling, and should be signed by the man who took the samples, and numbered to correspond with the number of the field report.

Economic Factors. In addition to determining the thickness, extent and character of the clay beds several important points must be considered while in the field.

Overburden. The amount and character of the overburden determines the amount of stripping necessary to obtain the clay. If the clay is not of high grade it will not pay to remove much overburden unless the latter can be used. If the clay is plastic or "fat," sandy overburden is frequently mixed with the clay to improve its working qualities. This is done in many Michigan brick yards using the soft mud process, but care must be taken to prevent injury to the products by using pebbly, calcareous or otherwise unsuitable overburden.

Frequently the overburden may be used for filling, as in bringing the worked parts of the deposit up to grade. If the overburden is clean sand it can often be used in foundries or by building contractors. Inclusions of worthless clay in a bank of otherwise good clay must receive consideration similar to that given the overburden.

Drainage. Drainage facilities must be considered. If the deposit lies below the level of the surrounding country, drainage will be more of a problem than if the bed outcrops on a hillside. Even then springs may

be a source of trouble. In places the clay is underlain by a stratum of water bearing sand, which should not be penetrated. In some cases underlying sand is dry and may greatly aid drainage.

Transportation. Transportation facilities are of prime importance whether the clay is to be sold as such or to be worked up into a finished product at the deposit. Transportation is necessary to supply the fuel needed as well as to market the product. As the manufacturer of brick, tile, and particularly pottery, require labor of a kind not easily available, the labor supply is a very important consideration.

Markets. Demand for the product must not be taken for granted. The local conditions and probable demand for the product must be carefully considered. If the plant is well located on a railroad and is producing a high grade product the local market conditions are not so vital, as the product can then be shipped some distance whenever the local market fails. But ordinary common brick must be sold locally as it cannot be shipped any distance at a profit.

Size of Deposit. About six pounds of clay are required to make one standard 8¼ x 4 x 2½ inch brick, or one cubic yard of clay is required to make about 450 bricks. An acre foot of recoverable clay represents potentially about 700,000 brick.

A single unit of a modern soft mud brick plant has a daily capacity of 40,000 to 50,000 brick, requiring 2 acre feet a month.

A single unit modern stiff mud machine has a daily capacity of from 50,000 to over 200,000 brick a day.

Although many plants of smaller capacity than 50,000 brick a day are operating in Michigan at the present time, the greatest efficiency is obtainable only when the plant is properly balanced so that all units can work to capacity. For this reason small deposits of clay containing less than 200 acre feet of recoverable clay are not suitable for use by a modern brick factory. However, these small deposits may be and are worked profitably in small brick yards when the overhead or fixed charges are kept at the minimum.

Quality. The clay deposit should always be carefully determined, sampled, and tested by a competent engineer before any money is spent in erecting a plant or purchasing equipment. It is impossible to tell the quality or value of a clay by any simple field examination. This fact is particularly true of Michigan clays, which are of glacial origin and vary widely in properties within short distances. Many brick and tile plants have been erected in Michigan and operated at a steady loss because the properties of the clay were unknown or misjudged by an incompetent person. The appearance and "feel" of a clay are no criteria of its economic value unless supplemented by careful burning and physical tests.

Chapter III

CHEMICAL PROPERTIES OF CLAY

CHEMICAL COMPOUNDS

Of all the elements found in nature, carbon and sulphur are the only ones ever found in the uncombined or elemental state in clays. The others are found in combination with each other. Silicon (Si) unites with oxygen (O) to form silica, a compound which contains one atom of silicon and two atoms of oxygen and is designated by SiO_2. Likewise, two atoms of aluminum (Al) unite with three atoms of oxygen (O) to form alumina (Al_2O_3). Iron gives two oxides, ferrous oxide (FeO) and ferric oxide (Fe_2O_3). Aluminum, silicon, and oxygen unite to form aluminum silicate (Al_2SiO_7 or $Al_2O_3 . 2SiO_2$). This compound is called aluminum silicate and not silicon aluminate, because silica is more acid than alumina. The compound formed by calcium, aluminum and oxygen ($CaAl_2O_4$ or $CaO.Al_2O_3$) is called calcium aluminate because the alumina is more acid or less basic than the lime (CaO). Generally acids tend to unite with bases, if the conditions are favorable, forming compounds which possess different degrees of stability depending upon conditions.

Clays contain a great many different chemical compounds, each of which represents a mineral species possessing definite physical properties, which could be easily noted if the particles of clay were large enough. This is not the case, and it is necessary to use a microscope[1] to identify the various minerals in any clay.[2]

MINERALS IN CLAY

The statement is often made that clay is a hydrated aluminum silicate corresponding to the formula $Al_2O_3 . 2 SiO_2 . 2H_2O$ which corresponds to the mineral kaolinite. While many clays contain some kaolinite, others consisting almost entirely of silica, alumina, and water do not correspond to the formula of kaolinite.[3]

The number of different minerals present in clay is often large and depends partly on the mineralogical composition of the rock from which the clay was derived, and partly on the extent to which the minerals have been weathered or decomposed. The minerals are difficult to iden-

[1] H. G. Schurecht, J. Am. Cer. Soc., 5, p. 3 (1922) compares the minerals in English and American white clays determined by microscopic examination.
[2] For a complete description of minerals, see Dana, System of Mineralogy.
[3] See Halloysite and Pholerite on following pages.
Wheeler, Mo. Geol. Surv., XI, p. 186 (1896).
G. P. Merrill, Non-Metallic Minerals, p. 217 (1904).
H. Ries, Clay Occurrence, Properties, Uses, p. 40 (1908).

tify as they are very finely divided and surrounded by decomposition products.[1]

The more important of these minerals may be considered here.

Hydrous Aluminum Silicates. *Kaolinite* ($H_4Al_2Si_2O_9$ or $Al_2O_3.2SiO_2$ $2H_2O$) corresponds to a composition of silica (SiO_2) 46.6 per cent; alumina (Al_2O_3), 39.8 per cent; water (H_2O) 13.9 per cent. It is soluble in hot sulphuric acid and sodium carbonate. When wet it is slightly plastic. It is pearly white, and crystallizes in the monoclinic system in small hexagonal plates with a hardness of 2-2.5 (Moh's scale[2]) and a specific gravity of 2.2-2.6. Its index of refraction (1.56) is the same as that of the Canadian balsam,[3] and its optical behavior is very similar to that of muscovite so that it can be distinguished from colorless mica only by analysis to prove the absence of alkali.[4] When stained with methylene blue the crystals are lamellar and exhibit a zonal structure parallel to the edge.[5]

Kaolinite is always of secondary origin, in most cases probably derived from feldspar. Although chemically possible, its derivation from other minerals has never been proved.[6] It may be formed from feldspar according to the equation given on page 16 or as follows:[7]

$$2KAlSi_3O_8 + 2H_2O + CO_2 \rightarrow H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3$$

Pure kaolinite is very refractory but a small addition of impurity decreases its refractory properties.

Halloysite is closely related to kaolinite, having the same relative amounts of alumina and silica but a greater amount of water, and an amorphous structure. Halloysite is massive, like clay, has a conchoidal fracture, and shows little or no plasticity. Its hardness is 1 to 2 and specific gravity 2.0 to 2.20. Its color is white, frequently with a gray green, yellow or red cast, with a pearly luster to waxy dull. When placed in water it swells and falls to a powder[8]. It is translucent to opaque,

[1]Chamberlain & Salisbury, U. S. Geol. Surv., 6th Ann. Rept., p. 245.
Ladd, Am. Geol., XXIII, p. 240 (1899).
Buckley, Wis. Geol. and Nat. Hist. Surv., Bull. VII, Pt. I.
Merrill, Rocks, Rock-Weathering and Soils, p. 335.
DeLage and Lagatu, Ann. de l'ecole nat. d'agrie de Montpellier VI, p. 200-220 (1905).
Comptes rend. CXXXIX, p. 1044 (1904).
F. Steinriede, Anleit. sur. min. Bodenanalyse, Halle (1889).
Dumont, Compt. rend. CXL, p. 1111 (1905).
Tebier, Comp. rend. CVIII, p. 1071 (1889).
Cameron and Bell, Bur. Soils, Bull. 30, p. 111 (1905) and Bull. 22, p. 12 (1903).

[2]A scale of hardness with diamond 10, corundum 9, topaz 8, quartz 7, orthoclase 6, apatite 5, fluorite 4, calcite 3, gypsum 2, talc 1.

[3]Rosenbusch, Physiography of Rock Making Minerals, Translat. by Iddings, p. 320 (1889).

[4]H. Ries, Clay, p. 42, 1908.
Vogt, Tonindustrie, Zeit, p. 140, 1893, Compt. rend. Acad. Sci. Paris, CX, p. 1199, 1890 quoted in U. S. Geol. Surv. 19th Ann. Rept., Pt. VI, p. 20, 1898.
W. and D. Asch, The Silicates in Chem. and Commerce (Constable).

[5]Rieke, Sprechsaal, XL, p. 33.

[6]Rösler, Beiträge zur kenntniss der kaolin-lagerstätten Neues Jahrb. f. Min. Geol. u. Pal. XV Beilage-Band 2nd Heft Fiebelkom, Baumaterialienkunde, IV, p. 280.

[7]VanHise, Treatise on Metamorphism, p. 352.

[8]H. Ries, Clays, p. 49.

sometimes becoming even transparent in water with an increase to one-fifth in weight.[1]

Halloysite found in a deposit five miles southwest of Aurora, Mo., and somewhat stained by yellow clay fused completely at cone 15 (2600°F) and has the following composition:

Silica (SiO_2)	44.12%
Alumina (Al_2O_3)	37.02
Ferric Oxide (Fe_2O_3)	.33
Lime (CaO)	.19
Alkalies (Na_2O K_2O)	.24
Water (H_2O)	18.48
	100.38

which agrees closely with the theoretical composition as given.[2]

Indianite[3] is found as a whitish clay with a composition very similar to Halloysite.[4]

Pholerite, a pure white pearly substance occurring in small hexagonal scales, soft and pliable to the touch, adherent to the tongue, and forming a plastic mass with water, has the composition Silica 39.3 per cent, Alumina 45 per cent, Water 15.7 per cent, which corresponds to $H_8Al_4Si_3O_{10}$ or $2Al_2O_3 . 3SiO_2 . 4H_2O$.[5]

Allophane occurs as thin incrustations with mammillary surface, amorphous with somewhat conchoidal fracture, shining to earthy. It is very brittle of variable translucent color. Hardness 3 and Sp. Gr. 1.85 to 1.89. Its composition is Silica 23.8 per cent, Alumina 40.5 per cent, Water 35.7 per cent corresponding to $H_{10}Al_2SiO_{10}$ or $Al_2O_3.SiO_2$ $5H_2O$.

Rectorite ($H_2Al_2Si_2O_8$ or Al_2O_3 $2SiO_2$ H_2O) is monoclinic in leaves or plates, soft, soapy, to the touch, with pearly luster and pure white in color.[6]

Newtonite ($H_{10}Al_2$ Si_2 O_{12} or $Al_2O_3 . 2SiO_2$ $5H_2O$) rhombohedral in soft compact masses, resembles kaolinite and is white in color.[6]

[1]A. B. Searle, Chem. and Physics of Clays, p. 412.

[2]Wheeler, Mo. Geol. Surv. XI, p. 186, 1896.
cf. H. Ries, Clays, loc. cit.

[3]Placed under Halloysite by Dana, Sys. of Min., p. 688, 1892.
Called Allophane in Ind. Geol. Survey, 29th Ann. Rept.

[4]Ky. Geol. Surv. Bull. 6, p. 50 (1905).
Ries, Clays.

[5]Guillemir, Ann. des. Mines XI, p. 489 (1825).
I. L. Smith, Am. J. Sci. ii XI, p. 58 (1859).
A. Knop, Neues, Jahrb. Minn. (1859).
Johnson & Blake, Am. J. Sci. XLIII, p. 361 (1867).
L. L. Koninck, Zeit. f. Kryst. u. Min. II, p. 661.
Wheeler, Mo. Geol. Surv. XI, p. 50 (1897).
Cook, N. J. Geol. Surv. (1878).
Greaves-Walker, Am. Cer. Soc. XIII, p. 297 (1906).
Ries, Clays, John Wiley & Sons.

[6]Brackett and Williams, Am. J. Sci. XLII, p. 16 (1891).

Cimolite $2Al_2O_3\ 9SiO_2\ 3H_2O$ + aq.
Montmorillonite $Al_2O_3\ 4SiO_2\ H_2O$ + aq.
Pyrophyllite $Al_2O_3\ 2\ SiO_2\ H_2O$.
Collyrite $2Al_2O_3\ SiO_2\ 9\ H_2O$.
Schrotterite $8Al_2O_3\ 3SiO_2\ 3H_2O$.[1]

The combined water in these minerals does not evaporate on drying, but is driven off as steam only at relatively high temperatures usually about 650-750°C.

LeChatelier suggests that if a small quantity of clay is rapidly heated,[2] at the moment of dehydration a retardation in the rise of temperature occurs due to the heat absorbed by the dehyration, and the temperature of this retardation may be used to establish a distinction between the various hydrated aluminum silicates. He found the following possessing distinctly different retardations:

Kaolinite ($H_4Al_2\ Si_2\ O_8$ or $Al_2O_3\ 2SiO_2\ 2H_2O$) retardation about 770°C and a slight acceleration about 1000°C.[3]

Halloysite ($Al_2O_3\ 2SiO_2\ 2H_2O$ + aq) retardation between 150° and 200C., and at 700C. followed by sudden acceleration at 1000°C.

Allophane ($Al_2O_3\ SiO_2$ + aq) retardation between 150° and 200°C and acceleration at 100°C.

Pyrophyllite ($Al_2O_3\ 4\ SiO_2\ H_2O$) retardation at 700°C and a less distinct retardation at 850°C.

Montmorillonite ($Al_2O_3\ 4SiO_2\ H_2O$ + aq) retardation at 200°C, 770°C and another less distinct at 950°C.

From X-ray analysis of Kaolin[4] it has been shown that kaolinite dried at 100°C is crystalline but that this crystalline structure is almost completely lost when the kaolinite is calcined at 700°C and is transformed into another crystalline structure at 900°-1000°C.

Minerals other than Hydrous Aluminum Silicates. *Quartz,* chemically silica (SiO_2), usually constitutes a large part of the sandy material and is found in nearly every clay; from less than one per cent in kaolins to 60 per cent in some sandy clays, usually in grains of microscopic size, which are translucent or transparent. If the clay is residual the grains are angular. In sedimentary clays the grains have been rounded by being rolled and ground while washed along the stream or by waves on the beach before being deposited in quiet water. Quartz has a hardness of 7 and is harder than glass, which varies from 4.5 to 6.50. It is non-

[1]Dana, System of Mineralogy.

[2]Comp. rend. CIV p. 1443 (1887).
Ding. polyt. J. CCLXV, p. 94 (1887).
Cf. A. Bigot. Compt. render., 176 p. 91-93 (1923).

[3]S. Satoh, J. Am. Cer. Soc. 4 p. 182, 1921, found that kaolinite from Japan lost weight very rapidly at 460°C.; exhibited a change in microstructure at 600°C., an exothermic reaction (acceleration of heating curve) between 900-1000°C., and between 1250-1300°C., and at 1400°C. when Sillimanite or some other compound began to develop.

[4]Bragg, Shearer & Mellor, Trans. Ceram. Soc. 22, p. 105, 110 (1922-23).

plastic and has a high, rather erratic expansion on firing. If very finely divided it may aid in the chemical union between the various minerals in clay but not so if present in large particles.

Flint or Chert is the name given to nodular masses of amorphous silica found in some clays.

Both quartz and flint are highly refractory when pure, softening at about 1800°C (cone 35).

Feldspar may be as abundant in clay as quartz, but as it decomposes so easily the grains are usually smaller. When undecomposed the grains have a bright luster, and split off with flat surfaces or cleavages.

The different species of feldspar vary in composition as follows:

	Formula.	Chemical Composition.				
		SiO_2	Al_2O_3	K_2O	Na_2O	CaO
Orthoclase (microline)	KAl Si_3O_8	64.7%	18.4%	16.9%	.....	.....
Albite	Na Al Si_3O_8	68	20	.....	12%	.....
Oligoclase	(Mixtures of Albite	62	24	.....	9	5%
Labradorite	and Anorthite)	53	30	.....	4	13
Anorthite	Ca Al_2 Si_2O_8	43	37	.....	.....	20

Feldspar is slightly softer than glass.

The fusing point of pure feldspar is about cone 9 (1310°C) but the different species vary somewhat, those containing CaO and Na_2O fusing at lower temperatures.[1] For this reason feldspar is used by potters to form vitrified ware at low temperatures.

Mica exists in a number of species of rather complex composition, all aluminum silicates with other bases.

Muscovite (white mica) SiO_2 45.2% Al_2O_3 38.5% K_2O 11.8% H_2O 4.5%, corresponding to $H_3KAl_3\ (SiO_4)_3$ occurs in flakes which fuse at about cone 12. When finely ground it appears to vitrify the clay body as low as cone 4 but in larger particles not until cone 8 or 10.[2]

Biotite (black mica) (H_2O or K_2O) . 2(MgO or FeO) (Al_2O_3 or Fe_2O_3) . $3SiO_2$.

Muscovite is more abundant in clay because it is less readily attacked by weathering agents.

Mica can be easily recognized by its thin scaly particles which are very bright and conspicuous even when small. Mica is present in nearly all clays even when washed because the light scales float off with the clay particles.

Lepidolite (KLi[Al.2 (OH, Fl)] Al $(SiO_3)_3$ occurs in some clays.[3]

[1]Seger, Ges. Schrift, p. 413.

[2]Trans. Am. Cer. Soc. IV p. 255.
N. J. Geol. Surv., VI, p. 68 (1904).

[3]N. W. Lord, Am. Inst. Min. Eng. Trans., XII, p. 505.

Iron is present in clays in a series of compounds that serve as ores of iron when found in sufficiently concentrated form.

Limonite has the same composition as iron rust Fe_2O_3 85.5%, H_2O 14.5% ($2Fe_2O_3 3H_2O$). Hardness 5.5, Sp. Gr. about 3.8. When evenly distributed through the clay, in places forming a film on the surface of the clay grains, limonite gives a yellow or brown color to the deposit. Sometimes it collects in small rusty grains, or forms concretions of spherical or irregular shape. In other clays it is found as stringers or crusts extending throughout the beds.

Limonite is most abundant in surface clays, especially if porous or sandy, so the oxidizing surface water may seep in easily. It is frequently found in weathered outcrops of many shales.[1]

Hematite, the red oxide of iron (Fe_2O_3) is present in some clays but readily changes to limonite when exposed to the air and moisture. Its hardness is 6 and its specific gravity about 5.2.

Magnetite (Fe_3O_4 or $FeO.Fe_2O_3$), the black magnetic oxide of iron, is sometimes found in clay. Its hardness is 6, sp. gr. about 5.1 and it is soluble in concentrated hydrochloric acid. Like hematite it changes to limonite.

Siderite, iron carbonate ($FeCO_3$ corresponding to FeO, 62.1% CO_2 37.9%) occurs in clay in a number of forms. If finely divided and evenly distributed through the clay or covering the other minerals as a film, it may give the bed a blue or slate-gray color. It occurs as concretions (clay-ironstones) ranging in size from a fraction of an inch to several feet in diameter, usually in more or less discontinuous beds parallel with the stratification of the clay; and as crystalline grains scattered through the clay. Its hardness is 3.5 to 4 and its specific gravity about 3.8.

Siderite may be present in surface clays but is generally more important in shales, as it weathers to limonite.

Pyrite, isometric form of iron sulphide, (FeS_2 corresponding to Fe 46.6%, S 53.4%) has a yellow metallic luster and occurs in some clays and many shales[2] in large lumps, small grains, or in flat rosette shapes. It is frequently found with lignite, the carbonaceous matter having reduced iron sulphate to the sulphide. Its hardness is 6 to 6½ and its specific gravity about 5. Pyrite weathers readily to the sulphate and then to limonite.

Marcasite is the orthorhombic form of FeS_2 and may be present in some clays.

Calcite, lime or calcium carbonate ($CaCO_3$, corresponding to CaO 56%, CO_2 44%) occurs in large amounts chiefly in recently formed clay, but is present in considerable quantities in some shales. It has a hardness of 3 and a specific gravity of about 2.72. It is generally colorless, white or amber with a vitreous or glassy luster. It dissolves rapidly in weak acids and may be easily detected, as hydrochloric acid or even vinegar causes it to effervesce violently. It occurs evenly distributed throughout the clay, or as concretions. Many of the lake and glacial clays of Michigan contain large amounts of calcium carbonate and limestone pebbles.

[1]Antrim Shale, as found at Walloon Lake is rusty in appearance due to formation of limonite from iron contained in the shale.

[2]The Antrim shale in many places as at Norwood shows nodules of pyrite.

Aragonite, an isomorphous calcium carbonate ($CaCO_3$) of hardness 3½ and specific gravity about 2.9 may be found in clays. Aside from these properties, it is similar to calcite.

Dolomite, calcium magnesium carbonate, ($CaMg(CO_3)_2$ or CaO 30.4%, MgO 21.7%, CO_2 47.8%. Hardness 3.5 to 4 Sp. Gr. about 2.8, and *Magnesite,* magnesium carbonate, $MgCO_3$ or MgO 47.6%, CO_2 52.4%. Hardness 4 to 5.5, Sp. Gr. about 3.1 are soft minerals resembling calcite but effervesce much more slowly with cold dilute acid.

Gypsum, hydrated calcium sulphate ($CaSO_4$, $2H_2O$ or CaO 32.6%; SO_3 46.5%; H_2O 20.9%) is found occasionally in large quantities, in a finely divided state or as crystals, plates, or fibrous masses of selenite. It is soft (hardness of 2) with a pearly luster and transparent.

Rutile, titanium oxide (TiO_2) may be generally present in clays as titanium is usually found when the proper tests are made in analyzing clays. It has a hardness of 6 to 6½, specific gravity of about 4.2, is red, brown red, or black in color and occurs mostly as bristle-like crystals.[1]

Ilmenite, iron and titanium oxide ($Ti_2Fe_2O_6$) may be present in a partly altered condition.

Glauconite, a hydrous potassium and iron silicate of variable composition is found in some clays.[2]

Hornblende and Garnet are complex silicates that may be present in many clays. The grains are of microscopic size, and they weather readily. The iron in them oxidizes and gives a deep red color to clays.

Vanadiates have been found in German clays.[3] If the vanadiates are soluble they will produce a green discoloration on the surface of the burned ware, which can be washed off with water but will return so long as any of the salt is present. They may be made insoluble by burning the clay to a point of vitrification.[4]

The following minerals may also be present in clay:

Sillimanite ($Al_2O_3 SiO_2$) and andalusite and cyanite of the same composition.

[1]H. Ries, Clays, etc., loc. cit.
J. J. H. Teall, Min. Mag. III, 201.
G. E. Ladd, Am. Geol., XXIII, 240, 1899.

[2]N. J. Geol. Surv. Fin. Rept. VI, p. 46, 1904.
Md. Geol. Surv. Eocene, p. 52, 1901.

[3]Seger, Ges. Schrift, p. 301.
Tonindus-Zeit, No. 46, p. 53 (1877).

[4]Seger, ibid.
Mellor, Clay and Pottery Industries, Chas. Griffin & Co., 1914.

Tourmaline, a complex silicate, $(Li_2Na_2Fe\,Mg\,etc.)_9\,Al_6\,B_4\,(OH)_4\,Si_8O_{38}$.

Wavellite $Al_6\,(OH)_6\,(PO_4)_4\,9H_2O$.[1]

Nontronite, the iron equivalent of kaolinite, $(Fe_2O_3\,.2SiO_2\,.\,2H_2O)$ weathers readily.[2]

Vivianite, iron phosphate ($Fe_2P_2O_8\,.\,8H_2O$, or FeO, 43%, P_2O_5 28.3%, H_2O 28.7%).[3]

Manganese oxides and rare elements[4] are occasionally found in clays.

CHEMICAL COMPOSITION OF CLAY

Chemical Compounds. Although the various elements are present in clay in different combinations as listed above, for practical purposes the ultimate chemical analysis of clays determines all the elements as their simple oxides. If calcite or calcium carbonate ($CaCO_3$) were present, it would be reported as lime (CaO) and carbon dioxide (CO_2) with the percentage of each given separately. Thus the ultimate analysis does not report the minerals present but simply the metals as oxides and is expressed:

Silica (SiO_2)
Alumina (Al_2O_3)
Ferric Oxide (Fe_2O_3)
Ferrous Oxide (FeO)
Lime (CaO)
Magnesia (MgO)
Alkalies { Potash (K_2O) / Soda (Na_2O) }
Titania (TiO_2)
Sulphur trioxide (SO_3)
Carbon dioxide (CO_2)
Organic matter
Water (H_2O)

Analyses. In most analyses the first eight are determined, except that all the iron is reported as ferric oxide (Fe_2O_3) and frequently the potash and soda are reported as combined alkalies. The last four may be reported collectively as "loss on ignition" as they are volatile at red heat. In the majority of "dry" clays[5] this loss on ignition is chiefly moisture, and some chemically combined water. In order to eliminate the variable

[1]G. W. Stose, U. S. Geol. Surv. Bull. 315, p. 474 (1907).
Ann. Rept. Pa. State College, 1889-1900, Appendix 3, p. 13.
[2]Weinschenk, Zeitschr. Kryst. u. Min. XXVIII, p. 150 (1897).
[3]Md. Geol. Surv. IV 228 (1902).
[4]H. Ries, Clays, etc., l. c.
J. R. Strohecker, J. Prakt., Chem. (2) XXXIII, p. 132.
Deutsch. Topf. u. Zieg. Zeit. 1880, p. 367; 1881, p. 387.
[5]Dried at 105°C. until weight is constant.

of moisture in clay all analyses should be made on a moisture-free or "dry" sample. Reporting the iron as Fe_2O_3 is in many ways misleading as the iron is usually present as ferrous oxide, carbonate or sulphide, and as Fe_2O_3 in weathered clays only. For this reason, many analyses in which the iron is reported as Fe_2O_3 total to over 100%.

Ultimate Analysis. Much has been said for and against the usefulness of the ultimate analysis of a clay to be used for burned clay ware. While an ultimate analysis is of value for particular and scientific work, the easiest, simplest, most accurate method of determining the physical properties of a clay, is by a direct actual test. For the manufacture of Portland cement the ultimate analysis of clay is of prime importance and the burning tests may frequently be omitted.

It is advisable and of advantage to have available the data of both chemical analysis and burning tests whenever clay is to be carefully or completely appraised, but the only safe way to determine the burning and physical properties is by actual test.

Clays vary widely in composition, sometimes even in the same deposit.

Rational Analysis. The "rational" analysis is an attempt to determine the amount of the different mineral compounds present in the clay, and to give a better conception of the true character of the clay. Most high grade clays and kaolins consist chiefly of some hydrous aluminum silicate such as kaolinite, quartz, and feldspar with some mica. If these three minerals are determined as such in different kaolins, the manufacturer can better ascertain how much quartz and feldspar should be added to each different kaolin to give the final mixtures similar properties. A rational analysis is useful only in connection with such mixtures of the high grade clays.

Frequently the rational composition of a clay may be calculated from the ultimate analysis about as well as it can be determined by a rational analysis as conducted by the present unsatisfactory methods.[1] This fact led Buckley[2] and others to compute the rational composition from the ultimate analysis. This was done by assuming that all the soda and potash were present in the feldspar, the alumina not necessary for the feldspar was present in the clay substance taken as kaolinite and any silica left over from the feldspar and kaolinite was present as quartz in other silicates. Sometimes there is not enough silica to go around when this method is used. Some of the alkali from about 0.08 to 0.25 per cent of the clay, is almost certain to be present as absorbed soluble sals.[3]

[1]Ries, Am. Inst. Min. Eng. Trans. XXVIII, p. 160 (1899).
Mellor, Clay and Pottery Industries, I, p. 109.
Zschokke, Baumaterialienkunde, VII, 165 (1902).
Henry S. Washington, J. Am. Cer. Soc. I p. 405 (1918).
[2]Wis. Geol. and Nat. Hist. Surv. Bull. 7, Pt. I, p. 267, 1901.
[3]Binns, Trans. Am. Cer. Soc. VIII, p. 198 (1906).

Such a computed rational composition has been called a "recalculated analysis."[1]

A rather elaborate method of rational analysis is given by Zschokke.[2]

MINERAL COMPOUNDS AND THEIR INFLUENCE ON CLAY

Silica is present in many different forms, uncombined, and combined with other more basic oxides. Free silica may be present as insoluble quartz or other crystalline form and as amorphous, hydrated, or colloidal silica. The insoluble sand, quartz, and silicates other than hydrated aluminum silicates, may vary from 5 per cent to over 70 per cent in different clays.[3] The total silica may vary from 32 to over 95 per cent.[4]

Free silica particularly quartz of all gradations of size is very common in clay. The insoluble silicates (those other than the hydrous aluminum silicates) are sandy or silty in character and have an effect on plasticity and shrinkage similar to that of quartz.

Sand (quartz and silicates) greatly diminishes the plasticity, tensile strength, and shrinkage of clays. The effect being more pronounced the coarser the sand. For this reason sand or loam is added to brick clay and ground flint to pottery clay.[5]

A very sandy clay will have a low fire shrinkage so long as none of the sand grains fuse; but when fusion begins (usually by forming a solution with other compounds) a shrinkage takes place.

Hydrous Silica (H_2SiO_3 or $SiO_2 \cdot H_2O$)[6] may be present with uncertain amounts of H_2O in some clays. W. H. Zimmer[7] found a kaolin 99.9 per cent soluble in sulphuric acid with the composition,

Silica (SiO_2)	57.00%
Alumina (Al_2O_3)	24.85%
Ferric Oxide (Fe_2O_3)	.25%
Lime (CaO)	.05%
Water (H_2O)	17.81%

The large amount of soluble silica leads to the conclusion that some free hydrated silica must be present. He found that free hydrated silicic acid, if present in quantity,

1. Increased the translucency
2. Improved the color
3. Increased the shrinkage

[1]A. B. Searle, Chem. and Physics of Clays, Ernest Benn, London, 1924, page 410.

[2]Baumaterialienkunde, VII, p. 165 (1902), abstracted in Ries, Clays, p. 71.

[3]Mo. Geol. Surv., Vol. XI, p. 54.
Ala. Geol. Surv. Bull. 6 (1900).
N. C. Geol. Surv. Bull. 13, p. 24 (1898).

[4]H. Ries N. Y. State Museum Bull. No. 35, p. 525.

[5]F. Krage, Tonindus, Zeit. XXXII No. 67, p. 934 (1908).

[6]See Fuller's earth. Page 166,

[7]Trans. Am. Cer. Soc., III p. 25 (1901).

4. Lowered the temperature of vitrification
5. Tended to make the clay warp on drying
6. Formed a hard coating on the ware due to deposition of H_2SiO_3 from the water.

Iron Oxides are very common in clay. They may be present in the free state, combined with silica, or they may be derived from carbonates (siderite), sulphates (milanterite), or sulphides (pyrite).

The free simple oxides are well prepared to enter into chemical combination with other elements in the clay when fusion begins. The sulphides and carbonates have to be decomposed, and the sulphur dioxide and carbon dioxide driven off before the simple iron oxides are formed. The silicates containing iron are complex and fuse at relatively low temperatures. Several of these silicates are easily weathered, the iron forming limonite.

The amount of ferric oxide (Fe_2O_3) may vary from a trace to over 30 per cent in clays.

Iron is the great coloring agent of both burned and unburned clays. In unburned clay, the yellow or brown color is due to the presence of limonite, the red color due to hematite; siderite or pyrite may be the cause of a blue or gray color, and iron silicate (especially glauconite) may give the clay a green color. The intensity of color is not always a true indication of the amount of iron in the clay. Organic or carbonaceous material may mask the color entirely. A coarse sandy clay shows a deeper color than a fine grained clay. For effective coloring the iron must be finely divided and evenly distributed, such as limonite in an amphorous or noncrystalline form which simply coats the surface of the grains.

In burned clay all of the iron ores will change to the red ferric oxide (hematite) if a sufficient supply of oxygen can enter thru the pores of the clay before it becomes vitrified. As vitrification takes place the iron slags with the silicates forming complex silicates, which are much darker in color running through a good brick red to a dark chocolate brown or reddish purple if the clay contains enough iron to be red burning. If the clay burns buff the silicates usually take on a greenish color as the clay vitrifies. The color produced by the iron depends on the amount of iron in the clay, the temperature of burning, the condition of the iron oxide, the condition of the kiln atmosphere, and other compounds present in the clay.

Usually 1 to 2 per cent of iron oxide imparts a yellow tint which is deepened to buff by 3 or 4 per cent and a full red by 5 to 8 per cent. However, the color of the burned clay is not influenced solely by the quantity of iron present and these limits frequently have to be increased

in Michigan clays containing large amounts of lime which reduces the coloring effects of the iron.[1]

The evenness of color is closely connected with the physical condition of the iron oxide, the colloidal oxide giving a uniformity of shade not obtained by adding very finely ground material.

The brilliancy of color depends somewhat upon the texture of the clay. The more sandy clays can be heated to higher temperatures without destroying the red color, than the more aluminous clays. Alkalies also seem to diminish the brilliancy of the iron coloration.[2]

Iron may exist as the ferrous oxide (FeO) or as ferric oxide (Fe_2O_3) during burning of the clay until the iron oxides combine with the other oxides present. The ferrous oxide is readily oxidized to the ferric condition when the clay is burned if the necessary oxygen is available. If carbon or sulphur are present this oxidation cannot take place, in fact these elements are reducing agents and reduce the ferric oxide to the ferrous oxide.[3] If the iron is not completely oxidized to the ferric condition, because of the presence of reducing agents, or because there is not enough oxygen in the gases in the kiln, or because the clay has become so dense as to prevent free circulation of the oxygen through it, the ferrous oxide may form ferrous silicates which impart a black or very dark color to the clay. The dark ferrous silicate cores or "black hearts" of improperly oxidized clay are formed in this way. If swelling accompanies the formation of this black core it may be due to sulphur.[4]

Iron sulphide (pyrite FeS_2) loses half of its sulphur at a red head (400°C).

$$FeS_2 \rightarrow FeS + S$$

In air the sulphur burns to sulphur dioxide (SO_2) but when liberated within the clay it may take the oxygen from ferric oxide forming ferrous oxide and sulphur dioxide. If exposed to oxidizing conditions the pyrite may be oxidized to ferrous sulphate which breaks down on further heating (550-650°C) to ferrous oxide.

Fine grained clays are difficult to oxidize because the small size of their pores prevent the circulation of the oxygen. Grog (ground burned clay) is often added to open the pores for this reason.

As the oxidation of the iron is dependent on the quantity of oxygen it receives during burning, the composition of the gases in the kiln is of great importance. If carbon monoxide is present the iron is reduced from the ferric to the ferrous condition as the carbon monoxide is oxidized to carbon dioxide, according to the equation,

[1]Seger's Collected Writings, Part I, p. 109.
Orton, Trans. Am. Cer. Soc., V., p. 380 (1903).
[2]Ries. N. Y. State Mees. Bull. 35, p. 515 (1900).
Orton, Trans. Am. Cer. Soc. V., p. 414 (1903).
[3]Orton, Trans. Am. Cer. Soc. V., p. 378 (1903).
[4]Orton and Staley, Third Rept. of Com. on Tech. Invest. 1908.

$$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$$

and the gases or fire is said to be reducing. If the gases contain an excess of oxygen so that ferric oxides are formed, the fire is said to be oxidizing. These conditions are often used to produce certain shades or colors in the ware. The beautiful shades of flashed brick are produced by having a *reducing* atmosphere in the kiln followed by an *oxidizing* atmosphere. The potter reduces the yellow tint in white ware by cooling the kiln as quickly as possible to prevent the iron from oxidizing.

Iron oxide is considered a fluxing impurity because it lowers the fusion point of clay. This effect is more pronounced if the iron is in a ferrous condition.[1]

Refractory clays have a low content of iron, averaging about 1.3 per cent ferric oxide, but not exceeding 3 per cent. Brick clays which are usually easily fusible contain from 3 to 7 or 8 per cent of iron oxide.

Calcium or Lime is present in many clays. In Michigan clays it is generally present in considerable and often in large quantities except near the surface where leached out by percolating waters. Such clays are usually classed as low grade. Lime may be present in any of a large number of minerals, all of which are included in the following groups:

1. Carbonates, calcite or dolomite
2. Silicates, feldspar and garnet
3. Sulphate, gypsum

Calcium carbonate is probably the most important form of lime. When present in a finely divided state it slags readily with the silicates in the clay and causes the clay to become viscous and soften or fuse at lower temperatures. For that reason it is called an active fluxing agent. In burning clays containing calcium carbonate carbon dioxide, (CO_2) is given off between 600°C and 900°C (probably most of it between 850°C and 900°C)[2] according to the reaction

$$CaCO_3 \rightarrow CaO + CO_2.$$

Driving off the carbon dioxide in addition to the chemically combined water, which passes off between 450°C and 700°C, leaves calcareous clays more porous than other clays up to the beginning of fusion.

If the burning is carried only to temperatures high enough to drive off the carbon dioxide (about 900°C) the quicklime (CaO) will absorb moisture from the air and slake. This may not be injurious if the lime

[1]Wheeler, Mo. Geol. Survey, l. c.
Ries, Clay, l. c.
Purdy and DeWolf, Ill. Geol. Surv. Bull. IV, p. 158 (1907).
[2]Bourry, Treatise on Ceramic Industries, p. 103.
Kennedy, Trans. Am. Cer. Society, IV, p. 146 (1902).
Bleininger and Emley, Trans. Am. Cer. Soc. XIII, p. 618 (1911) give 880°C.
Montgomery and Graves, Ibid. XVIII, p. 214 (1916) give 2.35 % per hour at 620°C. if atmosphere contains only small amounts of CO_2.

is finely divided and evenly distributed, but if present in lumps the swelling accompanying the slaking may split the brick. These "limepops" are a frequent source of trouble, generally caused by lumps or pebbles of limestone in the clays. If the burning temperature is raised much higher (900° to 1300°C, depending on the purity of the lime) the lime begins to slag with the iron, silica, and alumina of the clay forming silicates of very complex composition; or if present in lumps, becomes dead burned. In these conditions the lime is practically inactive with moisture and causes no injury by slaking.[1]

The state brickyard at Onondaga, Mich., makes a good brick from clay containing lime and lime pebbles. By fine grinding of the clay and giving the brick a soaking heat at a sufficiently high temperature "limepops" are practically eliminated. As this practice demands careful burning, which is impossible in the scove kilns, it is not of universal application.

In forming the complex silicate the lime unites with the iron and tends to destroy the red color caused by the iron, resulting in a buff color very similar to that produced in clays of low iron content. This bleaching action, if it may be so called, is most marked when the percentage of lime (CaO) is three times that of the iron oxide (Fe_2O_3).

Another very important effect of lime, if present in sufficient quantity, is to cause the clay to soften very rapidly, so that the clay becomes viscous at a temperature very near that at which it is hard burned. This rapid softening of calcareous clays is a very serious objection to their use, particularly for the manufacture of hard burned and vitrified products. Magnesia tends to counteract this, and quartz and feldspar have also been found to increase the temperature range between incipient vitrification and viscosity.[2] Many calcareous Michigan clays have a very narrow burning range, some not more than 50°C between incipient vitrification (hard burned) and viscosity.

Rieke[3] made very extensive tests of the effect of calcium carbonate and concluded that lime (1) decreases skrinkage, while magnesia increases shrinkage, that it (2) increases the porosity of the burned samples, if heated high enough to dispel the carbon dioxide and that (3) only the clays containing less than 10 per cent calcium carbonate (6 per cent CaO) burn to a dense body much below the fusion temperature, as a higher percentage brings the temperature of vitrification and viscosity close together.

Binns and Coates[4] concluded that lime particles large enough to be rejected by 12 mesh are objectionable even in small quantities, those

[1]Zimmerman, Tonind. Ztg., 44, p. 993 (1920).
[2]H. Seger, Collected Writings, Vol. I, p. 336.
[3]Uber die Einwirkung von Marmor auf Kaolin, Sprechsaal, XXXIX, No. 38 (1906).
[4]Am. Cer. Soc. XIV, p. 218 (1912).

passing 20 mesh are admissible up to 3% and those passing 36 mesh may be as high as 12%.

Lime-bearing silicates have much less pronounced effect than the carbonates. No volatile matter is given off to affect greatly the porosity and they do not cause a rapid softening of the clay although they are fluxing agents.

Gypsum, hydrated calcium sulphate, may have been formed from calcium carbonate by the action of sulphuric acid formed in decomposition of pyrite. Few clays contain large amounts of gypsum. Its properties are different from calcium carbonate. Mixed with clay, gypsum is completely dehydrated by about 1000°C,[1] and decomposed giving off most if not all of the sulphur trioxide (SO_3) by 1200°C.[2] The presence of silica appears to aid this decomposition giving off sulphur trioxide which may cause some of the swelling or blistering noticed in some wares after burning.[3]

Although lime (CaO) may be present in any amount up to 40 per cent, it does not usually exceed, 15 to 17 per cent in brick clays, 10 per cent in pottery clays, 1.6 per cent in fire-clays, or 2.5 per cent in kaolins.

Magnesia (MgO) is present in clays, usually less than 1.5 per cent in other parts of the country. Surface clays in Michigan frequently contain from 3 to 7 per cent of magnesia as do some of the shales. Magnesia may be present in silicates, carbonates, or as sulphate.

In most clays the silicates such as biotite (black mica), hornblende (chlorite and pyroxene) probably supply most of the magnesia. These minerals are scaly, of complex composition, containing from 15 to 25 per cent of magnesia, and decompose readily. Dolomite, the double carbonate of calcium and magnesium, is present in some clays and is a source of magnesia. Magnesium sulphate (Epsom salts) may be present in a few clays, and may form a white coating on the clay during weathering or drying. This is more likely to occur, if the clay contains pyrite (FeS_2) as the sulphuric acid formed by the decomposition of the pyrite may form magnesium sulphate from the carbonate.

On heating, both magnesium carbonate and dolomite lose carbon dioxide (CO_2). This decomposition is complete at 600°C, leaving Magnesia (MgO). Brill[4] found that magnesium carbonate ($MgCO_3$) loses carbon dioxide at 255°, 295°, 325°, 340°, 380°, 405°, and 510°C. Each point may show the successive formation and decomposition of a basic carbonate.

[1]Montgomery and Groves, Trans. Am. Cer. Soc. XVIII, p. 214-222 (1916), find that pure gypsum ($CaSO_4 \cdot 2H_2O$) is completely dehydrated by four hours heating at 105°C.
[2]Ries, N. J. Geol. Surv. VI, p. 63, 1904.
[3]H. E. Kramm, Trans. Am. Cer. Soc. XIII, p. 689, 1911, claims that the sulphur is all driven off at 1000°C.
[4]Zeit. Anorg. Chem. XLV, p. 277 (1905).

Magnesia has an effect upon the burning of clay that is quite different from that of calcium. Magnesia increases the shrinkage particularly at the higher temperatures, lowers the fusion temperature, but not to the degree that lime does, and, contrary to calcium, magnesia makes the clay soften slowly with a wider burning range (giving a hard burned product over a wider temperature range[1]). Magnesian clays can be made into wares of extreme length and very thin walls, which can be nearly vitrified without warping.[2] This influence of magnesia is greater in clays containing a number of active fluxing agents which vitrify at lower temperatures, than in refractory clays,[3] and is probably due to the fact that magnesia forms viscous silicates that react slowly, while lime forms fluid and corrosive silicates which rapidly attack the other particles causing rapid fusion of the ware.[4] Magnesia is not so strong as lime in masking or bleaching the red color due to iron oxide.

Magnesia may be present up to 7 or 8 per cent in brick clays, 5 or 6 per cent in pottery clays and fire clays, and about 2.5 per cent in kaolins.

The *alkalies* present in clays include *potash* (K_2O), *soda* (Na_2O), and *ammonia* (NH_3). The others are of rare occurrence.

Ammonia is present in some raw clays and exerts some effect on the physical structure, but it volatilizes easily and therefore has no influence on the burning properties.

Several common minerals may serve as sources of alkalies, particularly feldspar, muscovite (white mica) and glauconite; all complex silicates,[5] each with a fixed melting point. The temperature at which the alkalies flux with the clay depends on the minerals containing the alkalies and also on the grain size. If these minerals decompose, the alkalies are set free as soluble compounds. (See origin of clay).

Except in refractory clays, the strongly fluxing action of the alkalies is desirable as they serve, in burning, to bind the particles together in a dense hard body at a lower temperature. In the manufacture of porcelain, white earthen ware, encaustic tiles, and similar white wares of an impervious body, feldspar is used as an important fluxing agent. The action of feldspar in vitrification of bodies is noticeable at cone 1, but its effect on high heat bodies starts at about the melting point of feldspar (cone 9) unless finely ground,[6] when its effect is noticed at lower temperatures (cone 2 on Zettlitz kaolin).

Alkalies alone seem to exert little or no coloring influence on burned clay, but potash appears to deepen the color of a ferruginous clay.[7]

[1]Mäckler, Tonindustrie Zeitung, Vol. XXVI, p. 705 (1902).
[2]Nottinger, Trans. Am. Cer. Soc. V., p. 130 (1903).
[3]Barringer, Trans. Am. Cer. Soc. VI, p. 86 (1904).
[4]Rev. Mat. Constr. Trav. Pub. 140, p. 67-69 (1921).
[5]See minerals in clay.
[6]Berdel, Sprechsaal, No. 2-11, 1904.
[7]Ries, Clays, p. 103.

The alkalies contained in clays usually total from 1 to 2.5 or 3% and rarely exceed, 6% in kaolins, 5% in fire-clays, 7% in pottery clays or 14% in brick clays.

Titanium Oxide (TiO_2) is a common constituent in clays, but present in small amounts usually about 1 per cent or less and rarely over 2 per cent; it is generally ignored.[1]

Seger and Cramer[2] found that titanium oxide was an active fluxing agent upon Zettlitz kaolin at lower temperatures than silica. The curve A shown in figure 4[3] shows the effect of titanium oxide in the form of

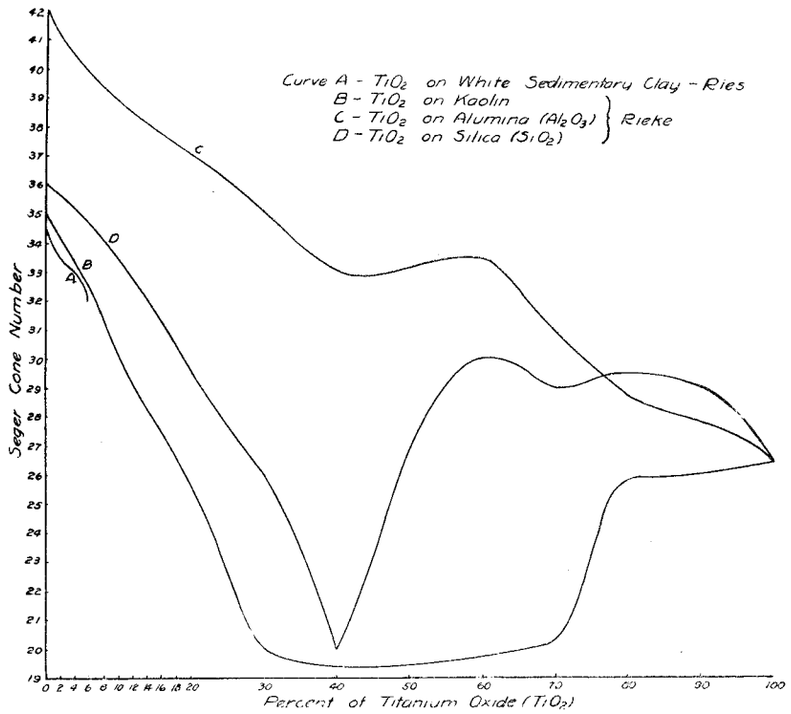

Figure 4.—Effect of Titanium oxide on fusion temperature.

finely ground rutile, on the fusion temperature of a white burning sedimentary clay fusing at cone 34. All the mixtures were vitrified when heated to cone 27 showing a deep blue fracture which was destroyed by

[1]Riley, Quart. J. Chem. Soc. XV, 311 (1862).
Cook and Smock, Clays of N. J. 1878, p. 276.
Second Pa. Geol. Surv., M.M. p. 261.
Orton, Ohio Geol. Surv., VII, Pt. I.
Wheeler, Mo. Geol. Surv. XI, p. 56.
Ries, Va. Geol. Surv. Bull. II.
Ries, Clays, p. 103.
Vogt, Tonindustrie-Zeitung XXVII, 1247 (1903).
Kovar, Sprechsaal (1891), p. 106 reports 10.06 per cent TiO_2.
[2]Seger's Collected Writings I, p. 519.
[3]Ries N. J. Geol. Surv. VI, p. 71 (1904).

the presence of a few per cent of silica. A mixture containing 5 per cent rutile burned yellow at cone 8. Curve B shows the effect of titanium oxide on the fusion temperature of Zettlitz kaolin, the mixtures being heated at the rate of one cone in 4 or 5 minutes. Curves C and D are similar curves[1] for alumina-titania, and silica-titania mixtures.

Water may be present in clays as moisture (mechanically held) or combined water (chemically combined with the clay). Moisture is held in the pores between the clay grains or particles largely by what is known as capillary action. If the pores are small the clay may absorb a large amount of moisture, but if the pores are larger and exceed a certain size they will no longer hold moisture by capillary action. Part of the moisture will pass off by evaporation in air at room temperature and most of it can be evaporated by heating the clay to 100°C (212°F), but a small amount is still held even then in the pores. The shrinkage, taking place as the moisture is driven off, varies from 1 per cent or less in sandy coarse clays containing a small amount of moisture to 10 or 12 per cent in very plastic fine grained clays. High moisture content means a high shrinkage in drying and often a danger of cracking the clay ware, particularly if dried rapidly. If the clay contains compounds soluble in water, during drying the moisture carries these compounds to the surface of the ware leaving them behind as the water vaporizes.

Chemically combined water is an essential part of some chemical compounds or minerals (kaolinite, muscovite, limonite, etc.) in the clay. When the combined water is driven off by heating these compounds are destroyed. This usually occurs between 400°C and 600°C.[2]

Carbonaceous Matter, generally of vegetable origin is found in nearly all sedimentary clays, having been incorporated with the clay during deposition. Although then it may have been fresh, long burial with the clay in the absence of air has often changed it into an asphaltic or coaly substance.

Vegetable tissue, (wood, leaves, etc.) is commonly found in surface clays of recent origin. It is usually present in small amounts, rarely exceeding 1 per cent, and burns out easily causing little trouble. It rarely affects the color of the raw clay.

Asphaltic or bituminous matter burns readily at a low red heat. It is found in some clays and in many shales, such as the Antrim shales of Michigan, and in shale associated with coal seams. Sometimes carbon

[1]Rieke, Spreschsaal XLI p. 406 (1908).

[2]E. Plenske, Sprechsaal, No. 21, p. 290 (1908). Noted a loss of combined water at 380° C. and a loss of 0.60 per cent when heated at 920° C.
Laubman, Tonindus.-Zeit. V., p. 400, 1881, noted dehydration at 360° C. and Muhlhauser, Ibid, p. 149, at 376°C.
Rohland, Sprechsaal p. 1745 (1905).
Bowry, Treatise on Ceramic Industries, p. 103.
J. W. Mellor, Iron and Coal Trades Rev. 82, p. 1045.
W. M. Kennedy, Trans. Am. Cer. Soc. IV p. 146.
Bigot, Compt. render. 179, p. 91 (1923).

is present in a hard or coaly formation, resembling anthracite, which burns more slowly.

Bituminous matter and carbon are generally strong coloring agents of raw clay, small amounts giving a gray or blue gray tint, and larger quantities a black coloration that may mask all other colors. Asphaltic material or carbon often cause much trouble in burning. If the bituminous matter exceeds 10 per cent the clay is generally considered not workable, and clay containing 5 or 6 per cent demands careful burning. Carbon is a very active reducing agent preventing the proper oxidation of the iron in the clay and may even reduce ferric oxide to ferrous oxide.

$$Fe_2O_3 + C \rightarrow 2FeO + CO$$[1]

This will cause "black hearts" and generally swelling and distorting of the ware. If the outer parts of the ware begin to vitrify before the carbon is completely burned out the carbon may react with the oxides present in the clay (particularly if sulphur is present) forming gases such as carbon monoxide that frequently bloat the viscous clay to three or four times its original size.

The carbon must be burned out at a temperature below that at which the clay may begin to vitrify. However, oxidation proceeds more rapidly at high temperatures, so that a compromise is necessary at some temperature just below that at which the clay begins to fuse. Usually 800° to 900°C is about the best temperature interval for burning off carbon,[2] but in the case of some clays which begin to vitrify at low temperatures, oxidation must be completed below 600°C.

The kiln gases must be oxidizing, i.e., they must contain an excess of oxygen, to burn the carbon and to oxidize the iron. This condition can be maintained only by supplying a much greater volume of air to the kiln than is necessary to burn the fuel. Because this oxygen has to permeate the clay, unite with the carbon, and the carbon dioxide so formed has to pass out through the pores in the clay, the clay should be porous and not dense. For this reason soft mud brick are more rapidly oxidized than brick made by the stiff mud or dry press processes, and the semi-dry press brick are the most difficult to oxidize.

If bituminous matter is present in considerable proportion the oxidation must not be allowed to take place too rapidly, or the heat given off by the combustion of the hydrocarbons may be sufficient to vitrify the ware before the oxidization is complete. This may be controlled by the amount of air admitted.

Sometimes brickmakers state that black coring (black heart) is caused by the brick being set in the kiln when too wet. Although this is not

[1]See iron oxide. Page 41.

[2]Orton and Griffin. Second Report Com. on Tech. Invest. Nat. Brick Maker's Ass., Indianapolis 1905.

strictly true there is an indirect relation in that so much heat is absorbed by the evaporation of the moisture in the early stages of firing that other changes such as the oxidation of carbon are retarded and the brick begins to vitrify before the process is complete.

Sulphur is present in many clays, but is seldom determined in the analysis unless the clay is used for the manufacture of Portland cement. It may be present as either sulphate (gypsum, $CaSO_4\ 2H_2O$; epsomite, $MgSO_4\ .7H_2O$) or as sulphide (pyrite, FeS_2 or marcasite). In either form the sulphur is rapidly removed from that part of the clay having free access to air during the burn up to 800°C and is removed, though more slowly, after that so long as the clay structure remains porous and permeable to air. In the inner parts of the clay, which the air cannot readily reach, the loss of sulphur may be much less and if bases such as FeO, CaO, or MgO are present with which the sulphur may combine it may not be expelled. Carbon interferes with the expulsion, as sulphur will not pass off to any extent until after the carbon is burned out, and by that time the clay may have become too dense for the oxidation of the sulphur.

The effect of sulphur is noticed only after the clay reaches a dense vitrified condition. The period of dense vitrification in all clays is followed after a longer or shorter interval by the development of multitudes of minute vesicles in the viscous body which becomes spongy and worthless (overburned). If sulphur is present this period of dense vitrification is greatly shortened or even eliminated. The sulphides and sulphates are decomposed chiefly by silicic acid, and the gas so evolved develops prematurely a spongy body. The method of overcoming the effects of sulphur in vitrifying clay bodies, is to apply a deliberate and complete oxidation treatment while the clay remains porous. This will rid the clay of most of the sulphur, and also prevent sudden or premature slagging by ferrous oxide if ferrous oxide actually has such a tendency.[1]

Pyrite breaks down into FeS and sulphur at 400°C.[2] Ferrous sulphate decomposes into ferrous oxide at 550°-650°C. Calcium sulphate decomposes[3] at higher temperatures and less completely. The action of carbon in checking the liberation of sulphur may be shown by the following equation:

$$FeO + S + C \rightarrow FeS + CO$$

showing that ferrous sulphide in clay cannot be decomposed without roasting in air, or interaction with silicic acid during vitrification.[4]

[1]Orton & Staley, Third Report of Com. on Tech. Invest. Nat. Brick Maker's Ass., Indianapolis 1908.

[2]See Pyrite and Iron Sulphate.

[3]See Gypsum and Ries N. J. Geol. Surv. 1904, p. 63.

[4]Orton, Trans. Am. Cer. Soc. V. p. 400.
Seger, Collected Writings II, p. 645, 1902.

Phosphoric acid may be present in clays, usually less than one-half per cent.[1] In sufficient amounts it may act to give translucency, improve the color, and act as a fluxing or vitrifying agent.[2]

Soluble Salts. In the formation of clay, soluble compounds are frequently formed by decomposition of the mineral grains. If the compounds are easily soluble in water they will be washed away in the process of weathering, but the less soluble salts tend to remain with the clay. During the drying, moisture carries these less soluble compounds to the surface of the clay when the moisture evaporates, these compounds are left as a scum on the surface of the air-dried ware *("Drier-White")*, or as a white coating on the clay after it is burned *("Kiln-white")*. The soluble salts contained in clays are usually sulphates[3] of lime, iron, or the alkalies, frequently formed from decomposition of pyrite in the clay. Carbonates are also set free by decomposition of the complex silicates, such as feldspar. In some cases soluble salts may be introduced into the clay by the water used for tempering, or by the artificial coloring materials sometimes used.[4]

"Wall-white" or *efflorescence*[5] is the name given to any superficial discoloration or coating developed on the surface after the ware has been burned and set in a structure or wall where it is subject to moisture. This type of coating may come from the mortar, either by direct introduction of soluble salts, or by reaction between carbonates of magnesium or alkalies in the mortar with calcium sulphate in the ware, or it may be derived from salts formed within the body of the ware during burning. If the fuel contains sulphur, as pyrite in the coal, sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are formed when the fuel is burned. These gases react with some salts in the clay, such as calcium carbonate, forming soluble sulphates.

The above coatings are all white in color. In some cases, the product is coated with a yellow or green stain caused either by the growth of vegetable matter on the surface of the ware or by soluble compounds of vanadium.

The amount of soluble salts present in clay is never large[6] but less than 0.1 per cent is often enough to produce a stain.

Prevention of Scumming. The following methods for the prevention of drier-white and kiln-white "scum," have been suggested:

[1]W. Va. Geol. Survey III, p. 21, 1906 reports on average of .319 per cent.

[2]C. W. Parmelee, Trans. Am. Cer. Soc. VIII, p. 238, 1906.

[3]Grimsley and Grout, W. Va. Geol. Surv. III, found some soluble salts high in Al_2O_3 and SiO_2 and showing no sulphate.

[4]Seger, Collected Writings I, p. 213, p. 369.

[5]C. W. Parmelee, J. Am. Cer. Soc. 5, p. 538 (1922), defines efflorescence as due to soluble salts, and scum as due to action of gases on ware during drying or burning.

[6]Măckler, Tonindustrie,—Zeitung No. 43, 1904—Found from 0.0134, to 0.7668 per cent of total sulphates of lime, magnesium, and alkalies, in fifty bricks examined.

1. Convert the soluble salts to insoluble compounds by precipitating the sulphates with barium salts.
2. Use the clay in a thoroughly weathered condition, thus permitting the soluble salts to be leached out.
3. Use the clay unweathered, before the soluble salts have had time to form.
4. Rapid firing to prevent concentration of the salts on the surface.
5. A reducing flame to prevent formation of the white stain, or coating the ware with flour or coal tar which burns rapidly with a reducing action.

Barium chloride ($BaCl_2$) and barium carbonate ($BaCO_3$) are usually employed to precipitate the sulphate as barium sulphate ($BaSO_4$). If sodium sulphate is present sodium chloride or carbonate will be formed, according to whether barium chloride or carbonate was used, and can be readily washed out as the sodium compounds are very soluble in water.[1]

Barium chloride is soluble in water and as a solution can be evenly distributed throughout the clay. But as it is soluble in water care must be taken to use very little more barium chloride than is necessary to precipitate the sulphates, for if any remains unchanged in the clay it may itself form a scum. The calcium chloride ($CaCl_2$) formed by the reaction, $CaSO_4 + BaCl_2 \rightarrow BaSO_4$ (insoluble) $+ CaCl_2$ is soluble but is decomposed on burning and leaves no scum. A clay containing 0.1 per cent of calcium sulphate would require about 26 pounds of barium chloride per thousand seven-pound bricks.

Barium carbonate is insoluble in water and must be finely powdered and carefully distributed throughout the clay, because it will react only when it comes into immediate contact with the sulphates. For this reason and because the action between barium carbonate and the sulphates takes place slowly, about 10 or 11 times as much barium carbonate is used as actually needed to precipitate the sulphates. For a clay containing 0.1 per cent of calcium sulphate about 100 pounds of barium carbonate would be needed for a thousand, seven-pound brick.

Efflorescence. Wall white, or efflorescence, is more difficult to control but may be prevented by keeping moisture out of the walls. This may be done by using well burned brick and proper drainage and waterproofing of the foundations. If efflorescence appears it may be partially concealed by a coat of paraffine or linseed oil, or by paint, if the paint will stick to the damp spots.[2]

[1]Seger, Collected Writings I, p. 396.

[2]Seger, Collected Writings I, p. 376, p. 381.
Guenther, Baumaterialienkunde I, p. 386 (1896).
Gerlach, Brickbuilder, p. 59 (1898).
Mäckler, Tonindustrie—Zeit. No. 43 (1904).
Lovejoy, Trans. Am. Cer. Soc. VIII, p. 355 (1906).
Jones Ibid VIII, p. 369 (1906).

Chapter IV

PHYSICAL PROPERTIES OF CLAY

PLASTICITY

Definition. Plasticity is probably the most important property of clay. Without it clay would be of comparatively little value for the manufacture of clay ware. Plasticity may be defined as the property which many bodies possess of changing form under pressure, without rupturing, and retaining their changed form when the pressure is removed.[1]

The amount of water required to develop the maximum plasticity varies with different clays.[2] Fine texture aggregates including clays assume a more or less hard condition when dry, the degree of hardness usually increasing with the plasticity. Hardening on exposure to heat is not necessarily a function of plasticity, but is due to the particles softening by fusion and becoming welded together. (See Burning Properties).

Causes. A number of theories have been advanced to explain the cause of this interesting physical property. The more important theories are mentioned below:

Plate Theory. In 1876 Johnson and Blake[3] suggested that plasticity is due to the presence of small transparent plates of kaolinite, the plasticity being more pronounced when the plates are smaller and not bunched together. This view has been supported by other investigators in this country and abroad.[4]

Interlocking-Grain Theory. Olchewsky[5] suggested that the plasticity and cohesion of a clay were due to the interlocking of the clay particles and kaolinite plates, and used the tensile strength of the air dried clay as a numerical value of the plasticity.[6]

Generally there is no constant relation between the tensile strength of the dry clay and its plasticity when wet, as this theory would suggest.

[1]Seger, Tonindustrie Zeit., p. 201 (1890).
Ries, Clays, p. 119.
A. B. Searle, Chem. and Physics of Clays, Ernest Benn (1924), p. 257.

[2]Wheeler, Mo. Geol. Surv. XI, p. 98, 1896, shows from 14 to 35 per cent water required for maximum plasticity.

[3]Amer. Jour. Sci. (2), p. 351 (1876).

[4]Bischof, Die Feuerfesten Thone, p. 23.
Hussak, Sprechsaal, p. 135 (1889).
Cook, N. J. Geol. Surv. Report on Clays, p. 287 (1878).
Haworth, Mo. Geol. Surv. Vol. IX, p. 104 (1896).
Wheeler, Ibid, page 106. Tried to prove this point by grinding minerals possessing a plate-like tructure. Calcite and gypsum when finely ground developed good plasticity and when air dried had tensile strengths of 100 and 350 lbs. per sq. in. respectively.

[5]Töpf. u. Zieg. Zeit. No. 29 (1882).

[6]U. Aleksiejew and P. A. Gremiatschenski, Zap. imp. russk. techn. obschtsch. XXX, pt. 6-7, (1896), conclude that plasticity is dependent not only on interlocking clay particles but also upon fineness of the grain, extremely coarse and extremely fine grains having less plasticity.

Water-of-hydration Theory. It has been suggested that the plasticity of clay is closely related to the hydrated aluminum silicates,[1] and disappears as the combined water contained in these compounds is driven off.

It is true that clay loses its plasticity when heated to a temperature high enough to drive off the combined water, but, so far as is known hydrated aluminum silicates bear no relation whatever to the plasticity of clay, as some of the most plastic clays contain very small amounts of hydrated aluminum silicates[2] and it seems more probable that a temperature necessary to drive off the combined water may also break up other structures closely related to plasticity.[3]

Molecular Attraction between the clay particles themselves or between the clay grains and the surrounding water, and the surface tension of the water films, have been suggested as important factors in determining plasticity.[4] The absorption of water into clay pores may give them a gelatinous coating[5] which may become more plastic by the addition of colloids such as tannin or solutions such as ammonia or alum.[6]

The Colloid Theory or some modification of it is receiving considerable attention and appeals to many investigators. The presence of colloids in clay was recognized by Way[7] in 1850. Later Van Bemmelen[8] noticed that nearly all metallic oxides and many salts have the power of entering into that peculiar non-crystalline hydrated condition called colloidal and forming glue-like[9] complexes with a peculiar relation to and dependency on water. The water content of these hydrogels varies continuously with the temperature and vapor pressure of water in the atmosphere surrounding them. When heated and dried at high temperature, they lose nearly all their water, but again absorb water to the same extent when cooled in moist atmospheres unless the temperature of drying is carried above a certain critical point, when this property is gradually lost and destroyed.

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[1]Vogt, Bull. d. l. Soc. d'encour. l'ind. nat., p. 633 (1897), among others.

[2]Ries, Clays, p. 121.
Ries, Geol. Surv. IV, p. 248 (1902), describes two clays of almost identical chemical composition and containing over 98 per cent of "clay substance" which differ widely in plasticity.
Seaman, Chem. Centralblatt I (1890), describes a highly plastic clay containing only 1.64 per cent of Al_2O_3.

[3]Ries, Clays, p. 121.
J. Keele, Trans. Am. Cer. Soc. 14, p. 154 (1912).

[4]Ladd, Ga. Geol. Surv. Bull. 6a, p. 29 (1898).
Zschokke, Tonindustrie—Zeit. No. 120, p. 1658 (1905).
Baumaterialienkunde No. 24, 25, 26 (1902); 12, 3, 4, 5, 6 (1903).
Whiting, U. S. Dept. of Agric. Bull. No. 4 (1892).
Briggs, U. S. Dept. of Agric. Bull. No. 10 (1897).
R. F. MacMichael, Trans. Am. Cer. Soc., 17, p. 616 (1915).
H. Chatley, Trans. (Eng.) Cer. Soc. 19, p. 1-2 (1919-20).

[5]Cushman, U. S. Dept. of Traus. Agric. Bull. No. 95 (1905).
Mellor Trans. Eng. Cer. Soc. V, Pt. 1, p. 72 (1905-6).

[6]Grout, W. Va. Geol. Surv. III, p. 54 (1906).

[7]Royal Agric. Soc. Journ. XI 1850, cf. Trans. Am. Cer. Soc. VI, p. 7 (1904).

[8]Zeitsch. anong. Chem. V, p. 466; XIII, p. 233; XVIII, p. 14; XX, p. 185; XXII, p. 313.

[9]Graham, Phil. Trans., p. 183 (1861).
Cushman, J. Am. Chem. Soc. XXV, No. 5 (1903).

The water so absorbed is called "Micellian" water and differs from the ordinary hydroscopic water in that it is absorbed into the particles of a hydrogel without producing any appearance of wetness.

Aluminum hydroxide, iron oxide, hydrated silica acid, and organic matter are all possible colloids and are commonly present in clays, in various amounts. Cushman[1] prepared some silicic acid as a hydrogel, and some alumina hydrogel, artificially and studied the effect of their addition to the clay. The silica gel increased the binding power and shrinkage but not the plasticity, while the alumina gel increased the plasticity but not the shrinkage or binding power. A mixture of the two, increased both the binding power and plasticity of the clay. Grout[2] found that the addition of 3 per cent of alumina cream to clay increased the plasticity of two clays 60 and 36 per cent respectively, but that after air-drying, powdering and remixing, the plasticity of the mass dropped to its original figure. In using a dilute solution of agar-agar he found 0.08 per cent just as effective as the 3 per cent of alumina cream, and the effect of the agar-agar was not destroyed by drying. From this he argues that since plastic clays do not lose their plasticity upon air-drying it is evident that such colloids as alumina cream do not explain plasticity, and that some colloid is required which is not irreversibly pektized by air-drying, a type that is extremely rare among inorganic compounds. He finds that a hydrated aluminum silicate acts exactly as alumina cream. Bigot[3] reports that clays are partially irreversibly pektized at 350-600°C and completely pektized between 600-700°F.

A mass of colloidal material itself does not show the solidity and cohesiveness of a plastic clay. It is as if it lacked some strengthening internal structure as might be supplied by a mass of mineral grains. According to these ideas it would seem necessary that in addition to colloidal matter a plastic clay should contain some fine grained mineral aggregate of exceedingly low plasticity to supply the solidity and cohesiveness.[4]

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[1]Trans. Am. Cer. Soc. VI, p. 7 (1904).

[2]W. Va. Geol. Surv. III (1906).

[3]Compt. rend. 179, p. 91 (1923).
cf. J. W. Mellor, Iron Coal Trades Rev. 82, p. 1045.

[4]Ia. Geol. Surv. XIV, p. 90 (1904).
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Albert Benke, Sprechsaal 53, p. 490.
Bole, G. A., J. Am. Cer. Soc. 5, p. 469 (1922

The essential nature of water in developing plasticity of clay must not be overlooked. It has been suggested that the strength of the dried clay is due to the cohesive forces between the dry grains as in any solid and that the addition of water introduces a disruptive force as due to the kinetic energy of the water. The balancing of these two forces is given as the cause of plasticity.[1] The very important effect of water on the behavior of the colloidal structure has been recognized for some time. H. E. Ashley[2] suggests that weathering is reabsorption of water squeezed out by rock pressure and suggests that viscosity shows plasticity of the clay, and that adsorption of salts varies as the plasticity. Grout and Poppe[3] suggest adsorbed water as the most important factor in plasticity with colloids contributing thereto, but inadequate in themselves to account for the entire plasticity. They believe that adsorbed salts cannot be the cause of plasticity any more than plasticity is the cause of the adsorbed salts, because clays with a high ability to adsorb salts are very plastic, while clays which cannot adsorb any more salts are very low in plasticity. Bigot[4] suggests that water lost while the clay is shrinking is colloidal water, while that lost after the clay has stopped shrinking is pore water. He suggests

$$\frac{\text{Colloid water}}{\text{Total water}} \times \text{shrinkage} = \text{plasticity}$$

and applies this formula to a number of clays.

Bacteria[5] are known to be present in clay, and are given the credit for the improved plasticity of clays which have been aged by storing in cellars, usually for six months to a year. Seger states that an acid, gradually developed by organic decomposition, destroys the alkalinity of the mass, and thereby improves its plasticity. By a process of normal growth the bacteria may add organic colloids (protoplasm) to the clay, increasing its plasticity.[6]

Improvement of Plasticity. Weathering a clay often increases its plasticity. This may be due to several causes such as mechanical disintegration, water soaking, oxidation of organic matter, or the production of colloids by hydrolysis or bacterial action.[7]

Frequently simply grinding, particularly wet grinding, will improve the plasticity.[8]

[1]R. F. MacMichael, Trans. Am. Cer. Soc. 17, p. 616-628 (1915).
[2]Trans. Am. Cer. Soc. XI, p. 530 (1909).
[3]Trans. Am. Cer. Soc. XIV, p. 71 (1912).
[4]Comp. rendu. 172, p. 755-8 (1921).
[5]Stover, Trans. Am. Cer. Soc. IV, p. 185 (1902).
[6]W. Va. Geol. Surv. III, p. 47 (1906).
[7]Ries, Clays, p. 129.
Rohland, Sprechsaal XLII, p. 1371.
[8]H. W. Donda, J. Am. Cer. Soc. 3, p. 885 (1920).

Measurement. Measurement of plasticity seems to be as difficult as finding the true cause of this property. The usual and about the most practical method consists in working the moist clay in the hands. Although not entirely satisfactory, this is the only method applicable in the field, and can be used with satisfactory results by an experienced investigator.

Forcing the wet clay through a cylindrical die and using as a measure of plasticity the maximum length of the extruded pencil of clay before it breaks of its own weight, has been suggested.[1] Care should be taken that the clay is worked up with the proper amount of water for maximum plasticity before this test is applied. This fact makes it necessary that the test be repeated with different moisture contents for consistent results.

The fundamental characteristic of plastic bodies is their deformability with a high degree of cohesion to prevent rupture. A fairly satisfactory method of determining these properties is to mold the thoroughly worked clay into cylinders and pull them in two with a special machine.[2] The amount of expansion shows the degree of deformation while the force required to pull the cylinder apart shows the cohesiveness or tensile strength. Zschokke calls the product of the two the plasticity coefficient.[3] He found that higher values, from 2 to 18 times as great, were obtained by stretching the bar rapidly or by a succession of short rapid strokes; so that rate of applying the load, or the rate of pulling the sample must be specified.

A similar method was used by Grout.[4] His cylinders were cut from an extruded pencil three-fourths of an inch in diameter, into two inch lengths, and were tested under compression instead of tension. The pressure necessary to compress the cylinder one-half centimeter was taken as a measure of its resistance to flow. This resistance was more satisfactorily measured by a Vicat needle seven square mm. in area, the weight necessary to cause the needle to sink three cm. in one-half minute being taken as the measure. The amount of flow was measured by the increase in area of the head of the cylinder when compressed to the point of fracture.

The adaption of a test originally developed for measuring the plasticity of lime plasters to measuring the plasticity of clay is described by W. E. Emley.[5] The test involves pushing a core into a rotating block of plastic material and measuring the tangential forces. Other tests

[1]Bischof, Die feuerfesten Thone, p. 84.
E. C. Stover, Trans. Am. Cer. Soc. VII, p. 397 (1905).
[2]Zschokke, Baumaterialienkunde No. 24, 1902, to No. 6, 1903.
[3]Tensile strength in kg. per sq. cm. multiplied by deformation in per cent (Cylinders 6 cm. long 3 cm. in dia.).
[4]W. Va. Geol. Surv. III, p. 40 (1906).
[5]Trans. Am. Cer. Soc. 10, p. 523 (1917).
Kirkpatrick and Orange, J. Am. Cer. Soc. 1, p. 170 (1918)

have been described by Langenbeck,[1] Ladd,[2] Bischof,[3] H. Green,[4] and F. P. Hall.[5]

TEXTURE

The texture or grain size exerts an important influence on all the physical properties of a clay. Most of the clay particles are so small that they can be seen only with the aid of a microscope, and cannot be separated with sieves, although many clays contain sand grains large enough to be visible to the unaided eye.

Determination of Grain Size. A determination of the grain sizes in clay is generally termed *mechanical analysis* and may be conducted in a number of ways.

Perrolt and Kinney[6] describe a method of determining particle size by direct microscopical examination.

The Beaker Method suggested by Whitney[7] consists in thoroughly shaking the sample with water for one or two days to disintegrate the clay forming a suspension. This suspension is then fractionally precipitated in beakers, into sand, silt, fine silt, and "clay," by allowing the suspension to settle until the desired size of grain is included in the precipitate, decanting the turbid liquid and repeating the sedimentation for finer material in another beaker. The grain size of the sediment is determined by microscopic examination so that the decantation may be properly timed. The process is repeated until the separation is sharp and complete. This is usually accomplished in six or ten days.

The *Schoene Method* consists in separating the coarser material by sieves and the finer particles by an upward current of water in a vertical tube in which the clay suspension is placed. The slower the current of water the finer the particles carried up. The velocity of the water current is kept constant until the effluent becomes clear indicating that the finest particles have been removed. The velocity of the current is then increased to carry off the larger particles. The device can be calibrated to carry off certain sized particles, since to every velocity there is a corresponding maximum size of grain that will be carried.[8]

Hilgard's *Churn Elutriator* is similar in principle to that of Schoene, with the addition of a churn in the lower part of the vertical tube, to break up any aggregations of fine particles that might form. About seventy-five to one hundred hours are required to complete a separation.

[1]Chemistry of Pottery, p. 19.
[2]Ga. Geol. Surv. Bull. 6a, p. 51 (1898).
[3]Die feuerfesten Thone, p. 88.
[4]Proc. Am. Soc. Test. Mat. 20 II, p. 451-94 (1920).
[5]J. Am. Cer. Soc., p. 346 (1922).
[6]J. Am. Cer. Soc. VI, p. 417 (1923),
[7]U. S. Dept. Agric. Bur. Soils, Bull. 4 (1896).
[8]H. G. Schurecht J. Am. Cer. Soc. 3, p. 355 (1920), Elutriation Tests on American Kaolins.

Krehbiel[1] uses a similar principle in an apparatus designed to separate all sizes simultaneously. In this way saving time and water.

Centrifugal Separation is probably one of the most satisfactory methods known. The disintegrated sample is centrifuged to precipitate everything except the finest particles which are decanted off. The sediment is then again stirred up and centrifuged at a lower speed, or for a shorter time, precipitating everything except the fine silt. The larger sizes are then separated by settling and screening.

Air Elutriation[2] of an oven dried powdered sample may be conducted on the same principle as Krehbiels' water elutriation.

Fineness or Surface Factor is taken as the reciprocal of the average diameter of grain size. The *"total factor"*[3] is taken as the sum of the products, of the surface factor of each group, multiplied by the per cent of that group present in the clay as in the following tabulation:[4]

Group.	Diameters.	Average Dia.	Surface factor × per cent.
1	0.12 to 0.04 mm.	0.08	12.5 x 10
2	0.04 to 0.025 mm.	0.0325	30.27 x 20
3	0.025 to 0.01 mm.	0.0175	57.14 x 20
4	0.01 to 0.0 mm.	0.0050	200.00 x 50
Total factor			118.83

SLAKING

Slaking is the spontaneous and complete disintegration of a clay mass in water. The time required for this varies from a few minutes in the case of soft porous clays to several weeks or more for tough shales.

For slaking tests finely ground clay passing a No. 30 sieve is mixed with an equal weight of "potter's flint" passing a No. 100 sieve, and the wet plastic mixture pugged into a slab which is cut into one inch cubes. These cubes are carefully dried in three stages:

1. Room temperature, until air dry,
2. 65°C-75°C for at least five hours,
3. 110°C until approximately constant in weight,

and cooled in a desiccator. Supported on a screen of about 2½ meshes

[1]Trans. Am. Cer. Soc. VI, p. 173, 1904.
[2]A. S. Cushman & P. Hubbard, J. Am. Chem. Soc. XXIX No. 4, April, 1907.
[3]Jackson, Trans. (Eng.) Cer. Soc. III, p. 16.
[4]Purdy, Trans. Am. Cer. Soc. VII, p. 441 (1905).
cf, Krehbiel l. c.
Binns, Trans. Am. Cer. Soc. VIII, p. 244 (1906).
Cushman & Hubbard, XXX l. c.
H. G. Schurecht, J. Am. Cer. Soc. 4, p. 812 (1921).
Sven Oden, Bull. Geol. Inst. Univ. Upsala 16, p. 15-64 (1919), for methods of measuring the rate of sedimentation and computing the mechanical analysis from the data so obtained.
C. W. Parmlee and H. W. Moore, Trans. Am. Cer. Soc. XI, p. 467 (1909, for a general review of methods.

to the inch the cubes are immersed in a vessel containing water maintained at 25°C and supported in such a way that the screen is at least one inch above the bottom of the vessel and the cubes covered with from ½ inch to one inch of water. The time required for the whole of the test piece to slake and settle through the screen is recorded. The slaking property is of some practical importance, as easily slaking clays temper readily; or if the material is to be washed, rapid disintegration is desirable.

ADSORPTION

Adsorption is the term used to indicate the ability of a clay to remove substances from solutions with which it is in contact. The action is selective[1] and in many cases very complete.[2] For some uses of clays, such as clarifying lubricating oils by Fuller's earth, this property known as adsorption is extremely important.

STRENGTH

Tensile Strength is the resistance to rupture offered by the air dried clay. It is an important property and has a practical bearing on the handling, molding, and drying of the clay, as a high tensile strength

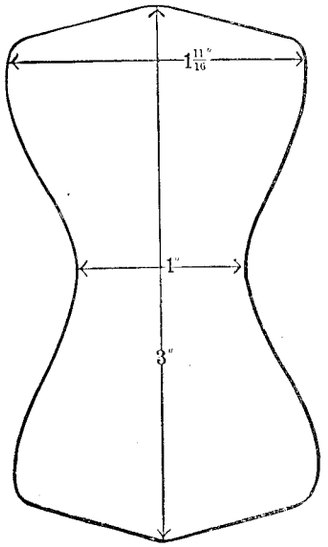

Figure 5.—Outline and dimensions of a briquette for testing the tensile strength of a clay. (After Ries.)

[1]T. Way Royal Agr. Soc., Jour. XI, 1880 (Cushman Trans. Am. Cer. Soc. VI, p. 7 (1904).
Bourry, Treatise on Ceramic Industries, p. 54 (1901).
Hirsch, Tonindustrie—Zeitung No. 26 (1904).
[2]H. Ries, Trans. Am. Cer. Soc. VI, p. 44 (1906).

enables the clay to withstand the shocks and strains of handling. Formerly plasticity and tensile strength were supposed to be closely related, but this view is not now generally accepted.

The tensile strength is determined by molding the thoroughly kneaded clay into briquettes one inch thick and of the form shown in figure 5, and pulling these briquettes apart when thoroughly dried. If carefully molded and dried the variation in breaking strength of individual briquettes should not exceed about twenty per cent.[1] At least ten samples should be pulled to get a fair average. The strength actually obtained must be corrected to the actual cross section of the test specimen since the clay shrinks on drying and is less than the molded area of one square inch.

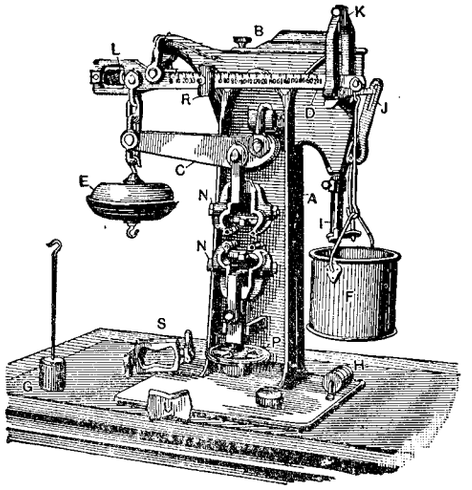

Figure 6.—Fairbanks tensile-strength machine. N. clips for holding briquettes; P, screw for applying strain to balance-lever C; F, bucket to hold shot fed in through I from the hopper K; J, automatic cut-off. (After Ries.)

The Fairbanks tensile-strength machine, Figure 6, was used in all tests reported in this bulletin. Other machines (such as the Riehle) equipped with similar jaws for holding the specimens but applying the load in a different manner will give similar results.

The tensile strength of different clays varies from a few pounds to over 400 pounds per square inch.[2]

The most probable cause of tensile strength is an interlocking of the grains. If the grains are all of uniform size they will be less interlocking

[1]Wheeler, Mo. Geol. Survey XI, p. 111.
Ries, Clays, p. 149.
[2]Wheeler, Mo. Geol. Survey XI, p. 111.
Beyer Williams, Ia. Geol. Survey XIV, p. 83 (1904).
Ries, N. J. Geol. Survey, Final Report VI, p. 85 (1904).

than if fine, medium, and coarse particles are all present in about equal proportions. By the same reasoning an excess of either coarse or fine grains would produce a clay with a lower tensile strength. This was found to be generally true in a test of five New Jersey clays.[1] Also, when two clays, one a slightly gritty clay with a strength of 182 pounds per square inch, and the other a plastic loam with a strength of 137 pounds per square inch, were mixed in equal proportions, the mixture had an average tensile strength of 258 pounds per square inch.

The addition of sand or non plastic material usually causes a diminution of the tensile strength directly as the diameter of the grains.[2]

Transverse Strength. Recently there has developed a definite tendency to discount the value of tests for tensile strength and to substitute tests for *transverse strength* of the air dried clay as being of greater value as more representative of the actual stresses developed in handling the ware. The transverse strength is determined by mixing the clay previously dried thoroughly at 65°-90°C, and crushed and screened to pass a No. 30 sieve, with 50 per cent by weight of standard silica sand passing a No. 20 sieve and retained on No. 30 sieve. The mixture is then made up to a soft plastic consistency with water and thoroughly pugged. The test pieces are formed in a suitable mold thinly oiled with kerosene, 7 inches long and one inch square in cross-section. The test pieces are carefully dried, first at room temperature, then at 65°-75°C, and finally at 110°C. After cooling in a desiccator the test bars are carefully measured for breadth and thickness; and then broken in a suitable machine having knife edges of ¼ inch radius set 5 inches apart, and applying the load at a rate of 100 pounds a minute. The modulus of rupture is computed by the formula,

$$M = \frac{3}{2}\,\frac{Pl}{b\,d^2}$$

Where M = modulus of rupture in pounds per square inch
P = breaking load in pounds
l = distance between knife edges in inches
b = breadth of bar in inches
d = depth of bar in inches

A variation of plus or minus 15 per cent from the average modulus of rupture of ten samples is allowable. Test pieces showing a greater variation should be rejected.

SHRINKAGE

Air Shrinkage. All clays shrink in drying, and this shrinkage is

[1]Ries, N. J. Geol. Survey, Final Report VI, p. 87 (1904).
[2]Orton, Trans. Am. Cer. Soc. II, p. 100, III, p. 198.

accompanied by a closer association of the particles. The more deliberate and complete the drying, the more strongly the particles can knit together, particularly with fine grained clay. Orton[1] found that the average tensile strength of the same clay varied from 182-205 lbs. per sq. in. accordingly as the clay was dried very rapidly or exceedingly slowly.

In a perfectly dry clay all the grains are in contact, with a variable pore-space between the grains depending on the texture of the clay. The volume of this pore-space is roughly indicated by the quantity of water the clay will absorb without changing its volume. This moisture may be termed *pore water.* If more water is added the mass will swell, and each grain is considered as surrounded by a film of water. In this condition the mass becomes plastic and yields readily to pressure. An excess of water separates the clay particles to such an extent that the mass softens and runs.

When plastic moist clay is set aside to dry, evaporation of the moisture begins and the particles of clay draw closer together, causing air-shrinkage. This process continues until the clay particles come into contact. As the pore water cannot be removed until the clay is heated for some time at 100°C. or above the air shrinkage may be complete before all the water is driven off.

The air shrinkage varies with the texture of the clay, from less than one per cent of the dry volume in coarse sandy clays to about 17 per cent in very plastic fine grained clays, and also directly with the amount of water added. Sandy material reduces the shrinkage and renders the mixture more porous, allowing the moisture from within the clay to escape more readily thereby reducing the danger of cracking. Acids when present in the plastic clay tend to decrease the shrinkage and alkalies tend to increase the shrinkage.[2]

Fire Shrinkage. Like air-shrinkage fire shrinkage varies within wide limits. Shrinkage begins at about a dull-red heat when chemically combined water begins to pass off. Up to about 600°C. the fire shrinkage is accompanied by a loss in weight, due to the loss of combined water of the silicates, limonite etc., and to the burning out of organic matter. During this period the clay should be heated slowly. From 600°C up to 1000°C. usually very little shrinkage takes place and the temperatures may be raised quite rapidly unless carbonaceous matter is present. Above 1000°C the temperature should be raised slowly as shrinkage usually begins again at this temperature due to some of the particles beginning to fuse and form an igneous solution. The finer the texture of the clay the easier and more rapidly vitreous solution may take place.

[1]Trans. Am. Cer. Soc. III, p. 202 (1901).
[2]Bleininger and Fulton, Trans. Am. Cer. Soc. 14, p. 827 (1912).

This may account for the observation made by Wheeler,[1] that the finer the texture, the greater the fire shrinkage.

In many clays the fire shrinkage is so great as to cause much loss from warping and cracking. If materials having no fire-shrinkage, such as sand (sandy clay) or ground burned ware (grog), are added, the shrinkages in drying and in burning are reduced. The ware is more porous, facilitating the escape of moisture in drying and the early stages of burning (water smoking), as well as enabling the product to be fired more rapidly without blistering. If sand, particularly fine grained, is added it may have a fluxing action at high temperatures. For this reason, among others, finely ground burned grog is always preferred for reducing the shrinkage in high class products.

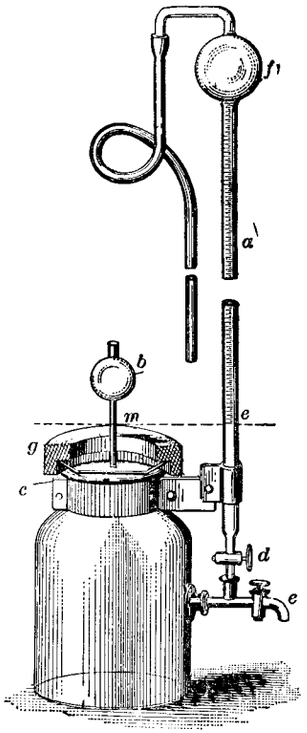

Figure 7.—Seger's volumeter.

Measurement. Exact knowledge of the air and fire shrinkage of the clay is necessary for the production of burned ware of specified dimensions. The linear shrinkage expressed as a percentage of the dried length may be determined by direct measurement, but for reasons of accuracy the linear shrinkage is usually computed from the volume or cubical shrinkage.

[1]Mo. Geol. Survey XI, p. 121 (1897).

A. Bigot[1] calls attention to the fact that clays show expansion on burning only when free silica (SiO_2) is present, except just before fusion when clays generally show an expansion. Artificial pumice stone may be made by rapidly heating schist and porcelain to the swelling temperature.

Seger Volumeter. The volume of clay briquettes is usually measured in a volumeter of the Seger type (figure 7). This consists of a wide mouthed, glass stoppered jar of ample size to receive the clay briquettes. The stopper is fitted with a short glass tube of small diameter, expanding above into a bulb and contracting again to a small funnel shaped top. The burette (a) has a capacity greater than that equal to the volume of the briquettes to be tested, and is graduated into tenths of a c.c. The upper part of the burette is expanded into a bulb to which is connected a glass tube for making connection to a suction line to draw the liquid into the burette.

In using the apparatus the volumeter is first filled with the liquid to be used,[2] so that the liquid stands at the scratch mark on the tube in the top (m), and on the zero point in the lower part of the burette (e). The burette is then drawn full of the liquid, the stopper removed and the specimen of clay placed in the volumeter. This can be done more easily without spattering the liquid if a float or wire frame is left in the volumeter to aid in placing the samples. The stopper is replaced and the liquid in the burette allowed to flow back into the volumeter until the mark (m) on the short tube in the stopper is reached. The volume of the clay sample is then equal to the displaced volume as indicated above the zero mark on the burette.

Overflow Volumeter. A direct reading overflow volumeter, that requires less attention and is simpler in construction than the Seger volumeter, has been described by H. G. Schurecht.[3] The volumeter bowl used at the Bureau of Mines is constructed of glass, but brass or copper has been found very satisfactory. The apparatus used in this investigation consists of a volumetric bowl, figure 8, containing an overflow tube which drains into a burette. The bowl is filled with an excess of liquid and allowed to drain to constant level. The volume of liquid in the burette is read, and the briquette lowered into the bowl by means of the holder. The briquette displaces a volume of liquid, equal to its bulk volume, which rises above the overflow orifice and flows into the burette. The volume of the briquette is equal to the difference of the two burette readings. The accuracy of this apparatus depends largely on its freedom from vibration if ample time is allowed (10 minutes) for draining, and is well within the limits desired for clay testing. A

[1]Compt. rend. 172, pp. 854-7 (1921).
[2]Kerosene of about 0.8 specific gravity is satisfactory for unburned clays.
[3]J. Am. Cer. Soc. 3, p. 730 (1920).

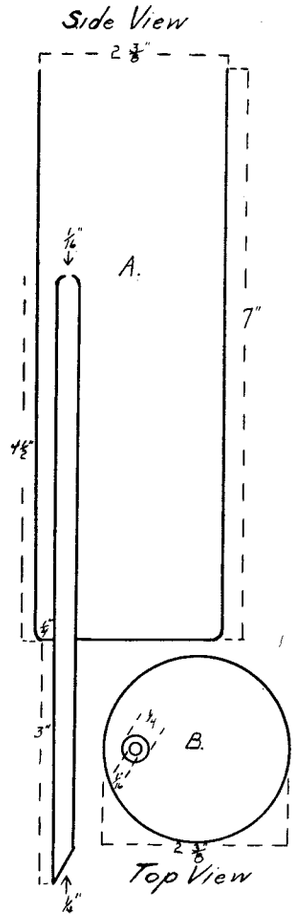

Figure 8.—Diagram of Schurecht overflow volumeter.

number of these volumeters may be set up in a battery to prevent delay due to the time required for draining.

E. F. Goodner* describes a satisfactory direct reading mercury volumeter that can be readily constructed from ordinary laboratory material.

POROSITY

Definition. *Porosity* may be defined as the volume of the pore-space between the clay particles expressed as a percentage of the total apparent volume of the clay. In the dry, unburned sample this is an index to the size of the particles. The maximum porosity would be found in a clay consisting entirely of spherical grains of uniform size. Such

*J. Am. Cer. Soc. 4, p. 288 (1921).

clays are practically unknown, and the porosity is found to vary with the shape, size, and size distribution of the clay particles. Thus two clays of the same porosity may differ greatly in grain size. The coarse grained clay absorbs water much more rapidly than the fine grained clay of the same porosity.

Porosity influences the amount of water absorbed by the clay, or the amount necessary to make a plastic mass. This in turn largely determines the air shrinkage. Large pores permit rapid absorption and rapid drying.

Porosity of the burned clay is a very important property. It is in many ways a good measure of the hardness and stage of burning, because as the sample approaches vitrification the pores close up, decreasing the porosity. The crushing strength of clay products increases as the porosity decreases, until the vesicular structure is developed.[1] The compressive strength seems to increase rapidly as the porosity is decreased below 3 or 4 per cent (.03-.04) and less rapidly as the porosity is decreased to this value.[2] In most products low porosity is desirable to increase resistance to the weather. If porous, the product will absorb water that expands on freezing. If the pores are large the pressure exerted by the expanding freezing water will be relieved by extruding small ice crystals through the pores, but if the pores are small the pressure may be so great as to rupture the ware. If burned to vitrification or if the clay has a fine close texture the porosity may be so small that not enough water will be absorbed to cause any damage.

Determination. The apparent porosity of the clay in either the raw or burned condition is determined from the following formula:

$$P = \frac{Ws - Wd}{S \times V} \times 100$$

where P = apparent porosity in per cent
Ws = weight of saturated test pieces in grams
Wd = weight of dry test piece in grams
S = specific gravity of oil used to saturate the test piece.
V = volume of saturated test piece in cubic centimeters.

In testing burned clay distilled water may be used instead of oil and S may be taken as unity.

In saturating the burned clay care must be taken that the test piece is thoroughly saturated.[3] The method usually employed is to boil the weighed test pieces in distilled water for two hours in a suitable vessel so that the test pieces do not come into contact with the heated bottom

[1]G. H. Brown, Trans. Am. Cer. Soc. XIV, p. 292 (1912).
[2]A. V. Bleininger, Trans. Am. Cer. Soc. XII, p. 564 (1910).
[3]Washburn and Bunting, J. Am. Cer. Soc. 5, p. 48 (1922) recommend methods for insuring saturation.

of the container and are completely covered by the water. The test pieces are cooled to room temperature while still immersed in the water. When cooled to 20°C. each test piece is carefully removed, dried lightly with a damp towel to remove the excess water and weighed. The test piece is then again immersed in distilled water until its Volume (V) is determined in the volumeter.

Washburn and Bunting[1] describe a method of measuring porosity by measuring the volume of air given off from the ware when under a reduced pressure. This method avoids wetting and drying and is reported to be accurate. The same authors also describe the use of the McLeod gage in determining the porosity of highly vitrified bodies,[2] and the application of this principle to an apparatus for determining the porosity of full sized brick.

E. W. Washburn[3] describes a method for measuring the pore size distribution in porous material by measuring the amount of mercury forced into the pores at different increasing pressures.

Absorption is generally expressed as the weight of water absorbed per unit weight of dry test piece. The same information is supplied by porosity as determined above.

Dry clay will absorb water from calcium chloride or concentrated sulfuric acid and this water may introduce an error in the dry weight of two per cent; but immersion in water, even under reduced pressure, is inadequate to complete the absorption of water.

SPECIFIC GRAVITY

Specific Gravity is a factor of slight economic importance, but is of use in some calculations and as an aid in determining other properties. In a number of tests on clays reported by different investigators, the values for specific gravity determined by different methods show very poor agreement.[4]

There are three different kinds of specific gravities:

1. *The Bulk Specific Gravity* is computed by dividing the weight of the dry test piece in grams by its volume in cubic centimeters.
2. *The Apparent Specific Gravity* is obtained by dividing the weight in grams by the volume less the volume of water or oil which can be soaked up by the pores.

[1]J. Am. Cer. Soc. 5, p. 112 (1922).
[2]J. Am. Cer. Soc. 5, p. 529.
[3]Proc. Nat. Acad. Sciences 7, p. 115 (Abst. in J. Am. Cer. Soc. 4, p. 1003).
[4]N. J. Geol. Surv. Final Report Vol. VI, p. 114 (1904).
N. J. Geol. Surv. Report on Clays, 1878.
Ia. Geol. Surv. Vol. XIV, p. 116 (1904).
Mo. Geol. Surv. Vol. XI, p. 562 (1896).

$$\text{Apparent Sp. Gr.} = \frac{Wd}{V - (Ws - Wd)}$$

Where Wd = dry weight of test piece in grams
V = volume of test piece in cu.cm.
Ws = weight of test piece saturated with distilled water.

3. *True Specific Gravity* is the specific gravity of the finely ground clay as determined by a pycnometer of the usual type. The clay is finely ground so as to possess no voids that cannot be filled by the water.

While the clay remains porous or only partially vitrified, its pores or voids are very largely permeable by water if boiling or a vacuum be relied upon to remove the air from the pores. Under these conditions the apparent specific gravity closely approximates the true specific gravity. When fusion progresses to the point of sealing up the voids, or creating new blebs by evolution of gas from within the viscous matrix, the gas in the voids cannot be replaced by water and the apparent specific gravity is less than the true specific gravity.

The apparent specific gravity is the most useful of the three. If, in burning a clay, the apparent specific gravity decreases rather suddenly, the clay is certainly deteriorating in structure, because the decrease in apparent specific gravity is caused by the growth of sealed blebs or cavities indicating the development of a pasty, sticky stage of vitrification.[1]

BURNING PROPERTIES

Burning properties of clays are of the greatest practical importance. If the clay has the desired plasticity its value is determined largely by its burning properties.

Factors Affecting Burning Properties. All clays fuse or become liquid at some temperature, that is determined by a number of factors among which the following are probably the most important:

1. The minerals and chemical compounds present in the clay and their melting or fusion points.
2. The relative amounts of the different compounds present as determining the formation of eutectics and eutectic mixtures.
3. The size of grain of the various compounds and minerals as limiting the intimacy of contact between the different compounds.
4. The amount and character of the volatile matter driven off during heating, leaving voids which retard the rate of fusion.
5. The firing conditions, whether oxidizing or reducing, and the rate of firing.

[1]Worcester, Manufacture of Roofing Tiles. Geol. Surv. of Ohio, Series 4, Bull. 11 (1910).

Chemical Composition as Determining Eutectic Mixtures. The effect of different chemical compounds on the fusion of clay is similar to the effect of ordinary salt upon the fusion or melting of ice. Ice under atmospheric pressure melts at 0°C and salt at 805°C. If ice is crushed and mixed with salt some of the ice melts forming a solution of salt and water which is in equilibrium with ice at a temperature below 0°C. This is the familiar "freezing-mixture" from the system, water-salt. The phase equilibrium diagram of this system is shown in figure 9.

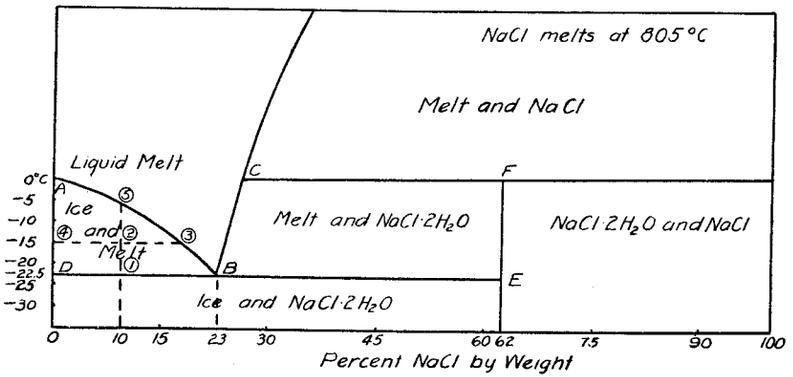

Figure 9.—Phase equilibrium diagram salt water at atmospheric pressure.

Referring to this figure, suppose some salt (NaCl) is added to crushed ice at — 30°C. so that the mixture so formed contains 23% salt. First of all the salt (NaCl) will combine with some water to form the solid hydrate (NaCl . $2H_2O$). This process consists in the water vapor which exists in equilibrium with the ice condensing and uniting with the anhydrous salt to form the hydrate. The system of the two co-existing solid phases, ice and hydrated salt, is then in equilibrium. If this mixture is carefully heated its temperature will rise until — 22.4°C. (B) is reached when the two solid phases begin to melt. As the melt at — 22.4°C. contains 23% of NaCl which is the composition of the solid mixture, the entire mixture of ice and salt melts at — 22.4° C just as if it were a pure substance such as ice. This mixture of ice and salt containing 23% salt is called a eutectic mixture. The word "eutectic" means most easily melted. At the eutectic point (B) the liquid or melt is in equilibrium with a solid mixture of the same composition and the solid melts or the liquid freezes at a definite temperature as if the eutectic mixture were a pure substance such as a water.

If salt is added to crushed ice at — 30°C. so as to form a mixture containing 10% salt, the hydrate (NaCl . $2H_2O$) will form as above; but when this mixture containing 10% salt is carefully heated to — 22.4°C. only enough ice will melt at — 22.4°C. to form a liquid solution containing 23% salt, with all the salt present in the solution. This condition

is indicated by point (1) on the diagram where the composition is 10% salt at — 22.4°C., the equilibrium conditions being a melt, or solution, containing all the salt in a 23% solution, and ice. As this batch containing 10% salt is heated to higher temperatures more ice will melt continuously diluting the solution or melt. At — 15°C. (2) the melt contains all the salt in a solution of about 19% of salt (3) and the solid is ice (4). As heat is added the temperature rises steadily, more liquid is formed, as the solid phase gradually melts until the melt has the same composition as the original entire mixture. At this point — 4°C (5) all the ice has melted and the system consists of a liquid solution containing 10% salt.

Ice melts completely at 0°C. A mixture of ice and salt containing 10% salt begins to melt at — 22.4°C., where about 3/7 of the mixture melts, the melting continues as the temperature rises and is complete at — 4°C. A eutectic mixture (23% salt) melts entirely at — 22.4°C. A mixture of ice and salt containing 40% salt begins to melt at — 22.4°C. but some solid salt remains at temperatures above 100°C.

This brief explanation and diagram of the water-salt system has been introduced to associate the familiar fact that ice melts at a lower temperature when mixed with salt, with the similar properties of mixtures of the refractory oxides.

As clay, the basis of the ceramic industries, consists largely of hydrous aluminum silicates a knowledge of the system silica (SiO_2) alumina (Al_2O_3) at high temperatures is fundamental to an understanding of the burning behavior of the better grades of clay. The equilibrium diagram is shown in figure 10.* Silica (SiO_2) melts at about 1710°C. When mixed with alumina (Al_2O_3) the mixture begins to soften somewhat at about 1545°C. due to the formation of the eutectic containing 5½ per cent of alumina. This eutectic is very silicious and viscous so that the softening of the mixture takes place slowly. The compound sillimanite (Al_2O_3 . SiO_2 or Al_2SiO_5) is not stable above 1050°C. but does not decompose until 1545°C. forming the silicious eutectic melt and the compound 3 Al_2O_3 . 2 SiO_2 because the entire mass is solid and any change in crystal form takes place extremely slowly.

If this mixture of equal molecular proportion of Al_2O_3 . SiO_2 is heated to higher temperatures more and more of the 3 Al_2O_3 . 2 SiO_2 will dissolve in the melt until a temperature of 1810°C. is reached when the compound decomposes into corundum (Al_2O_3) and silicious melt. As the temperature is raised the corundum dissolves in the melt until simply one liquid phase exists. As has been noticed by Bowen and Grieg the compound 3 Al_2O_3 . 2 SiO_2 is much more refractory than sillimanite because the former shows no signs of fusing below 1810°C. while sillimanite begins to soften at 1545°C. These mixtures of silica and alumina

*Bowen and Grieg, J. Am. Cer. Soc. VII, p. 238 (1924).

containing high percentages of alumina are used to form very satisfactory "super refractories." The mixture is fused in an electric furnace to form the stable compound 3 Al_2O_3 . 2 SiO_2 which is then bonded, molded into the desired shape, and burned. Pure corundum (Al_2O_3) does not melt below about 2050°C., but in the pure state a substance is worthless as a practical refractory as it cannot be formed or molded into the desired shape which will be retained, because there is nothing to hold the grains together. If corundum were mixed with a small amount of silica molded into the desired shape and burned at a temperature of 1810°C. or a little higher, some of the melt would form and

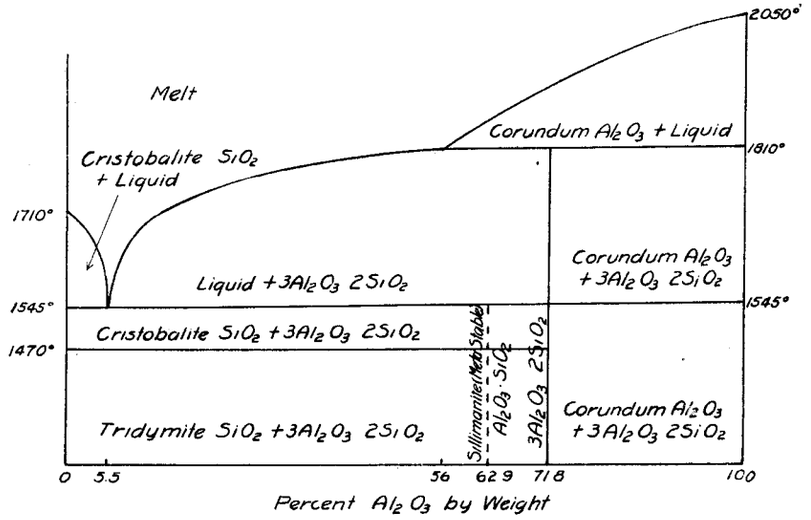

Figure 10.—Phase equilibrium diagram of silica (SiO_2)—alumina (Al_2O_3).

cement the grains of corundum together so that when cooled the mixture would be a well bonded mass of corundum and the compound $3Al_2O_3$. $2SiO_2$. It will be noticed that any mixtures of silica and alumina containing 71.8 per cent or more alumina will begin to show some softening at 1810°C. and any mixture containing less alumina than 71.8 per cent will begin to soften at 1545°C.

Figures 11 and 12 are the equilibrium for the systems lime (CaO)—alumina (Al_2O_3), and lime (CaO)—silica (SiO_2). Figure 13 is from a photograph of a model of the system CaO—Al_2O_3—SiO_2.

A comparison of the diagram of the system CaO—Al_2O_3 (Figure 11) with the diagram of the system MgO—Al_2O_3 (Figure 14) may partially explain why lime (CaO) in clay causes rapid softening and failure of the ware, while magnesia (MgO) does not. The lime-alumina system has eutectics melting at about 1400°C., while the system magnesia-alumina has eutectics melting at 1925°C. and 2030°C. Lime is known to

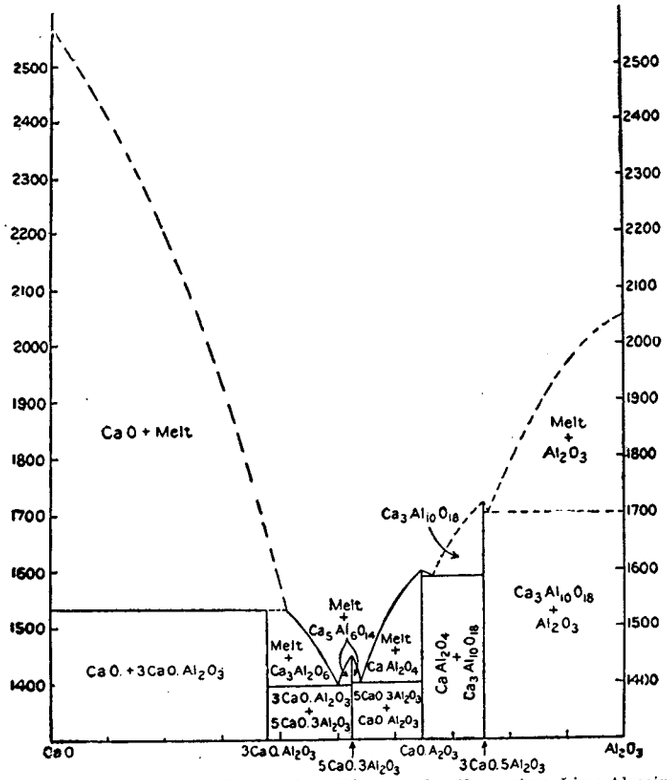

Figure 11.—Concentration-Temperature Diagram for the system Lime-Alumina. (After Washburn).

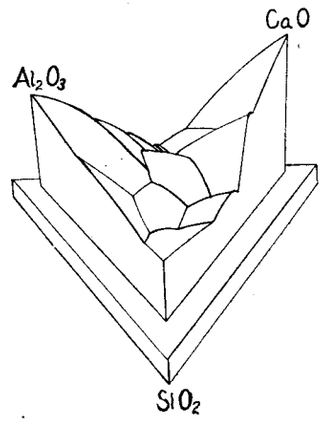

Figure 13.—Phase equilibrium model of the system silica—(SiO_2), lime (CaO), and alumina (Al_2O_3).

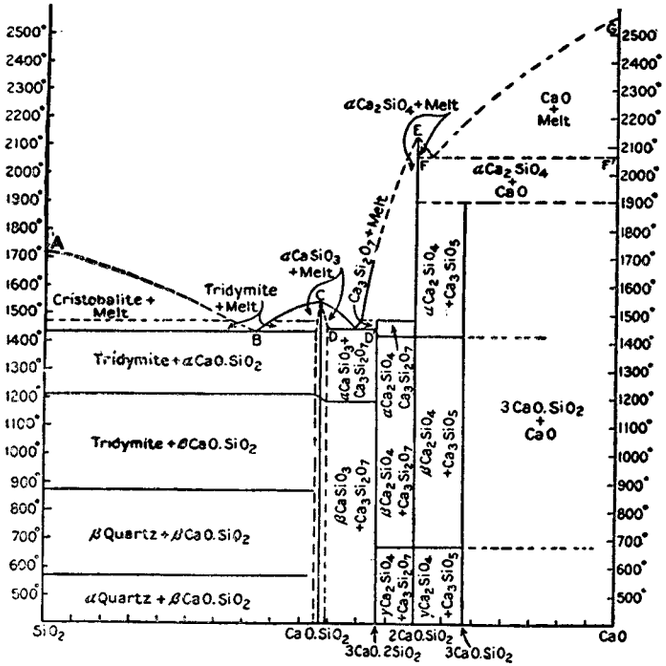

Figure 12.—Concentration-Temperature Diagram for the system Lime-Silica. (After Washburn).

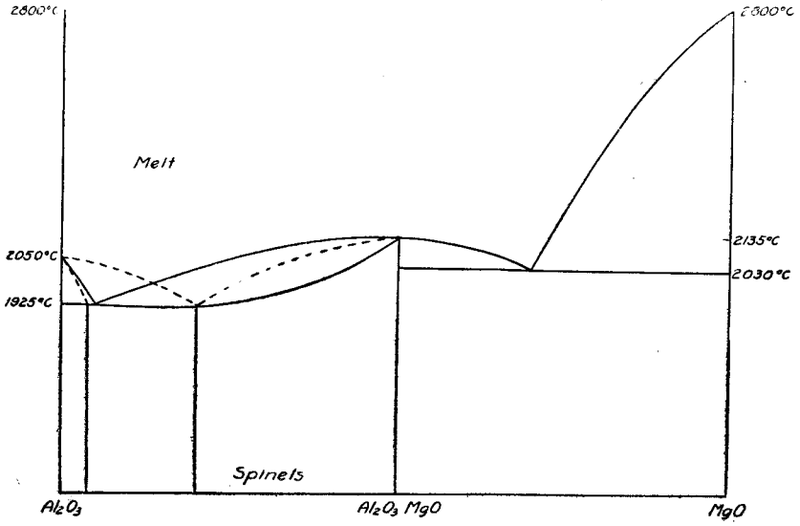

Figure 14.—Phase equilibrium diagram of magnesia (MgO)—alumina (Al_2O_3).

form fluid and corrosive silicates which rapidly attack the ware at low temperatures, while magnesia under the same conditions forms viscous silicates which react slowly.[1]

The melting point of the eutectics of a binary system are generally lowered by the addition of a third substance. This is true with every eutectic in the equilibrium diagram of the system CaO—Al_2O_3—SiO_2 (figure 13). The addition of iron as ferric oxid (Fe_2O_3) will also lower

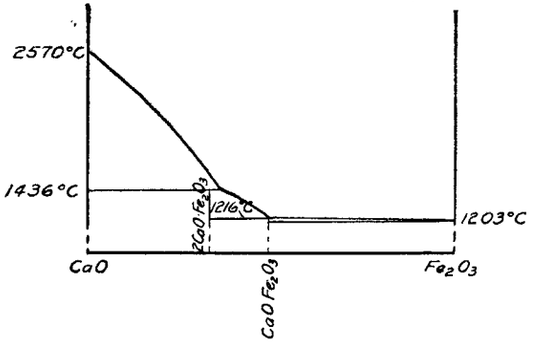

Figure 15.—Phase equilibrium diagram of lime (CaO)—iron (Fe_2O_3).

the melting points of the eutectics and cause the clay containing it to soften at a lower temperature. The same effect is caused by soda (Na_2O) or potash (K_2O) and other so-called "impurities" in the clay.[2]

Grain or Texture. The size of grain or texture of the clay determines largely the speed with which equilibrium conditions are approached. The equilibrium diagrams given above represent the ultimate condition that is permanent at the indicated temperature and composition. In many cases this condition of equilibrium is approached very slowly because the particles in the clay cannot readily react to form the melt, and because the air spaces in the clay act as heat insulation and allow the outside of the ware to be heated more rapidly than the inner parts. Under these conditions the eutectic does not form readily, and softening of the clay may not take place until the melting point of the easily fusible compounds originally in the clay is reached. A fine grained clay will

[1] Rev. Mat. Constr. Trav. Pub. 140, pp. 67-69 B (1921).

[2] For phase diagrams of other ceramic systems and further references see:
A. B Searle, The Chemistry and Physics of Clays, Ernest Benn, London (1924).
Sosman, Trans. Faraday Soc. 12, 170 (1917).
P. Eskola, Am. J. Sci. 4, 331-375 (1922).
Jaeger & VanKlooster, Sprechsaal 52, 256 (1919).
Washburn & Libman, J. Am. Cer. Soc. 3, 634 (1920).
Ferguson & Merwin, Am. J. Science 48, 6 (1919).
Wallace, Trans. Eng. Cer. Soc. 9, 175 (1909-10).
B. A. Rice, J. Am. Cer. Soc. 6, 525 (1923).
A. S. Watts, Trans. Am. Cer. Soc. 19, 453 (1917).
Rankin & Merwin, Am. J. Sci. 45, 301 (1918).
N. L. Bowen, Am. J. Sci. 38, 307 (1914).
Stetzner, Neues Jabert Min. 1, 170 (1882).
Schurecht, J. Am. Cer. Soc. 4, 128 (1921).
Bleininger, Trans. Am. Cer. Soc. 10, 259 (1908).
Ferguson & Buddington, Am. J. Sci. 50, 131 (1920).
Kirkpatrick—Trans. Am. Cer. Soc. 18, p. 575 (1916).

approach equilibrium more rapidly than a coarse grained clay, partly because the particles are in more intimate contact, and, as the formation of the melt due to the reaction between two or more grains begins on the surface of the grains and works inward toward the center, the fine textured clay presents a greater surface for the formation of the melt which then forms more rapidly.

In the early stages of fusion or softening, the clay is a mixture of fused melt supported by a skeleton of solid grains giving a hard porous product with little shrinkage. As fusion proceeds the skeleton of solid grains is dissolved by the melt until the spaces or pores are completely filled, giving a vitrified product with maximum shrinkage and minimum porosity. Any condition, such as fine texture, that allows the melt to form readily will hasten development of the vitrified structure and also the final failure or viscosity of the clay.

Volatile Matter. If relatively large volumes of gas are given off during the formation of the melt in the early stages of fusion, small bubbles will form in the melt, leaving voids which reduce the intimacy of contact and in general have somewhat the same effect as large grains.

Firing Conditions. Firing conditions are very important in influencing the fusion of clays. If the fire is reducing, the iron in the clay will be in the form of ferrous oxide (FeO) which readily forms easily melted mixtures with the other oxides present. For this reason ferrous oxide is frequently spoken of as a "powerful fluxing agent". If the fire is oxidizing the iron is oxidized to the ferric condition and is present as ferric oxide (Fe_2O_3) which forms eutectics that melt only at higher temperatures than those composed of ferrous oxide. For this reason ferric oxide (Fe_2O_3) is considered a "less powerful fluxing agent" than ferrous oxide (FeO). Unless the fire is oxidizing, carbonaceous material and sulphides will not be destroyed. Both of these materials cause early failure of the clay in forming easily fusible mixtures and in giving off large volumes of gas at temperatures well within the proper burning range of the clay, prematurely developing viscous bleb structure with extreme bloating of the clay to two or three times its normal size. Reducing conditions in the fire generally tend to develop early failure of the clay.

If the firing is forced so that the temperature rises very rapidly sufficient time is not allowed for the melt to form until the temperature is above that indicated in the equilibrium diagrams. On the other hand, when the clay is fired rapidly even under oxidizing conditions and sufficient time is not allowed for the carbonaceous matter or the sulphur to be oxidized, these materials, if present in the raw clay, will cause early failure. Rapid firing, within limits, of thoroughly oxidized ceramic material free from iron, such as is used to make up the pyrometric cones, delays softening to higher temperatures.[1]

While the rate of firing is very important, the prime importance of temperature and equilibrium conditions must ever be kept in mind. Bleininger and Boys[2] found that temperature is more important than time in the vitrification of shale. Lemon Parker[3] noticed that pressure has an influence causing earlier and more dense vitrification.

K. Endell[4] describes the uses of the Leitz thermal microscope for studying vitrification.

Effects of Burning. The softening of a clay usually takes place slowly over a rather wide temperature range, as the eutectic forms slowly and usually in small amounts which gradually increase as the temperature is raised. If the burning of a clay is discontinued at a temperature slightly above that at which the melt begins to form and the clay has softened sufficiently to make the grains stick together so as to prevent the recognition of any except the larger grains, but not sufficiently to close up all pores of the mass, the clay is said to be *hard burned,* or burned to *incipient vitrification.*[5]

If the burning is continued further for about 20° to 120°C., or in some cases even more, some of the grains dissolve in the melt. The melt becomes less viscous as the temperature is raised, so that all the pores are finally closed, rendering the mass impervious. The cold ware then shows a smooth fracture with a slight luster. Clays burned to this condition representing the maximum shrinkage and minimum porosity are completely *vitrified.*

A still further but variable rise in the temperature causes the clay to warp and sag, slightly at first but more so as the temperature is raised, and to swell or blister and soften until it flows or becomes *viscous,* as most of the solid grains are dissolved in the melt; chemical reactions take place which give rise to the gas bubbles, causing the clay to swell giving it a vesicular structure evident on breaking.

To recognize precisely the exact attainment of these three conditions is often difficult, as the clay may soften so slowly that the change from one to the other is very gradual and continuous. *Incipient vitrification* is usually recognized by the clay becoming so hard that it cannot be scratched with a knife. This corresponds to a hardness of 6 to 6.5 on Mole's scale. The difference in temperature between the points of incipient fusion, or incipient vitrification, and viscosity varies from about 30°C. in calcareous brick clays to about 300°C. in refractory clays such

[1]Rieke, Sprechsaal Vol. 40, Nos. 44, 45, 46, Trans. Am. Cer. Soc. X, p. 314 (1908).
A. V. Bleininger, Trans. Am. Cer. Soc. X, p. 259, 1908.
L. I. Dana, Paul D. Foote, Chem. Met. Eng. XXII, p. 23 (1920).
[2]Trans. Am. Cer. Soc. XII, p. 387 (1911).
[3]Trans. Am. Cer. Soc. XIV, p. 822 (1912).
[4]Met. and Erz. XVIII, No. 8 (1921).
[5]Wheeler, Mo. Geol. Survey Vol. XI, p. 130 (1896).

as are used in making glass pots. This temperature range between incipient vitrification and viscosity is generally called the *burning range* because the most valuable products are usually obtained by burning the clay to incipient vitrification or complete vitrification. If the temperature of complete vitrification is exceeded the clay fails due to the formation of the vesicular structure accompanied by swelling and warping.

If the burning is continued beyond viscosity, all of the particles are finally completely dissolved in the melt which becomes thin enough for the gases set free by the chemical action to escape, and the clay resembles so much slag. It is then said to be *completely fused* and on cooling gives a dense compact stony or vitreous fracture. Some clays fuse completely to a good glaze at low temperatures and are used as slip clays for glazing.

Frequently the term fusibility is applied to the softening of clays produced by heating. This softening is so gradual and indefinite that the fusion of clay differs greatly from the melting of any pure substance.[1]

Many of the terms used in describing the burning and fusion of clays may appear confusing. For this reason the following brief explanation of the common terms is included:

Fuse, as a verb, to become liquid by the influence of heat, a general term to cover fusion taking place at a definite temperature as the melting of a pure substance and readily recognized, or fusion proceeding over a wide temperature range so slowly as to be barely preceptible.

Fusible, capable of fusing.

Fusibility, quality of being fusible.

Melt, as a verb, to change from solid to liquid, usually a distinct change in phase from solid to liquid.

Melt, as a noun, a melted mass.

It will be noticed that "fusion" is the act of becoming a liquid under the influence of heat, and that "melting" is the act of changing from a solid phase to a liquid phase. These two terms are frequently used interchangeably. At other times a distinct difference in meaning is made by limiting the use of "melting" to that particular type of fusion which is initiated and completed at the same temperature such as the fusion or melting of a pure substance (ice) or a eutectic, as distinct from the fusion (not melting) of a mixture of substances, such as butter, ice-cream, or brick-clay, which has no definite melting point but softens slowly over a wide range in temperature.

Vitrify, to become glass or a glassy material by heat or by fusion.

Virtrification, act of vitrifying or becoming a glassy material.

[1]See R. C. Purdy, Trans. Am. Cer. Soc. XIII, p. 75 (1911), for a discussion of fusion of clay and H. F. Staley, Trans. Am. Cer. Soc. XIII, p. 668 (1911) for a discussion of melting points and deformation point eutectics.

Viscous, adhesive or sticky, yielding continuously but slowly to the smallest stress. "When the smallest stress, if continued long enough, will cause a constantly increasing change of form, the body must be regarded as a viscous fluid, however hard it may be."—Clerk Maxwell, Heat, p. 276.

Viscosity, a state of being viscuous.

A number of attempts have been made to express the fusibility or softening of clays as a function of their chemical composition.[1] Such methods are very unreliable as they usually ignore the physical condition of the clay and apply rather arbitrary rules as to the effect of the different oxides on the softening temperatures. Moreover a complete chemical analysis of the clay must be available in order to apply any of the suggested formulas and it is usually easier to make a complete burning test and determine the burning properties of the clay directly and accurately than to make a complete chemical analysis, let alone trying to guess the burning properties from the analysis.

The physical condition of the clay is also a very important factor in determining its softening on heating. Unless the particles of the different chemical compounds are uniformly distributed through the mass they cannot produce their maximum effect in forming easily melting or eutectic mixtures. For this reason *homogeneity*[2] is frequently given as a factor influencing the burning properties of a clay.

Method of Measuring Fusibility. From what has been said concerning the effect of firing conditions upon the softening and burning of clay, it is evident that simple temperature measurements, although the most important consideration, are not entirely adequate in defining the burning conditions under which a test piece of clay is burned or fused. The chemical composition of the gases and the rate at which the temperature is raised are also important considerations.

At the present time the most modern forms of temperature measuring devices (i. e. pyrometers), and the very old methods, are used in the ceramic industries. Among the oldest methods is Wedgewood's pyroscope based on the contraction of clay as the temperature rises. However the contraction of the clay is not uniform and occurs only over a limited range. While Wedgewood's method, which served its purpose until better methods were available, has been abandoned, the same principle is used in the "Veritas firing system."[3] When these firing

[1]Bischof—Die feuererfesten Thone, p. 71 Leipzic (1876).
Dingler's Journal CLXV, p. 378.
Richter—Dingler's Journal CXCI, p. 59 (1868).
Seger—Tonindustrie Zeitung, p. 290 (1877); p. 332 (1889); p. 339 (1893).
Cramer—Tonindustrie Zeitung No. 40, 41 (1895).
Ludwig—Tonindustrie Zeitung XXVIII, p. 773 (1904).
Simons—Sprechsaal No. 29, p. 390 (1907); No. 30, p. 402 (1907).
Wheeler—Mo. Geol. Survey XI, Clay Deposits, p. 146 (1896).
Flach—Sprechsaal No. 44, pp. 171-3, 187-9, 205-7, 219-21.
Montgomery and Fulton, Trans. Am. Cer. Soc. XIX, p. 303 (1917).

[2]Ries, Clays, Occurrence, Properties, and Uses, p. 174, John Wiley & Sons.

[3]U. S. Bur. of Standards Paper No. 40 (1914).

rings are made of the same mixture as the clay ware, the effects of time and kiln gases on the clay are partially reproduced on the firing ring.

The melting points of metal alloys were developed to indicate the temperature scale from the melting point of silver through that of gold, palladium up to the melting point of platinum.[1] These metals are alloyed and hammered into small cubes and cones (¼ to ½ inch high) and carefully placed in the furnace so that they cannot mix when melted. When cold they can be hammered into their original shapes and reused. These metal alloys represent the true temperature more accurately than Seger's cones, but they are not influenced by the rate and condition of firing, and therefore do not possess that peculiar advantage common to the cones and rings made of ceramic material in being affected by firing conditions in much the same way as the ware being burned. For this reason as well as the inconvenience and expense involved, these metal alloy pyroscopes are now obsolete.

Bischof[2] tried to measure the fusibility of a clay as the amount of a mixture of equal parts of pure silica and alumina required to increase the refractoriness of a definite amount of clay up to that of cone 36. Hofman and Demond[3] tried a somewhat similar method of adding calcium carbonate and silica to refractory clays, and silica and alumina to brick clays. Later Newell and Rockwell[4] developed the same idea using cone 26 as standard with more satisfactory results. These methods are mainly of historical interest as they are impossible for control of burning, or routine testing.

Pyrometric Cones. An improvement over Wedgewood's pyroscope was announced in 1886 by Seger[5] who had constructed a series of fusible cones, (small tetrahedra) of different mixtures of washed Zettlitz kaolin, Rörstrand feldspar, Norwegian quartz, and Carrara marble. At that time (1886) no practical pyrometer was available to the ceramic industry for measuring the temperatures attained in the different kilns, and Seger suggested the use of these fusible cones for practical comparison of the firing temperatures attained in the ceramic industries. The cones were prepared by moistening the dry finely ground mixture with a solution of arabic gum, forming it into triangular pyramids 5 cm. (2 in.) high with the side of the base 2 cm. (0.8 in.) long.[6]

[1]Lauth & Vogt, Thonind. Zeit. XI, p. 81 (1887).
[2]Dingler's Polyt. Jour. Vol. CXCVI, p. 438, 525; CXCVIII, p. 396.
[3]Trans. Am. Inst. Min. Engrs. XXV, p. 3 (1896).
[4]Trans. Am. Inst. Min. Engrs. XXVIII, p. 435 (1899).
[5]Thonindustrie—Zeitung X, No. 14, p. 135 (1886).
[6]Seger, Thonindustrie Zeitung X, No. 15, p. 145 (1886).

The modern cones are about 2½ inches high and ½-¾ in. on the base. In use the cones are mounted in fire clay so that one of the long sides is vertical. The temperature or firing conditions corresponding to the fusing point of a cone are reached at the instant the cone is so warped that the tip of the cone has bent over and touched the horizontal plane on which the base of the cone rests. In order to associate this temperature scale expressed in cone numbers with the more usual scale in degree centigrade, Seger[1] took the fusing temperature of cone No. 1 as about the same as that of an alloy containing 90 per cent gold and 10 per cent platinum, or about 1145°C. Cone 20 softened at about the highest temperature attained in a porcelain kiln which Seger supposed to be about 600°C. above cone 1. He then suggested that each cone from 1 to 20 be taken as representing an equal interval of temperature or 30°C. above the cone of the next lower number. In testing his cones, however, Seger[1] noticed that when his cones were placed in a kiln fired under uniform conditions, cones 1, 2, 3, and 4 went over in about equal intervals or 10 to 15 minutes, cones 5, 6, and 7 in 5 minute intervals, and the more refractory cones of higher number in ¼ to ½ hour intervals. Seger noted that cones 5, 6, and 7 have about the same softening point and that the cones do not actually indicate the temperature in degrees, but suggested their use as of great practical aid in the industry. In 1886[2] Seger announced that the cones could be obtained for 5 Mks. per 100 (about 1 cent apiece). Apparently urged to designate the temperature represented by the softening of each cone Seger[3] reluctantly published the temperature of each cone from 1 to 20, beginning with cone 1 at 1150°C. and each succeeding number representing a temperature 29°C. above the previous one up through cone 20, indicating a temperature of 1700°C. The system was soon extended to cone 36 supposed to melt at 2180°C.

These temperatures given by Dr. Seger are purely arbitrary and therefore meaningless as indicating the temperature on the standard centigrade scale. The cone scale of temperature is affected by rate of heating and composition of the kiln gases as well as by the temperature proper (Tables I & II).

[1]Thonind. Zeitung X, No. 17, p. 168 (1886).
[2]Thonindustrie Zeit. X, No. 22, p. 217 (1886).
[3]Thonind. Zeit. X, No. 23, p. 229 (1889).

TABLE I

Softening Points of Cones, °C.*

Cone.	Rate of heating °C/hour.			
	42.5	27.5	20.0	12.5
010	885	885	880	910
09	920	930	950	890
08	950	970	970	965
07	960	975	950	970
06	990	1,000	990	995
05	1,015	1,035	1,025	1,030
04	1,040	1,055	1,040	1,045
03	1,055	1,065	1,050	1,050
02	1,065	1,070	1,065	1,060
01	1,080	1,080	1,080	1,070
1	1,100	1,085	1,090	1,070
2	1,110	1,090	1,100	1,075
3	1,120	1,110	1,110	1,080
4	1,130	1,125	1,115	1,090
5	1,140	1,135	1,125	1,110
6	1,170	1,140	1,135	....
7	1,185	1,155	1,140	1,125
8	1,200	1,170	1,160	1,150
9	1,230	1,190	1,180	1,190

*Brown and Murray, U. S. Bur. Stand. Tech. Paper No. 17.

TABLE II.

Softening Temperatures, °C. of Cones in Various Atmospheres.*

Cone No.	Per cent of Fe_2O_3 in cone formula.	Softening temperatures in—			Differences H_2-H_2O and CO-CO_2 atmospheres.	H_2-H_2O and air.
		Atmosphere of equal parts of H_2 and H_2O.	Atmosphere of equal parts of CO and CO_2.	Air.		
06	8.52	1,018	1,026	1,040	+ 8	+22
04	8.54	1,089	1,062	1,085	−27	− 4
02	8.57	1,119	1,119	1,178	0	+59
1	8.58	1,146	1,164	1,182	−18	+36
2	4.38	1,165	1,170	1,181	+ 5	+16
4	None	1,221	1,240	1,250	+19	+29
6	None	1,281	1,292	1,286	+11	+ 5
8	None	1,332	1,330	1,366	− 2	+34
10	None	1,358	1,340	1,334	−18	−24
12	None	1,358	1,370	1,367	+12	+ 9

*Fieldner, Hall, and Field, U. S. Bur. Mines Bull. No. 129 (1918).

These effects are greater and more irregular for cones melting in the lower ranges, as developed by Cramer[1] and Hecht,[2] because of the admixtures of reducible and volatile fluxing agents. The fact that the effects of time and of kiln gases on the softening of cones are somewhat similar to the effects of these variables on the progress of firing the ware is generally assigned as the reason for the successful and continued use of the pyrometric cones. They do not, however, give an accurate measure of either of these effects for they are never of the same material as the ware being fired. The real reasons for the wide use of cones, instead of the more modern types of pyrometers, are probably that the cones are cheap, easily used even in inaccessible places by ordinary workmen, and are very satisfactory in commercial use for controlling the burning process, in spite of their many serious shortcomings when used for measuring temperature.

The unfortunate attempt to indicate the temperature of softening of the cones has caused a great deal of confusion and discussion[3]. The cones are usually given as made of the following mixtures and softening at the indicated temperatures which vary 100°C. or more depending upon firing conditions.

[1]From No. 1 at 1150°C, in supposedly regular intervals of 19°C, down through No. 010 (or 1-10), at about 960°. Tonindustrie Zeit. XVI, p. 155 (1892).

[2]Thonind, Zeit. XI, p. 185 (1887); XII, pp. 73, 85 (1888).

[3]Bischof, Thonindust. Zeit. XI, pp. 42, 81 (1887).
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