DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 22

EFFECT OF OVERFIRING UPON THE STRUCTURE OF CLAYS

BY

A. V. BLEININGER, Ceramic Chemist

and

E. T. MONTGOMERY, Laboratory Assistant

Bureau of Standards

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CONTENTS

I. INTRODUCTION

1. CAUSE OF VESICULAR STRUCTURE

Clays, like rocks of all kinds, contain considerable amounts of gaseous constituents in the form of dissociable compounds, occluded and dissolved gases. During the firing constant evolution of gas takes place. In the earlier stages the hygroscopic water is expelled as steam, followed later by the combined water of the clay substance, carbon dioxide from the combustion of carbon, and the dissociation of carbonates, sulphur di- and trioxide from pyrites and gypsum, oxygen due to the reduction of ferric oxide. On the other hand, during the firing, absorption of air, hydrocarbons and other gases may occur at times while the temperature is constant or is temporarily lowered.

The firing of clays brings about a decrease in the initial pore space, a process which as it approaches completion is called vitrification. This closing up of the pore space is caused by the softening of the mass and the effect of surface tension which operates to bring about a condition of minimum surface area.

The progress of vitrification then can be followed by means of porosity determinations, provided the structure of the material in question is sufficiently open to allow of the ready escape of the gases evolved. If at any time the evolution of gaseous matter is rapid enough so that pressure is produced within the clay, bloating is certain to take place and a vesicular structure will be formed.

2. OPEN AND INCLOSED PORE SPACE

Assuming that normal conditions prevail and that vitrification progresses steadily, one aspect of the decrease in porosity must receive attention. Starting with maximum porosity immediately after the dehydration of a clay it is found that the total pore space is practically measured by the volume of water absorbed in vacuo. This indicates that the pore system is open and the capillaries communicate with each other. During vitrification some of the fine channels are closed and thus cut off a portion of the pore space. The system therefore is no longer open and must be divided into open and inclosed pore space. Gas evolved within one of the inclosed pores must break its way through the walls in order to escape. Since the viscosity of most clays still remains very considerable, it is readily seen that gas vesicles may be under considerable pressure before they are released, when they leave behind greatly enlarged spaces. Anywhere throughout the clay mass, especially in connection with cavities left during the molding, gas accumulations may occur.

The practice of "oxidizing" the clays, so well presented by Orton in his valuable researches, thus becomes a matter of primary importance. The oxidation stage consists in holding the clay at a practically constant temperature, surrounded by an excess of air, between 750° and 800° C until all of the carbon is consumed, the sulphides are decomposed, and any ferrous oxide is changed to the

ferric form. But even though the oxidation has been completed, clays differ widely as regards their tendency to give off further gases, a condition aggravated by the presence of sulphates which are not completely decomposed during this stage of the burn.

Owing to the fact that the presence of gaseous matter likely to be evolved throughout vitrification is always objectionable, due to the serious effects upon the final structure of the clays, causing a general decrease in strength and impermeability, it is evident that clays containing the smallest amounts of such matter are by far the safest and most valuable ones.

3. VITRIFICATION BEHAVIOR OF CLAYS

It is important, therefore, that methods of testing be employed which bring out clearly the qualities in question. From the practical standpoint this question concerns chiefly dense products like paving blocks, sewer pipe, porcelain, stoneware, etc., where serious harm may be done by the overdevelopment of vesicular structure.

Considered from this standpoint, clays might be divided into the following classes as regards the character of structure developed during the highest burning temperatures:

1. Open structure; no vitrification possible.
2. Sound vitrification, with no immediate development of vesicular structure.
3. Vesicular structure developed before vitrification; sound vitrification impossible.
4. Vesicular structure developed, coincident with or immediately after vitrification.

The first group of materials consists principally of the pure clays kaolins, flint clays, etc., or silicious clays in which the amount of fluxing material is insufficient to bring about vitrification. Owing to the open pores the development of vesicular structure is impossible.

The second group embraces the most valuable and useful clays and represents the best types of paving-brick shales, stoneware clays, and similar materials burning to an impervious structure.

In the third class are represented those shales and clays which show a decided development of vesicular structure before vitrification has been completed. This is especially true of many shales which fail to make satisfactory paving blocks. In the preliminary testing of shales this matter does not receive the attention it deserves, as is indicated by the frequent attempts to use materials of this description in the industry.

In the fourth class, clays are found which either offer the same difficulties as the third group or possess such a short vitrification range that their proper firing under commercial conditions becomes practically an impossibility.

In the development of vesicular structure both the physical constitution of the clay, as regards compactness and fineness of grain, as well as the mode of shaping, are of as great, if not greater, importance than the amount of constituents present which form gases. It is obvious that a silicious clay will be able to release more of the gaseous material than one of dense and close structure. Similarly, a dust-pressed body is more open than a plastic molded one.

II. DESCRIPTION OF WORK

The subject of vesicular structure has received the consideration of several workers. Purdy especially has called attention to its importance in several of his investigations, although actual determinations have been reported only in one paper where a fire clay was made the subject of study.[1]

In the present work six clays were examined and their total and inclosed pore space determined after firing to several temperatures, starting from the point at which good maturity had been reached.

These clays were as follows:

No. 1. Surface clay, weathered shale, Cleveland, Ohio.

No. 2. Surface clay, glacial, Curtice, Ohio.

No. 3. Shale, Galesburg, Ill.

No. 4. Shale, Cleveland, Ohio.

No. 5. No. 2 fire clay, Union Furnace, Ohio.

No. 6. No. 2 fire clay, Kittanning, Pa.

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[1] Trans. Am. Ceram. Soc., 13, p. 602.

Each batch of these clays was tempered to uniform consistency, and all the specimens were molded from the same lump, rendered as homogeneous as possible. The molding was done in brass molds and the trial pieces were practically cubes, weighing about 130 grams in the burnt state. The drying was carried on slowly at room temperature. In burning, a constant temperature increase of 20° C per hour was maintained. Due to the use of natural gas this was easily possible and the heating curve proposed was followed very closely. The temperature measurements were made by means of a thermocouple and a Siemens-Halske recording millivoltmeter. Part of the time a second couple was inserted through the back of the kiln in order to check the uniformity of the heat distribution. Cones were placed in each burn.

The cold junctions were kept in glass tubes cooled in ice water. At each of the selected temperatures three trial pieces were drawn for the purpose of checking the results. Upon drawing, the sets of specimens were cooled in a pot furnace previously fired to a red heat.

The trial pieces were then weighed, saturated with water in vacuo, followed by the usual determination of the suspended and wet weights. An average sample of the briquettes was then obtained, which was pulverized for the estimation of the true specific gravity by means of the pycnometer.

From these values the per cent of apparent porosity was calculated from the relation $100\,(W - D) \div (D \div S_1)$. The pore space is expressed here in terms of the true clay volume, viz, dry weight, divided by the true density. Similarly, the per cent volume of the inclosed pore space was reckoned from the following formula:

$$\frac{100\left(\frac{D}{S_2} - \frac{D}{S_1}\right)}{\frac{D}{S_1}} = 100\left(\frac{S_1}{S_2} - 1\right)$$

In these expressions:

D = dry weight of specimen.

W = wet weight.

S_1 = true specific gravity.

S_2 = apparent specific gravity of saturated piece.

The total porosity, of course, represents the apparent pore volume plus the volume of the inclosed pore space, all of the values being expressed in terms of the true clay volume. It is quite evident that the apparent specific gravity of the piece equals the true specific gravity only under two conditions, viz, when there are no pore spaces or when all of the latter are open and may be occupied with water. The former case is impossible, the latter is frequently realized with open-grained fire brick and similar materials.

In this investigation overburning was studied rather than normal conditions in order to bring out the readiness, varying for different clays, with which they become spongy, and to determine if possible how important a factor the inclosed pore space is in bringing about the swelling. At the same time it seemed desirable to follow the changes in density upon heating the clays beyond the stages of maximum strength and dense vitrification.

III. RESULTS

1. POROSITY DETERMINATIONS

In the following table the results of this work are compiled. Attention might be called at this point to the regularity with which the cones went down in the different burns, which is due to the fact that the same rate of firing was maintained throughout. This emphasizes the importance of associating the softening points of cones with definite rates of heating. It should become common practice to compare cone temperatures on the basis of time-temperature curves.

TABLE 1

Porosity Determinations on Specified Clays and Shales

CLAY NO. 1. CLEVELAND SURFACE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C											
1070	1	148.4	141.3	85.6	2.54	2.53	2.63	13.2	13.4	4.1	17.5
		144.2	137.2	83.0	2.53			13.5			
		143.3	136.3	82.4	2.53			13.5			
1090	2	138.0	132.9	80.6	2.54	2.53	2.61	10.0	9.2	3.1	12.3
		145.0	146.0	84.7	2.53			9.3			
		138.1	133.8	80.6	2.52			8.4			
1100	3	139.7	136.1	80.9	2.47	2.45	2.59	6.8	6.2	5.4	11.6
		140.6	137.6	81.2	2.44			5.7			
		142.3	139.0	82.4	2.46			6.1			
1130	6	149.4	139.7	78.0	2.26	2.31	2.57	17.7	19.3	10.7	30.0
		145.0	136.2	77.6	2.32			16.6			
		148.8	136.2	77.8	2.33			23.7			
1150	7	149.7	135.0	72.8	2.17	2.20	2.55	27.7	28.4	13.3	41.7
		149.8	135.3	73.0	2.17			27.0			
		152.3	135.9	75.5	2.25			30.7			
1170	8	153.8	136.9	77.6	2.31	2.28	2.55	31.4	29.8	12.4	42.2
		148.4	133.2	74.6	2.27			29.1			
		157.3	141.3	78.9	2.26			29.0			
1190	9	158.0	143.2	75.4	2.13	2.13	2.52	26.0	33.4	18.1	51.5
		152.2	134.0	71.0	2.13			34.3			
		160.3	138.1	73.3	2.13			40.0			
1210	10	167.0	140.2	75.6	2.17	2.18	2.51	48.0	50.6	14.7	65.3
		171.5	141.7	77.0	2.19			53.2			
1230	.....	123.4	110.4	59.4	2.16	2.14	2.49	30.0	31.6	15.3	46.9
		177.6	156.6	82.6	2.12			33.3			

93212°—13——2

TABLE 1—Continued

CLAY NO. 2. CURTICE SURFACE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C											
1030	03	114.1	113.8	66.5	2.41	2.41	2.61	0.7	0.7	8.2	8.9
		108.1	107.8	63.1	2.41			.6			
1050	02	113.1	113.0	63.8	2.29	2.27	2.57	.0	.0	15.0	15.0
		109.7	109.6	60.6	2.24			.0			
1070	1	119.8	119.8	52.7	1.79	1.81	2.52	.0	.0	41.0	41.0
		115.0	115.0	50.7	1.79			.0			
		117.2	117.2	54.3	1.86			.0			
1090	2	143.8	116.2	35.5	1.44	1.38	2.515	60.0	47.4	82.4	129.8
		126.2	110.0	28.0	1.34			37.0			
		135.5	114.8	31.5	1.38			45.4			
1100	3	155.8	115.8	37.8	1.48	1.48	2.51	87.0	83.5	71.3	154.8
		152.6	116.0	37.3	1.47			80.0			
		149.6	109.9	37.3	.....			.....			
1110	4	133.1	109.6	29.3	1.36	1.30	2.495	53.4	47.0	92.0	139.0
		127.4	108.5	24.1	1.30			43.6			
		127.0	108.3	20.4	1.23			44.0			
1130	6	163.4	106.3	53.8	2.02	2.02	2.49	134.0	136.0	23.4	159.4
		167.0	107.2	54.1	2.02			139.0			
		174.2	115.4	54.7	.....			.....			
1150	7	154.8	102.7	51.9	2.02	2.00	2.485	126.0	126.3	23.0	149.3
		140.7	94.0	46.8	2.00			123.0			
		165.6	108.8	54.3	2.00			130.0			
1170	8	138.2	95.2	49.6	2.09	2.10	2.485	112.2	112.0	18.4	130.4
		127.2	87.7	46.0	2.10			112.0			
		116.5	80.6	42.6	2.12			111.1			

TABLE 1—Continued

CLAY NO. 3. GALESBURG, ILL., SHALE

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total percent true porosity
°C											
1030	03	143.7	129.3	79.0	2.57	2.56	2.67	30.0	29.0	4.2	33.2
		139.2	126.1	76.7	2.56			28.0			
1050	02	140.4	131.4	78.7	2.50	2.50	2.655	18.2	19.3	6.2	25.5
		141.6	131.5	78.9	2.50			20.4			
1070	01, 1	132.4	125.6	76.9	2.57	2.57	2.635	14.3	14.1	2.5	16.6
		138.4	131.1	80.0	2.56			14.6			
		134.3	127.8	78.8	2.58			13.4			
1090	2, 3	128.2	127.5	73.6	2.36	2.40	2.625	1.5	1.7	9.2	10.9
		125.0	124.1	72.3	2.40			1.9			
		127.1	125.8	73.4	2.40			1.7			
1110	4	127.7	127.5	73.5	2.36	2.35	2.605	.4	.4	11.3	11.7
		128.9	128.8	74.0	2.35			.2			
		128.9	128.6	74.2	2.35			.6			
1130	5, 6	134.5	123.5	70.2	2.32	2.35	2.59	23.0	25.2	10.8	36.0
		137.1	125.2	71.9	2.34			24.6			
		148.1	133.6	77.5	2.38			28.1			
1150	7	150.9	129.0	75.9	2.43	2.41	2.555	43.3	43.6	6.0	49.6
		149.1	127.2	74.4	2.41			43.8			
		143.5	122.6	71.7	2.41			43.7			
1170	8	155.4	129.9	73.9	2.32	2.32	2.535	49.8	48.5	8.7	57.2
		151.8	127.2	72.7	2.33			49.1			
		150.2	126.9	71.8	2.30			46.6			
1190	9	152.5	124.5	69.8	2.28	2.32	2.53	56.9	59.2	8.1	67.3
		155.7	125.7	72.1	2.34			60.3			
		157.7	127.3	73.0	2.34			60.4			
1210	10	179.4	143.7	78.9	2.22	2.20	2.495	62.0	59.2	13.3	72.5
		131.9	106.5	57.9	2.20			60.0			
		108.7	88.9	47.0	2.12			55.5			

TABLE 1—Continued

CLAY NO. 4. CLEVELAND SHALE

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C											
1030	03	131.7	130.4	78.4	2.51	2.51	2.65	3.2	3.3	5.7	9.0
		131.6	130.0	77.9	2.51			3.3			
1050	02	128.6	128.5	75.4	2.42	2.42	2.63	.0	.0	8.7	8.7
		135.2	135.1	79.3	2.42			.0			
1070	01, 1	134.8	134.2	75.4	2.28	2.28	2.595	1.1	1.4	14.1	15.5
		127.9	126.9	70.7	2.26			2.0			
		126.9	126.3	71.7	2.30			1.2			
1090	2, 3	149.4	138.7	70.8	2.04	2.05	2.57	20.0	21.5	24.0	45.5
		135.8	124.6	64.2	2.06			23.0			
1110	4	159.0	133.7	73.6	2.22	2.23	2.565	48.5	49.8	17.0	66.8
		133.6	111.3	62.1	2.26			51.3			
		157.0	131.6	73.1	2.20			49.5			
1130	5, 6	171.6	130.7	71.3	2.20	2.20	2.56	80.4	75.7	18.0	93.7
		158.7	131.3	72.0	2.21			73.3			
		176.7	137.3	74.0	2.17			73.5			
1150	7	194.5	136.9	72.8	2.13	2.13	2.55	107.2	108.1	20.0	128.1
		194.5	134.7	72.1	2.15			111.0			
		188.0	132.7	69.2	2.10			106.3			
1170	8	220.2	132.7	63.0	1.90	1.90	2.53	167.0	165.6	33.2	198.8
		210.8	127.2	61.3	1.92			166.2			
		179.6	109.1	49.6	1.83			163.6			
1190	9	252.3	132.5	52.6	1.66	1.66	2.50	226.4	223.0	51.7	274.7
		247.2	130.7	51.5	1.65			222.7			
		248.6	132.6	53.5	1.67			220.0			

TABLE 1—Continued

CLAY NO. 5. UNION FURNACE NO. 2 FIRE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C.											
		147.1	135.0	79.8	2.44			23.8			
1090	3	142.7	131.9	77.6	2.43	2.45	2.655	22.0	23.7	8.8	32.5
		146.7	133.9	79.8	2.47			25.4			
		142.4	132.3	78.9	2.47			20.0			
1110	4,5	148.8	140.3	81.6	2.40	2.42	2.62	16.0	17.3	9.3	26.6
		144.6	136.4	79.2	2.40			16.0			
		136.6	130.3	75.8	2.40			12.6			
1130	6	142.9	136.5	78.9	2.39	2.39	2.61	12.2	12.3	9.1	21.4
		142.0	136.0	78.5	2.37			12.0			
		134.2	127.5	75.3	2.44			14.0			
1150	7	139.8	133.1	79.0	2.46	2.45	2.60	13.0	13.3	5.6	18.9
		143.6	136.7	81.1	2.46			13.1			
		144.0	137.6	81.6	2.46			12.0			
1170	8	134.5	131.5	74.8	2.32	2.37	2.58	6.0	8.0	10.0	18.0
		142.2	139.1	79.5	2.34			6.0			
		133.7	130.9	74.0	2.30			6.0			
1190	9	129.7	127.7	71.2	2.26	2.27	2.57	4.0	4.6	14.0	18.6
		140.0	138.1	76.9	2.26			3.7			
		147.8	137.5	80.3	2.40			20.0			
1210	10	139.4	130.6	76.0	2.39	2.38	2.55	17.0	17.4	7.4	24.8
		139.0	131.2	75.4	2.35			15.3			
		143.1	130.3	75.6	2.38			24.8			
1230	11	149.4	134.7	78.3	2.38	2.38	2.53	27.6	26.1	7.0	33.1
		151.1	137.0	79.2	2.37			26.1			
		154.2	137.9	79.5	2.36			30.0			
1250	12	149.7	134.6	77.6	2.31	2.33	2.505	30.0	29.3	8.4	37.7
		145.1	130.5	75.2	2.31			28.1			

TABLE 1—Continued

CLAY NO. 4. KITTANNING NO. 2 FIRE CLAY

Temperature	Cone	Wet weight W	Dry weight D	Suspended weight	Approximate specific gravity	Average approximate specific gravity S_2	True specific gravity S_1	Approximate per cent porosity	Average approximate per cent porosity	Per cent true porosity due to sealed pores	Total per cent true porosity
°C.											
		159.0	149.6	90.3	2.52			16.4			
1090	3	145.5	137.1	82.4	2.51	2.51	2.62	16.2	16.2	4.4	20.6
		145.3	137.0	82.3	2.51			16.2			
		149.3	142.6	85.8	2.50			12.2			
1110	4,5	153.5	146.7	88.3	2.51	2.50	2.605	12.0	11.8	3.7	15.5
		148.9	142.8	85.6	2.50			11.1			
1130	6	142.2	136.6	81.8	2.49	2.48	2.58	10.6	9.6	4.0	13.6
		152.7	147.9	87.9	2.48			9.7			
		142.3	138.9	81.9	2.44			6.2			
1150	7	138.5	134.4	79.5	2.45	2.45	2.545	7.7	7.2	4.0	11.2
		154.3	149.8	88.7	2.45			7.6			
		145.2	143.3	83.4	2.39			3.3			
1170	8	143.5	141.7	82.2	2.38	2.39	2.525	3.2	3.4	5.2	8.6
		146.2	144.0	83.9	2.39			3.8			
		140.0	138.9	80.5	2.38			2.0			
1190	9	151.6	150.8	86.9	2.36	2.38	2.520	1.6	2.0	6.0	8.0
		146.0	144.7	83.9	2.38			2.2			
		142.2	141.6	81.4	2.35			1.0			
1210	10	145.1	144.4	83.0	2.36	2.35	2.510	1.2	1.1	6.4	7.5
		147.0	146.3	84.2	2.35			1.1			
		136.2	135.9	76.7	2.30			.5			
1230	11	144.8	144.4	82.1	2.31	2.31	2.495	.7	.5	7.3	7.8
		142.7	142.5	81.1	2.32			.4			
		147.6	146.8	81.0	2.23			1.4			
1250	12	144.3	143.4	79.5	2.24	2.24	2.480	1.5	1.7	11.1	12.8
		146.4	145.1	80.5	2.24			2.2			

In Figs. 1 to 6, inclusive, the results of the porosity determinations are shown graphically. In each figure the ordinates of the lower curve are the inclosed pore space; those of the upper curve are the total pore space; the difference between the two gives the open pore space.

No. 1. Cleveland Surface Clay (*Fig. 1*).—In considering results of this kind it is well to remember that the accidental factors entering into this question are quite prominent. The initial structure of the clay, the method of molding, the rate of heating, the character

of the kiln atmosphere, shorter or longer periods of overfiring, all influence the porosity conditions. In the present case we have minimum absorption (2.4 per cent) and minimum porosity at 1110°, followed by a rather sudden increase in porosity. The clay does not become densely vitrified at any temperature. Overburning begins within one cone of minimum absorption with decided development of vesicular structure. Facts as these clearly show the impossibility of using such clays for the manu-

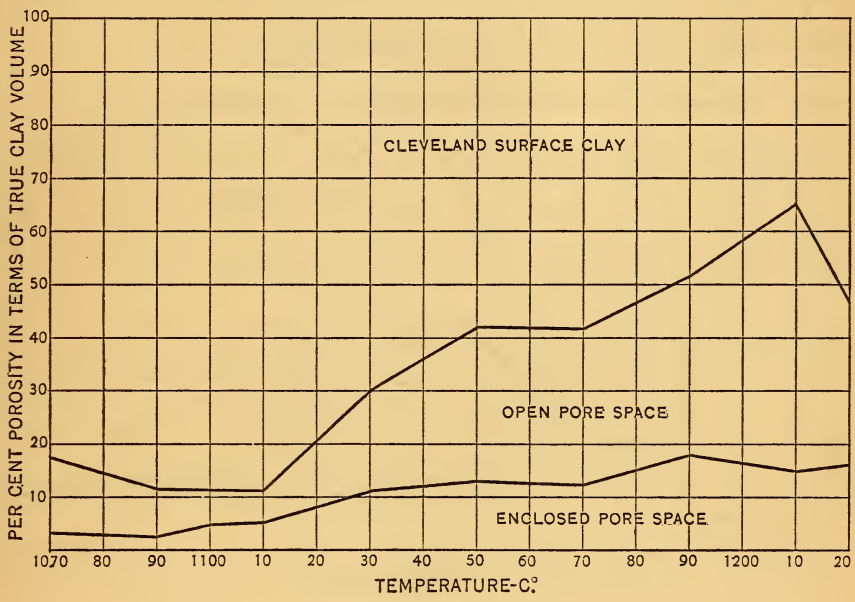

Fig. 1

facture of paving brick. The inclosed pore space also increased, though not so markedly as might be expected from the development of the porosity.

No. 2. Curticè Surface Clay (*Fig. 2*).—The conditions are very similar to those in the preceding case, with the exception that the vesicular structure develops very strongly and then subsides decidedly as the gases escape. In time, of course, still higher temperatures would cause more or less complete expulsion of the gases and reduction of total porosity, so that finally we should have a glass of no apparent porosity but still possessed of a system of inclosed pores.

No. 3. Galesburg Shale (Fig. 3).—This material reaches minimum absorption at between 1090° and 1110°, 0.5 per cent at 1090°, and zero at 1110°. At these points the open pore space is negligible in volume, but the vesicular structure has developed rapidly, beginning with 1070° C. For best results, therefore, the proper burning temperature should not exceed 1090°. The margin of safety of this material has clearly been shown to be small, as is

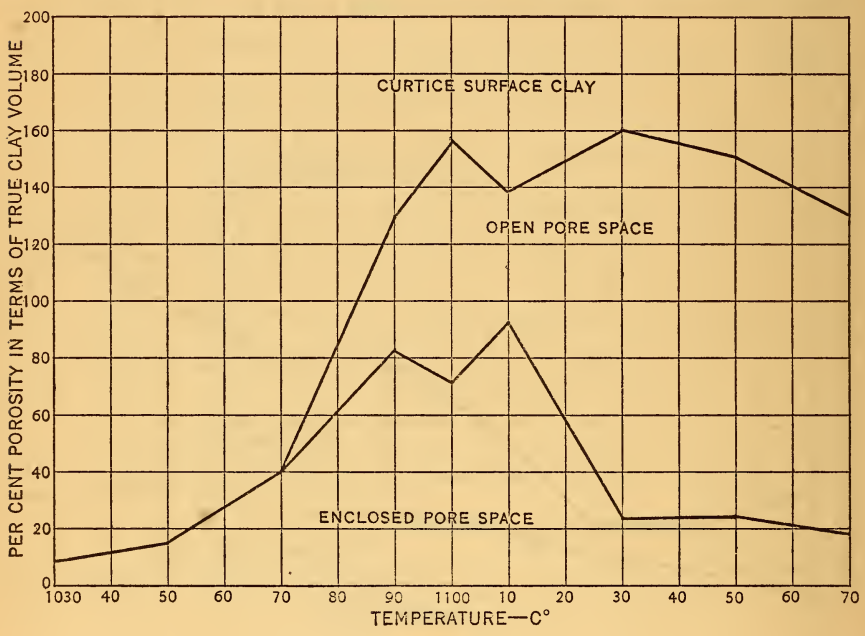

Fig. 2

typical of many Illinois shales. The importance of following the development of the vesicular structure is thus clearly indicated, since the ordinary porosity curve would fail to bring out the weakening influence of the factor in question. It is noted that the inclosed pore space diminishes again, though the total porosity is increased rapidly.

No. 4. Cleveland Shale (Fig. 4).—This material differs markedly from the preceding one inasmuch as the range of nonabsorption is very much longer. It is noted that the pore space represents practically altogether inclosed "bleb" structure up to 1070°.

From this point on the total porosity increases quite rapidly and the inclosed pore space more slowly.

No. 5. Union Furnace No. 2 Fire Clay (Fig. 5).—This clay shows a gradually decreasing total porosity with diminishing absorption,

Fig. 3

interrupted between 1130° and 1170° by the increased vesicular structure. The lowest absorption is 2.14 per cent (in terms of the dry weight) and is reached at 1190°. From this point on the total porosity gains rapidly, although at the same time there is a

marked decrease in inclosed pore space. The diagram shows clearly that this clay can not be vitrified to a dense structure at commercial temperatures and hence would not be suitable for the manufacture of stoneware or similar products.

No. 6. Kittanning No. 2 Fire Clay (Fig. 6).—This material shows a markedly different behavior from the preceding clay of the same

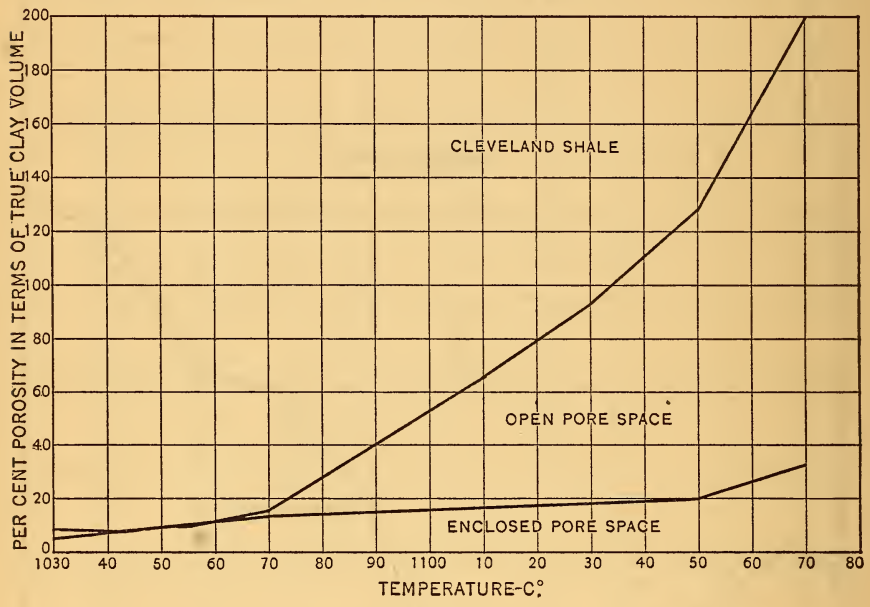

Fig. 4

type. Starting with an absorption of 6.28 per cent at 1090° it reaches practically complete nonabsorption, which condition is retained up to 1250°. At 1250° vesicular structure is developed, although the open pore space is not increased in volume. The diagram shows very strikingly the excellent qualities of this clay and its suitability for all products requiring dense structure and safe firing behavior.

2. SPECIFIC-GRAVITY DETERMINATIONS

The increase in the specific volume of these clays is shown by the tables, as well as by the curves of Fig. 7. It is at once observed that in no case a constant condition has been reached, but that the

density continues to decrease at a steady rate. This is further evidence tending to show that we are dealing here with a state far from equilibrium, which is reached only when complete fusion

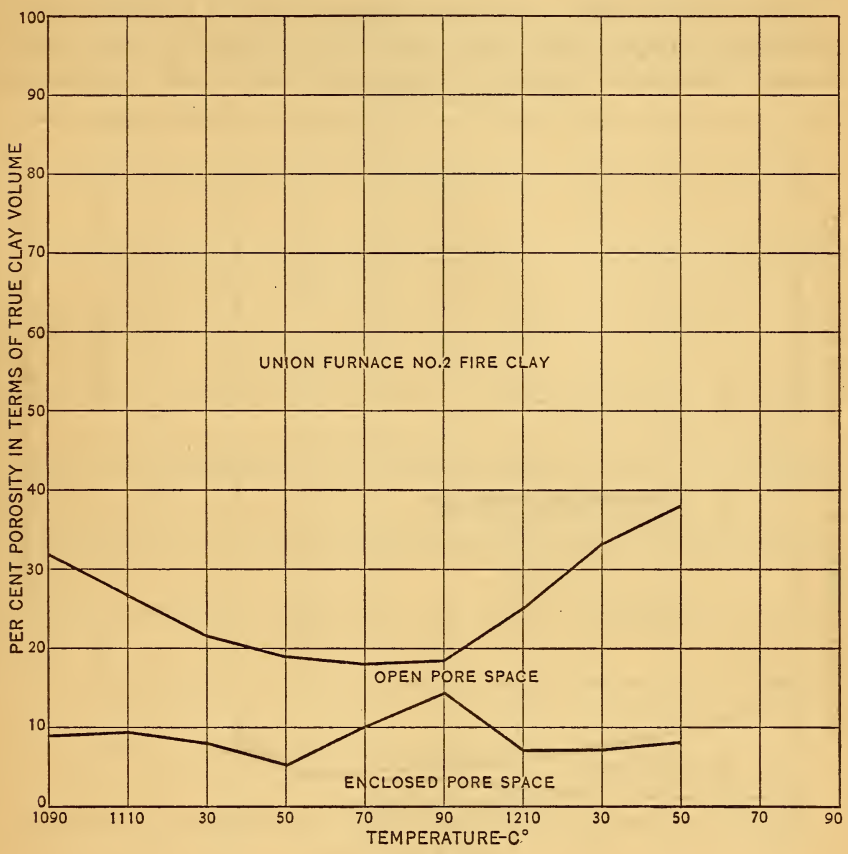

Fig. 5

has been brought about. It is interesting to note the drop on the specific gravities, which are as follows:

Clay	Maximum density	Minimum density	Difference
Cleveland surface clay	2.63	2.49	0.140
Curtice surface clay	2.61	2.485	.125
Galesburg shale	2.67	2.495	.175
Cleveland shale	2.65	2.500	.150
Union Furnace No. 2 fire clay	2.655	2.505	.150
Kittanning No. 2 fire clay	2.62	2.48	.140

IV. EFFECT OF THE CONDITIONS OF SHAPING

1. DESCRIPTION OF WORK

As has already been mentioned, the conditions of molding are of considerable importance, not only with reference to the initial porosity, but also in regard to the density developed at different

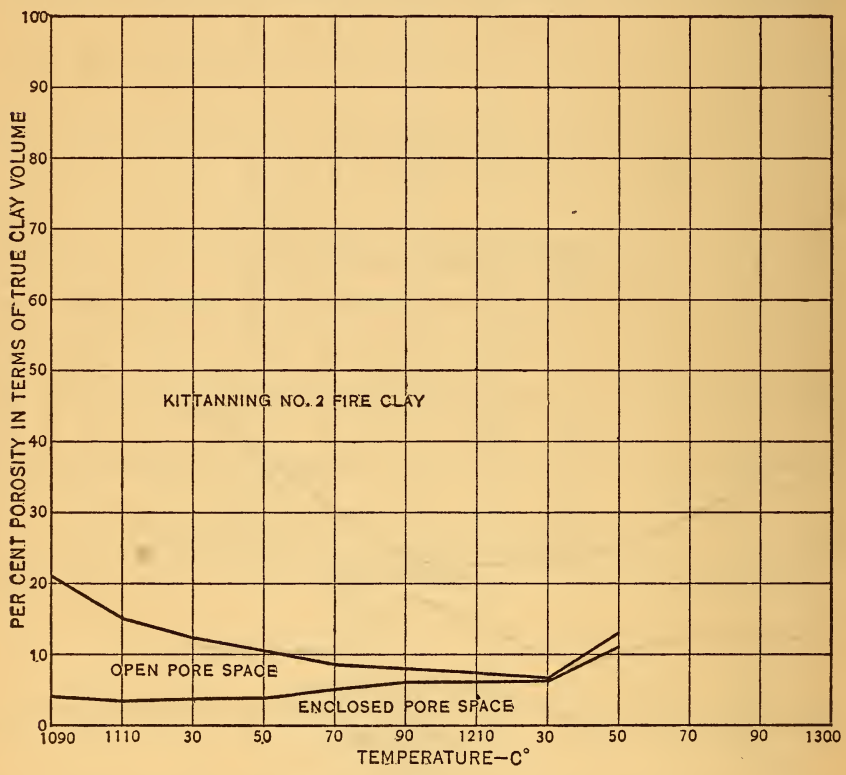

Fig. 6

temperatures. The comparison is especially interesting when the question of "overburning" is considered.

In order to illustrate the differences thus obtainable, the following experiment was made. A lot of Canton, Ohio, shale, well known for its safe vitrifying properties, was thoroughly mixed in the dry, ground state so that it truly represented a uniform sample. Part of this material was made up into brickettes in the plastic state; part was dry pressed in the moist condition, containing

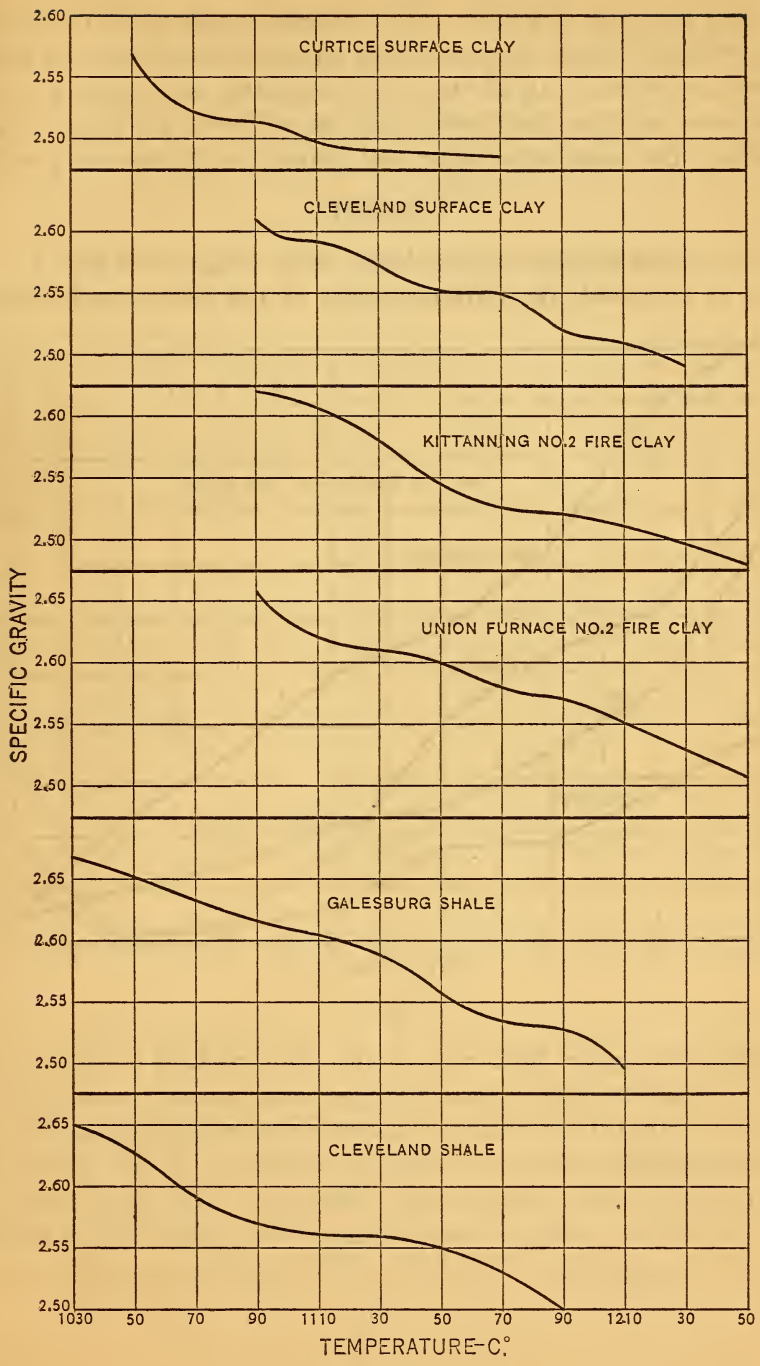
CURTICE SURFACE CLAY
CLEVELAND SURFACE CLAY
KITTANNING NO.2 FIRE CLAY
UNION FURNACE NO.2 FIRE CLAY
GALESBURG SHALE
CLEVELAND SHALE
SPECIFIC GRAVITY
2.60
2.55
2.50
2.65
1030
50
70
90
1110
30
50
70
90
1210
30
50
TEMPERATURE-C.°

Fig. 7

about 9 per cent of water. The specimens made from the plastic clay weighed about 80 grams when burned; the dry-pressed trials, about 40 grams. All of the dried brickettes were placed in the kiln close together and fired at the rate of 20° C per hour. After burning, the usual absorption and porosity weighings were made.

2. RESULTS

The results are shown graphically in the diagram of Fig. 8. As is to be expected, the initial porosity of the dry-pressed body is

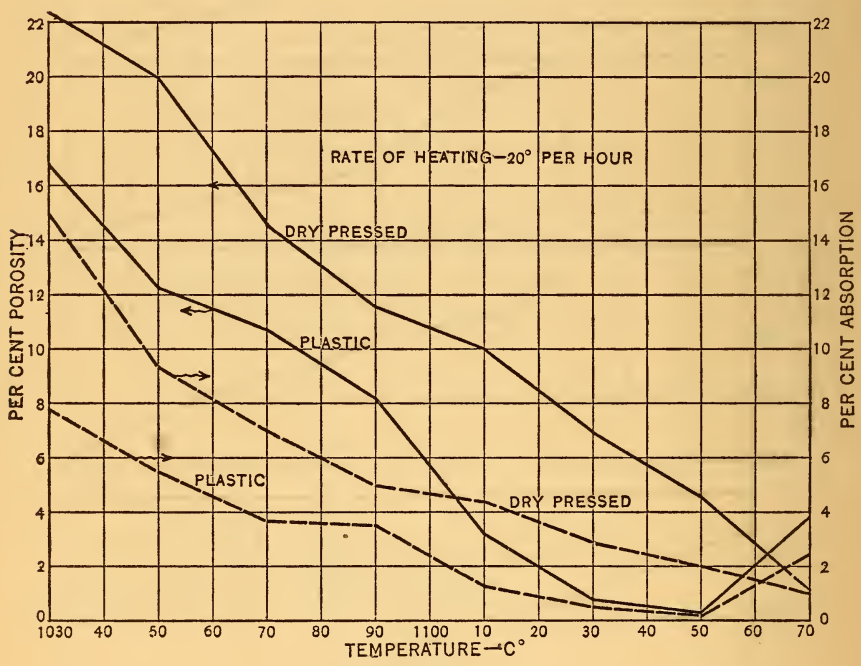

Fig. 8

considerably higher than that of the shale molded in the plastic state. Starting with 22.8 and 16.8 per cent porosity, respectively, the contraction of both kinds of specimens proceeds fairly uniformly and progressively down to about 3 per cent. At this point the contraction of the plastic body shows up. All along the two curves, however, points of equal porosity are separated by a considerable temperature interval, which becomes greater as the

3 per cent line is approached. Thus, a porosity of 6 per cent is reached by the plastic molded body at 1100°, by the dry-pressed body at 1138°. Similarly, 3 per cent porosity is obtained in the first case at 1111°; in the second at 1159°. Within the temperature limits employed the condition of nonabsorption is not reached at all by the dry-pressed body, while the plastic molded clay not only becomes impervious but even decidedly vesicular at 1170° C.

Here we have a case where the influence of physical factors is shown most prominently. The identical body presents an entirely different behavior according to whether it is made up in the plastic or the dry-pressed condition. At the same time, the well-known practical observation that dust-pressed clays require a higher maturing temperature is confirmed. If the two conditions of preparation were not known, the two curves would be considered to represent two clays of varying behavior.

V. SUMMARY

In the testing of clays the question of development of vesicular structure should receive careful attention and should be included in every complete report. Owing to the fact that the conditions of firing and other factors enter into the formation of inclosed pore space, carefully conducted burning is essential.

A definite rate of firing after the complete oxidation of the material should be maintained. The study of vesicular structure is more important in the case of materials where sound vitrification is required, as in the case of sewer pipe, paving brick, stoneware, electrical porcelain, etc., than for open-grained products. It is advisable to express all volume relations in terms of the true clay volume.

The continuous decrease in the specific gravity of the overburned clays shows that molecular changes are still going on and that equilibrium is by no means reached at the stages of complete and viscous vitrification.

Clays in the dust-pressed condition require a higher maturing temperature than when shaped in the plastic state and are less subject to the formation of vesicular structure.

WASHINGTON, May 15, 1913.