

## SILICA REFRACTORIES.<sup>1</sup>

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### Previous Work.

A great deal of work has been done on the stability relations of the silica minerals, the results of which are probably summarized best by Fenner.<sup>2</sup> More recently, the results of these studies have been applied in the optical examination of silica brick. McDowell<sup>3</sup> has been one of the foremost investigators along this line, and at the present time Insley<sup>4</sup> is conducting an exhaustive study of silica brick made from practically all of the leading varieties of materials used commercially in the United States for this purpose.

The present status of our knowledge along these lines is briefly as follows: The specific gravity of quartz is 2.65, that of cristobalite is 2.33, and that of tridymite, 2.27. Upon heating, alpha-quartz (the stable form at atmospheric temperatures) is inverted to beta-quartz at 575° C. In the presence of a flux, this beta-quartz is transformed into beta-tridymite at 870° C. This, in turn, is transformed at 1470° C into beta-cristobalite—which is the stable form from this temperature to its melting point, 1715° C. "In the absence of a flux, the beta-quartz is transformed directly to cristobalite—which in this case is the final form."<sup>5</sup> In the manufacture of silica brick two per cent of lime (CaO) is mixed with the quartzite. Upon heating, the lime

<sup>1</sup> By permission of the Director, Bureau of Standards.

<sup>2</sup> C. N. Fenner, "The Stability Relations of the Silica Minerals," *Am. J. Sci.*, **36**, 331-384 (1913). In this connection it is of interest to note that work recently published by the Geophysical Laboratory of the Carnegie Institution, indicates that the melting point of pure cristobalite is probably  $1715^{\circ} \pm 10^{\circ} \text{C}$  instead of  $1625^{\circ} \text{C}$  as previously reported.

<sup>3</sup> J. Spotts McDowell, "A Study of the Silica Refractories," American Institute of Mining Engineers, *Bull.* **119**, p. 1916.

<sup>4</sup> H. Insley, U. S. Bureau of Standards, Pittsburgh, Pa.

<sup>5</sup> *Am. J. Sci.*, **36**, 339 (1913).

combines with a small amount of the silica to form a glass, or, in some cases, possibly a little mono-calcium silicate ( $\text{CaO} \cdot \text{SiO}_2$ ). The quartz of a silica brick is transformed first to cristobalite, but as the lime constitutes a small amount of flux, continued heating causes the silica to be slowly converted into tridymite—after approximately two-thirds of it has been transformed into cristobalite.

McDowell<sup>1</sup>, Bell,<sup>2</sup> Le Chatelier<sup>3</sup> and others have also studied the differences in finished silica wares due to the use of the different quartzites and to variations in the methods of manufacture.

#### Usual Method of Manufacture.

Ordinarily, silica brick are manufactured by crushing the quartzite so that it will pass through a 2-inch ring. The crushed material is then fed in batches into wet pans and ground until the largest particles are approximately 0.2 inch in diameter, during which period two per cent by weight of  $\text{CaO}$  as milk of lime is added along with enough water so that the resulting mix can be molded into bricks. When dry, the bricks are burned in fire-brick kilns of the usual type.

#### Nature of the Present Work.

Some three years ago, the writer began a study of the silica refractories under the direction of Mr. A. V. Bleininger. The present paper is an attempt to set forth a summary of the data obtained since that time and to present some applications of the same. In taking up the data we shall first consider the raw materials, then manufacture and burning, and lastly some of the properties of the burned ware.

#### Raw Materials.

By far the largest part of the silica brick in all countries are manufactured from quartzites of comparatively early geologic age, although in some cases, chalcedony, chert, quartz sand, or pebbles cemented together with chalcedony, have also been

<sup>1</sup> *Loc. cit.*

<sup>2</sup> C. E. Nesbitt and M. I. Bell, "Silica Refractories," *Proc. Am. Soc. Testing Materials*, 1917.

<sup>3</sup> *Rev. métal.*, June, 1917.

used. Suitable quartzites range from the hard, highly metamorphosed varieties having tightly interlocking grains, to the medium soft rocks which are slightly porous. Loose grained quartzites and sand stones are, however, of little value. The quartzites now being used range from the very young rocks to the oldest sedimentaries.

The following microscopic method may prove of value in judging the suitability of quartzites for the manufacture of silica brick. In the metamorphosis of sandstones to quartzite, the rocks which received but little alteration consist of hard, usually rounded grains of quartz imbedded in a ground mass of a softer material. If a thin section of a rock of this kind is viewed under the microscope, the softer material appears as cloudy areas between the quartz grains. These cloudy areas consist of fragments of silica (probably quartz) and impurities such as hydrated iron oxide. As the metamorphosis proceeded, the interstitial silica, frequently augmented by silica from water solution, crystallized on the larger grains and shows the same orientation as these grains. Silica crystallizing in this way is pure—except for occasional inclusions. Hence, the impurities are segregated. In thin sections of highly metamorphosed quartzites these segregations appear as sharply defined lines between the tightly interlocking, built-up grains of quartz. The quartzites which have been found most satisfactory for the manufacture of silica refractories are those which have moderately to tightly interlocking grains, while those materials which merely show cloudy areas between the harder grains have been found to be less desirable. The specific gravity of quartz is 2.65. The specific gravity of chert rock—although practically the same as that of quartz—is usually slightly below this figure as shown by No. 29 (Table 1) (2.585). This is borne out by Mellor.<sup>1</sup>

Screen analyses (by the wet method) and porosity determinations were made on 15 leading varieties of unburned silica brick. These are presented in Table 2, together with the porosities and specific gravities of bricks of the same varieties which have received regular commercial burning.

<sup>1</sup> J. W. Mellor, *Trans. Eng. Ceram. Soc.*, 15.

TABLE 1.

Geological formation from which derived.	Materials. Remarks.	Sample No.	Specific gravity.	Per cent porosity.	Micro-Composition.		
					Quartz plus silicates.	Cristobalite.	Tridymite.
Medina.....	{ Commercial brick, reheated for 11 days; 4 days at 1450° C and finally 1 day at 1500° C.	33	2.321	29.45			
	Commercial brick, reheated 40 times to 1450° C on bag wall of test kiln.	34	2.275	31.85			
	{ Commercial brick, reheated 10 times in commercial silica brick kiln to cone 14.	35	2.271	27.25			
	{ Commercial mix, heated 9 times at successively higher temperatures from 1200-1500° C. by 50° intervals—last 3 heatings were to 1500° C.	36	2.304	25.19			
Baraboo.....	{ Commercial brick which received 9 years' service in Koppers by-product coke oven.	37	2.314	19.94	No. { 1 8 3 2 20 13 3 31 24 45		
	{ Micro-analysis 1 is from the side exposed to heating flue; 2 from center of brick; and 3 from coke chamber side.						
Homewood.....	Raw rock.	38	2.626	6.52			
	{ Raw rock	39	2.585	1.83			
	{ Rock calcined rapidly (6 hours) to cone 20.	40	2.272	14.33			
	{ Commercial brick made from chert rock.	29	2.273	25.64	5	12	83
	Commercial German brick, Stella Werke (gives good service).	45	2.372	20.07	20	78	2
	{ Test brick, California quartz + river sand + 2% CaO, 2 heatings in commercial clay brick kiln.	41	2.437	30.02			
	Alabama mica quartz schist rock.	42	2.690	4.52			
	Test brick made from above schist.	43	2.616	34.07			
	{ Test brick made from slightly impure silica sand from Georgia + 8% Ca(OH) <sub>2</sub> .	44	2.527	30.40			

TABLE 2.  
Screen analyses (by the wet method) of raw commercial silica brick mixes. The porosities of the raw and burned bricks and the specific gravities of the burned bricks of the same brands are also shown.

			MEDINA.					BARABOO.			HOMERWOOD FORMATION.		
Screen. No. mesh.	No. of brick.		6	2	7	3	5	4	18	21	14	16	
	% on screen.	%											%
4	..	1.69	2.44	1.43	1.27	9.97	1.41	3.58	1.72	3.25	11.96		
8	..	19.85	24.18	20.22	14.35	15.63	23.46	27.38	20.98	19.09	11.96		
20	..	11.74	9.67	9.15	10.79	10.01	16.07	15.66	17.86	6.09	6.20		
30	..	3.31	6.36	9.15	9.84	7.76	3.75	5.77	8.84	1.89	4.95		
40	..	10.07	9.67	9.69	15.34	17.23	10.93	4.90	7.97	10.22	29.62		
60	..	18.65	13.97	17.13	16.48	12.17	15.02	12.20	5.73	26.35	16.94		
80	..	1.58	5.70	4.99	3.85	2.97	3.60	2.23	4.24	2.29	2.81		
100	..	3.17	4.26	3.76	3.46	3.27	5.68	3.97	3.32	2.07	5.55		
150	..	4.25	3.33	4.10	2.94	2.32	3.91	3.14	2.60	3.87	1.83		
200	..	3.35	2.45	3.07	2.47	1.51	2.90	2.77	2.76	2.55	1.78		
Through 200	..	9.46	6.63	6.25	5.84	2.88	4.39	8.57	11.27	6.89	8.48		
Floated	..	12.84	11.34	11.06	13.37	14.28	8.90	9.84	12.80	11.38	9.89		
Porosity, raw brick	..	26.70	26.15	25.93	27.20	21.22	25.45	23.54	23.20	27.50	28.54		
Porosity, burned brick	..	26.35	25.84	28.35	28.52	22.80	27.16	23.91	23.45	30.58	26.55		
Sp. gr., burned brick	..	2.291	2.295	2.375	2.424	2.340	2.393	2.381	2.390	2.496	2.517		

Screen. No. mesh.	COLORADO.			Mo.	CHERT.	EASTERN PENNA.	Average of all varieties.		Theoretical <sup>1</sup> for minimum porosity. <sup>1</sup>	Diameter of holes between wires. Inches.
	No. of brick.	28	27				%	%		
4	..	0.23	3.27	0.54	0.37	0.39	2.24	0.40	0.18	
8	..	14.17	16.18	11.09	15.47	21.76	18.85	28.10	0.093	
20	..	16.55	22.53	18.15	25.00	22.04	14.52	28.20	0.034	
30	..	3.25	12.58	9.90	12.14	6.31	7.06	10.30	0.0198	
40	..	4.09	10.06	9.80	4.77	6.45	10.72	4.40	0.0150	
60	..	12.05	7.09	11.87	7.55	11.57	13.66	6.10	0.0087	
80	..	3.62	1.95	3.43	2.37	3.03	3.51	2.50	0.0068	
100	..	3.08	4.10	4.09	3.93	3.81	3.83	2.50	0.0055	
150	..	3.92	4.40	3.16	2.78	3.32	3.32	2.53	0.0041	
200	..	5.04	4.21	3.03	2.48	2.97	2.89	1.75	0.0029	
Through 200	..	21.32	9.57	9.83	11.44	9.83	8.46	13.50	..	
Floated	..	12.65	9.53	15.37	11.66	8.53	11.56	..	..	
Porosity, raw brick, ....	..	26.52	22.93	25.30	24.70	20.32	...	...	..	
Porosity, burned brick, ....	..	24.51	24.63	24.70	25.64	23.10	...	...	..	
Sp. gr., burned brick, ....	..	2.387	2.393	2.393	2.273	2.480	...	...	..	

<sup>1</sup> Taylor and Thompson, "Concrete, Plain and Reinforced," p. 775. Formula for construction of curve is  $d = P^2D/10000$ , where

$D$  = Diameter of largest grain.

$d$  = Any given diameter.

$P$  = The per cent of mixture smaller than any given diameter.

Largest grain = 0.182 inch diameter.

Curves showing the results of screen analyses made on quartzites that have been crushed ready to be molded into brick, when compared with the theoretical curve for minimum pore space,<sup>1</sup> show that there is always an excess of material of the sizes which correspond to those of the quartz grains.

In crushing, sandstones and quartzites that are but slightly metamorphosed break mostly to individual sand grains and yield an excess of these sizes.

Moderately metamorphosed material, *i. e.*, material that is still slightly porous, follows the theoretical curve quite closely. In this case the breaking is usually through the interstitial material between the built-up grains. However, the interstitial material breaks free from some of the original rounded grains and still other grains are broken in two.

In the case of highly metamorphosed quartzites, *i. e.*, those in which the crystalline quartz is practically continuous, the breaking is usually through the grains, but a fair percentage of rounded grains also break free from the interstitial material. This breaking away of the interstitial material from the rounded grains is particularly noticeable in the highly metamorphosed Baraboo quartzites.

Inspection of the screened material revealed the fact that in the Medina, Baraboo, Homewood, Missouri, and Eastern Pennsylvania materials, the original rounded grains which broke free from the interstitial material practically all passed through a 30-mesh (0.503 mm. diam.) screen, and that but very few particles passed through a 60-mesh (0.221 mm. diam.) screen—the great majority being caught on the 40-mesh (0.381 mm. diam.) and 60-mesh screens, in varying proportions. In Fig. 1 are shown photographs of samples of material remaining on the 40-mesh screen. No. 6 consists largely of material broken through the interstitial material between the built-up grains, and some that has broken through the grains. A slight amount of finely ground material still adheres to the particles. No. 21 shows a large percentage of the original rounded grains which have broken free from the material of the built-up grains. No. 12 contains a large percentage of material broken through the grains and

<sup>1</sup> Taylor and Thompson, "Concrete, Plain and Reinforced," p. 775.

also material in which the breaking was between the original rounded grains and built-up grains. A slight amount of finely ground material still adheres to the particles. In No. 14, the original grains of the material appear more angular than is the case with the other quartzites examined. In No. 31, many

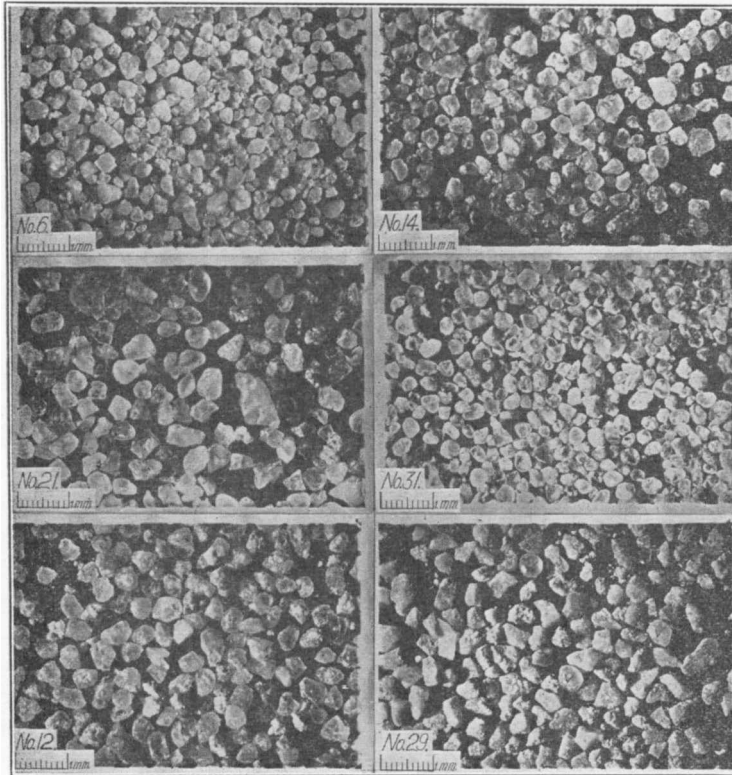


FIG. 1.—Materials (caught on 40-mesh sieve) resulting from wet screen analyses of raw commercial silica brick mixes. Magnified.  
(Microphotographs by Dr. R. Thiessen, U. S. Bureau of Mines, Pittsburgh, Pa.)

of the original rounded grains have broken free from the chalcedony bonding material. In No. 29, the grains in the chert are extremely fine, hence, as might be expected, it breaks into angular fragments. A slight amount of finely ground material

still adheres to the particles. The three grains checked are of a different material which was accidentally included.

At the present time, McDowell is carrying on a study of the sizes of the built-up interlocking grains of several quartzites.

Of the quartzites, the loosely bonded varieties yield the most porous raw brick, and the strongly bonded varieties, in which the breaking is across the grains—thus avoiding an excess of material corresponding to the grain sizes—yield raw brick of the least porosity. Material No. 12 (Table 2) is of this type and has the lowest porosity of any of the unburned brick tested. The chert material, No. 29, is next, this being closely followed by the mixes made from Baraboo quartzite, while the large majority of the raw mixes made from the Medina quartzite, of Blair and Huntingdon counties, Pennsylvania, show in turn somewhat greater porosities than do the Baraboo materials.

#### **Innovations in Methods of Manufacture.**

Finished silica brick frequently show quite wide variations in their physical properties when subjected to strength tests, etc. These variations may be due in part to differences in grind from one pan to the next, and, in part, to the human factor in hand molding. To overcome such difficulties in special cases, the following changes in the methods of manufacture have been suggested:

The material is ground and, by screening, is divided into three sizes. These are then mixed in the desired proportions in a machine similar to that used for mixing concrete. To avoid storage in bins,<sup>1</sup> the material might be ground directly in a wet pan having raised mullers. The lime is added at this point. The brick are then machine molded. This should insure greater uniformity of texture, shape, amount of material per brick, and should tend to slightly reduce the porosity. Nesbitt and Bell<sup>2</sup>

<sup>1</sup> When crushed materials are poured from a spout into a bin there is a tendency for the coarse material to segregate from the fines. This trouble may be largely obviated by frequently changing the position of the spout while a bin is being filled. It is essential to keep this in mind when using bins for the storage of ground silica brick materials.

<sup>2</sup> *Loc. cit.*



have suggested that 1500 pounds per square inch is the most desirable pressure for use in the manufacture of machine molded silica brick. Fine surface cracks appear to be characteristic of machine-pressed silica brick. However, in most cases these should be of no serious detriment to the bricks. In making silica brick by machine, the water content need not be quite so great as for the hand-made brick. However, an abnormally low water content is apt to result in an open brick of weak structure—both in the raw and burned condition.

### Effects Produced by Burning.

Since the specific gravities of cristobalite (2.33) and tridymite (2.27) are considerably lower than that of quartz (2.65), the relative position of the specific gravity of any sample of silica brick between these limits should indicate, quite accurately, the degree to which its quartz has been transformed to the lower specific-gravity forms.

To accurately determine the specific gravities of solids by means of a pycnometer bottle, using finely powdered material, is a rather tedious operation. Hence, an effort was made to determine the specific gravity by using a two-inch cube of the material. This was first weighed dry, then saturated with water and weighed wet, and finally the saturated piece was weighed, suspended in water. From these data, the specific gravity was calculated. Saturation was obtained by placing the pieces in boiling water and subjecting them, while thus submerged, to a vacuum equivalent to twenty-four inches of mercury for a period of four hours. This method, when carefully conducted, has been found to give the specific gravities with sufficient accuracy for our present purpose.

The specific gravities of most of the leading varieties of commercial silica brick, manufactured in the United States, have been determined in this way (see Table 3) and, thus far, all lie between 2.65 (the specific gravity of quartz) and 2.27 (the specific gravity of tridymite). The results of our own work, and more recently of that of other investigators of silica refractories, indicate that this gives a definite and satisfactory indication of the degree to which a brick has been burned.

TABLE 3.—POROSITIES AND SPECIFIC GRAVITIES OF PRINCIPAL BRANDS OF COMMERCIAL SILICA BRICK MADE IN THE UNITED STATES.

Quartzite from which the brick were made.	Sample No.	Specific gravity.	Per cent porosity.
Medina (Tuscarora).....	1	2.375	27.15
	2	2.296	25.84
	3	2.424	28.52
	4	2.393	27.16
	5	2.340	22.80
	6	2.291	26.35
	7	2.375	28.35
	8	2.336	31.52
	9	2.321	25.97
	10	2.358	26.10
	11	2.291	29.56
	12	2.460	23.10
	13	2.340	29.88
Av., 2.357		Av., 27.07	
Homewood sandstone.....	14	2.496	30.58
	15	2.448	28.95
	16	2.517	26.55
Av., 2.470		Av., 28.69	
Oneida.....	17	2.274	25.66
Baraboo.....	18	2.381	23.91
	19	2.430	25.15
	20*	2.325	31.41
	21	2.390	23.45
	22	2.395	24.79
Av., 2.399		Av., 24.30	
Quadrant formation (Montana).....	23	2.495	23.22
	24	2.490	22.66
	25	2.537	22.96
Alabama, probably Weisner formation.	26	2.311	29.75
Dakota and Comanchian (Colorado) ..	27	2.393	24.63
	28	2.387	24.51
Indiana chert.....	29	2.273	25.64
Saint Louis district.....	30	2.363	25.73
	31	2.393	24.70
Eastern Pennsylvania.....	32	2.335	26.85
Grand average of all varieties.....	Av., 2.384		Av., 26.34

\* Calcined quartzite.

Using the specific gravities of the materials in this way, our data (Table 4 and Fig. 2) indicate that at the end of heating to 1500° C (conducted as follows: heating to 800° C in 18 hours, heating from 800° C to 1500° C in 6 hours, and held at 1500° C

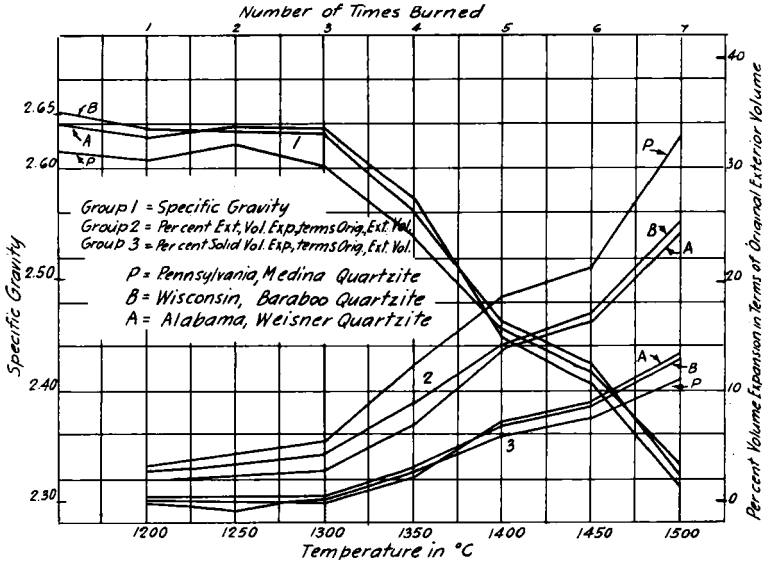


FIG. 2.—Changes in exterior and solid volumes and specific gravities of Medina, Baraboo and Alabama quartzites, caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

for 1½ hours) the amount of transformation that had taken place was approximately the same in the Baraboo, Alabama, and Medina quartzites. The specific-gravity curves show that, for the repeated heatings at from 1300° to 1400° C, the Medina quartzite appears to be transformed slightly more than the other two. The average specific gravity (Table 3) of commercial brick made from the Baraboo quartzite is somewhat higher than that of brick made from the Medina quartzite. Hence, since the chief part of the burning received by average commercial brick is between 1300° and 1400° C, it is probable that at these temperatures Baraboo quartzite is actually transformed at a slightly slower rate than is the Medina

TABLE 4.—SPECIFIC GRAVITIES OF QUARTZITES BEFORE AND AFTER HEATING FOR 1½ HOURS AT 1500° C.

Material.	Specific gravity. Raw quartzite.	Specific gravity of quartzite after 1500° C. burn.
Medina quartzite.....	2.635	2.303
Baraboo quartzite.....	2.650	2.293
Alabama quartzite.....	2.640	2.295
Homewood sandstone.....	2.630	2.326
Montana quartzite.....	2.638	2.306

quartzite. When quartz is transformed to cristobalite, the action is progressively from the surface and along cracks towards the interior and hence is most rapid in the varieties having the greatest surface areas. In accordance with this we would expect the slightly porous Medina quartzite to be transformed somewhat more rapidly than the more highly metamorphosed, non-porous, Baraboo quartzite. At temperatures above 1400° C, however, the transformation of quartz to the lower specific-gravity forms is so rapid in all varieties that the above effect is apparently obscured.

In silica brick, the transformation from cristobalite to tridymite apparently takes place first in the fine material of the ground mass and then progressively from the surfaces to the centers of the larger particles. This is illustrated in Fig. 3, which shows a

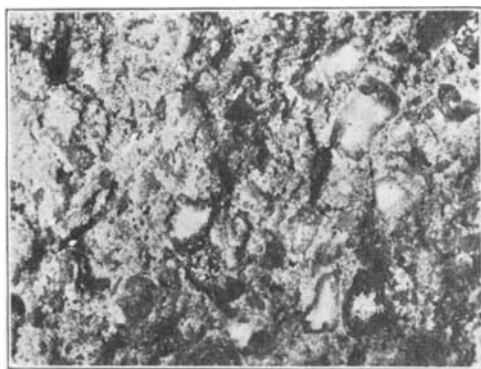


FIG. 3.—Brick made from Medina quartzite, after 40 heatings to 1450° C. Ground mass is tridymite, gray outer portion of large particles is tridymite in glass, and white centers of large particles are cristobalite (natural size).

fractured surface of a brick which has been burned to an advanced stage. In this case the quartz has almost entirely disappeared and practically all of the cristobalite that remains is represented by the light patches present at the centers of the larger particles. In the course of the transformation of quartz through cristobalite to tridymite, the original crystal form is largely lost, so that the final product shows a considerable quantity of interlocking crystals which were not present in the unburned brick.

In accordance with Mellor,<sup>1</sup> we found that chert is transformed to the lower specific-gravity forms much more rapidly than quartz. Thus, brick 29 (Table 3) (micro-analyses shown in Table 1), which was made from a chert rock, received one regular burn in a commercial silica brick kiln. Its specific gravity is lower and the sum of its contents of cristobalite and tridymite is much higher than is usually the case with single burn bricks made from quartzite.

A comparison of the porosities of raw and burned brick (Table 2) shows that the porosity of the burned brick depends largely upon the porosity of the raw mix. However, it was found, by repeated trials, that if a raw brick mix was heated to 1500° C in one day the resultant product was porous, weak and friable, while if fourteen days were consumed in reaching the same maximum temperature, with a protracted soaking at from 1200° to 1350° C, the resultant brick showed no undue increase in porosity and was sound and strong. In fact, in cases where the conversion of quartz has been practically completed at the soaking temperatures, the final increasing of the temperature to the maximum actually causes the porosity of the brick to decrease. As a rule, the increased porosity (punkiness) of rapidly burned brick is much more pronounced with loosely than with firmly bonded quartzites.

Number 37 (Table 1) represents a piece of brick which received long soaking in use in a by-product coke oven at moderately high temperatures. The differences in micro-composition from the hot (heating flue) side of the brick to the cold (coking chamber) side are very marked. For the specific gravity and porosity determinations, pieces were taken which extended entirely across

<sup>1</sup> *Loc. cit.*

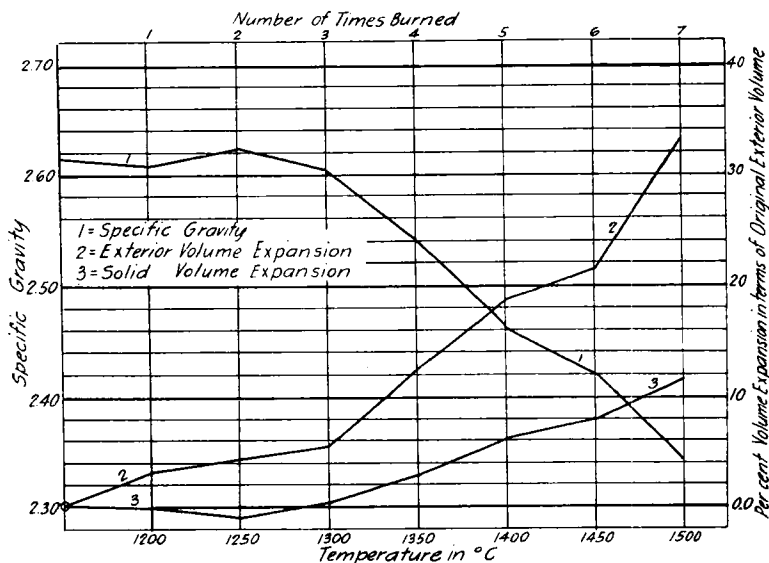


FIG. 4.—Changes in exterior and solid volume and specific gravity of Medina quartzite, caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

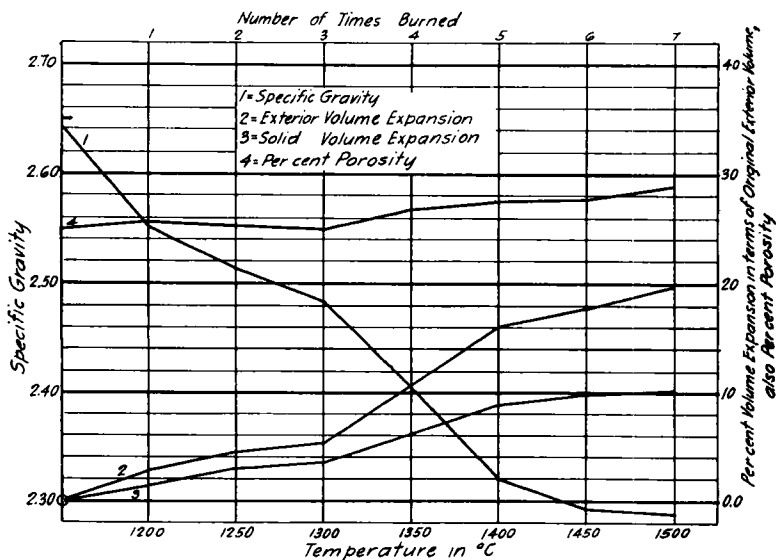


FIG. 5.—Changes in exterior and solid volume, specific gravity and porosity of Medina raw mix—caused by repeated burnings to successively higher temperatures from 1200°–1500° C.

a section of this brick. The abnormally low porosity of this brick was in all probability caused by the protracted soaking at high temperatures which it received in use. This brick is of particular interest because of its low cristobalite content, even at the coke side—where there is considerable quartz + silicates present.

A comparison of the specific-gravity curves in Figs. 4 and 5 indicates the way in which the lime increases the amount of transformation produced by a given heat treatment. Increasing the lime content above two per cent appears to further increase the rate of transformation. Sodium chloride apparently has a similar effect. On the other hand, plastic clay, pure calcined alumina (ground to pass through a 60-mesh screen), and iron oxide appear to have very little effect on the rate of transformation. Small percentages of fluorspar ( $\text{CaF}_2$ ) were tried in conjunction with lime, and although our data is not conclusive, the indications are that the fluorspar has very little effect on the rate of transformation.

### Properties of the Burned Brick.

The results of cold cross breaking tests (Table 5),<sup>1</sup> in conjunction with the natures of the materials broken, and their specific gravities, porosities (Table 3), micro-analyses, etc., indicate that, with brick made from quartzites, the strength of slightly to moderately burned brick probably depends largely upon the

TABLE 5.—CROSS BREAKING TESTS. (MODULUS OF RUPTURE.)

Test No.	Material.				
	(18) Baraboo.	(6) Medina.	W. Va.	(29) Chert.	Medina. <sup>2</sup>
1.....	565	1557	664	446	...
2.....	593	709	1143	...	...
3.....	544	452	782	...	...
4.....	546	1003	645	...	...
5.....	527	863	809	...	...
Av.....	555	915	809	...	793

<sup>1</sup> Bricks set on edge with six inches between supports.

<sup>2</sup> As given by McDowell.

state of metamorphosis of the raw material and the porosity of the raw brick and the lime-silica bond formed in the burning. On the other hand, well burned silica brick appear to have their strength somewhat increased by the formation of interlocking crystals—occasioned by the transformation of the quartz to the lower specific-gravity forms. Seaver<sup>1</sup> likewise maintained that the interlocking crystals of well-burned silica bricks increases their strength.

If all other properties of a silica brick made from quartzite are found satisfactory, it is not usually found that the brick will fail in use because of lack of strength. The Baraboo and Medina varieties (Table 5) have both been thoroughly tried out in steel furnace and coke oven work and both give consistently satisfactory results. The great variations in strength of the Medina brick, as compared with the Baraboo, may be due to an unequal development of interlocking crystals in the individual specimens of the former.

In Table 6 is presented the data of crushing tests made upon "Star" silica brick at various temperatures as reported by

TABLE 6.—CRUSHING STRENGTH OF SILICA BRICK AT VARIOUS TEMPERATURES (LE CHATELIER).

Temperature ° C.	Crushing strength of hot brick.	
	Kg./sq. cm.	Lbs./sq. in.
15	170	2418
520	158	2247
670	150	2133
800	139	1977
950	125	1778
1050	120	1707
1200	85	1209
1320	62	882
1460	50	711
1540	37	526
1600	30	427
1700	12	171 <sup>2</sup>

<sup>1</sup> K. Seaver, "Manufacture and Tests of Silica Brick for the By-Product Coke Oven," *Trans. Am. Inst. Mining Eng.*, **53**, 125-139 (1916).

<sup>2</sup> Extrapolated.



Le Chatelier.<sup>1</sup> The 1700° C figure has been extrapolated by a continuation of the curve. This curve would seem to indicate that hot crushing tests, to be of the most value, should be made at a temperature that corresponds to the working conditions—such as the temperatures of the crowns of steel furnaces. Or, if made at any other temperature, the strength obtained should be compared to that at the corresponding temperatures on previously prepared curves of the above nature. Such prepared curves should of course include varieties of materials similar to those under test.

McDowell,<sup>1</sup> in his tests of silica brick which had been burned from one to ten times in a commercial kiln, found that at the end of the first few burns the strength had reached a maximum—after which it declined slightly. His theory is that this decrease is due to a slight rupture of the brick—caused by repeated heating and cooling—rather than to an inherent weakness of one or both of the low specific-gravity forms of silica.

In making load tests on silica brick, it was soon found that, if heated to 700° C at the same rate as clay brick (270° C in 20 minutes, 520° C in 40 minutes, and 670° C in 60 minutes), the specimens invariably spalled; and that spalling apparently ceased when the rate of heating below 500° C was decreased to 50° C in 15 minutes. Measurements of the linear expansion of bricks during the load tests indicate that the spalling is practically all due to the alpha-beta cristobalite inversion—which takes place at from 220–275° C.<sup>2</sup> In Table 7 is given the data of such a test. From this data it is seen that there is a decided expansion at the lower temperatures. This is followed by a gradual but very slight expansion until a temperature of approximately 1400° C is reached—at which point a rather decided increase in the rate of expansion is noted. This expansion, which becomes apparent at 1400°, is approximately equivalent to the permanent expansion of the brick. Or, in other words, this ex-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> The temperature depends upon the previous heat treatment which the material has received.

TABLE 7.—EXPANSION OF BRICK NO. 27 UNDER A LOAD OF 25 POUNDS PER SQUARE INCH.

Time in hours.	Temperature ° C.	Per cent linear expansion.
0.00	19	0.0
1.00	200	0.0
2.50	500	0.340
3.00	650	0.363
4.50	1200	0.403
4.75	1250	0.408
5.00	1300	0.431
5.25	1330	0.431
5.50	1360	0.657
6.00	1400	0.657
6.50	1400	0.657
7.00	1400	0.703
7.50	1400	0.840
Measured cold after test.....		0.158
Total expansion.....		0.840 Per cent
Permanent expansion.....		0.153 Per cent
Difference compared to 0.657 at 1360° C.....		0.682 Per cent

pansion may be considered as due to the actual transformation of silica from the high to low specific-gravity forms.

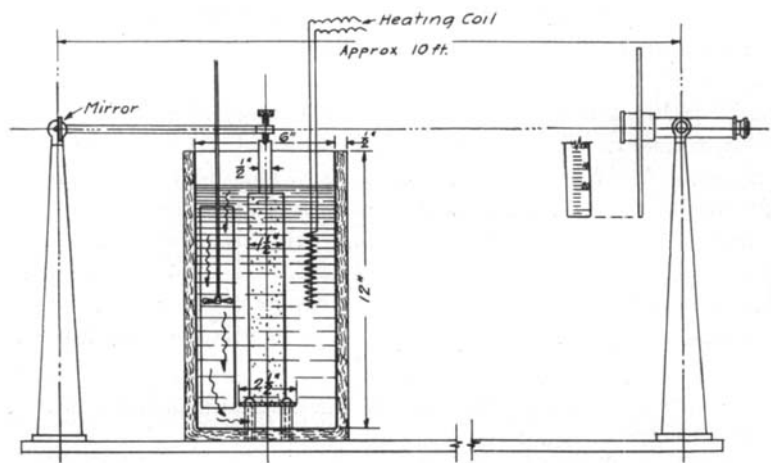


FIG. 6.—Extensometer, designed to measure the expansion of silica brick between atmospheric temperatures and 300° C.

In Fig. 6 is shown an apparatus for measuring the expansion of silica brick up to  $300^{\circ}\text{C}$ . It consists of a lever arm to register expansion and an attached mirror for magnifying the readings to any desired extent by means of a telescope and graduated scale. The test specimen is immersed in a bath of "Crisco," which is heated electrically by means of a nichrome grid. The temperature throughout the bath is kept uniform by stirring the liquid with a paddle. The supports between the specimen and bed plate are of quartz glass, as is also the rod between the specimen and the lever arm. It would be of interest to determine the exact temperatures at which the chief expansions take place for bricks made from each of the leading varieties of quartzite, and also the time required for a standard 9-inch brick to reach its maximum expansion when the temperature is kept constant.

#### Load Test.

The load test on silica brick is conducted in the usual form of load test furnace.<sup>1</sup> The load is 25 pounds per square inch. The heating rate is  $50^{\circ}\text{C}$  in 15 minutes from atmospheric temperature to  $500^{\circ}\text{C}$ ,  $75^{\circ}\text{C}$  in 15 minutes from  $500^{\circ}\text{C}$  to  $800^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$  in 15 minutes from  $800^{\circ}\text{C}$  to  $1200^{\circ}\text{C}$ ,  $50^{\circ}\text{C}$  in 15 minutes from  $1200^{\circ}\text{C}$  to  $1350^{\circ}\text{C}$  and  $30^{\circ}\text{C}$  in 15 minutes from  $1350^{\circ}\text{C}$  to  $1500^{\circ}\text{C}$ . A temperature of  $1500^{\circ}\text{C}$  is maintained for  $1\frac{1}{2}$  hours—after which the firing is discontinued. When cold, the brick should not have increased in length more than two per cent ( $\frac{1}{4}$ " per foot), nor decreased in length more than one per cent ( $\frac{1}{8}$ " per foot). The Refractory Materials Committee of the American Gas Institute has set one per cent permanent expansion as the limit in such tests. This one per cent limit is a desirable one if materials which will satisfy it can be regularly obtained.

#### General Results.

Among the more highly metamorphosed quartzites, those which crush largely by breaking through the original grains are apt to yield brick of lower porosity than those in which the breaking is largely through the interstitial material between the built-up

<sup>1</sup> U. S. Bur. Standards, *Tech. Paper 7*.

grains—or those in which a large proportion of the original grains break free from the interstitial material—while the more friable materials, which crush almost entirely to individual grains, show a very high porosity and yield brick which are weak and friable.

Innovations in the methods of manufacture may be advisable in special cases in order to obtain greater uniformity of product. One such innovation is to control the grind so that the percentages of the various-sized particles in the mix will remain constant at all times and to then machine mold the brick at a pressure of approximately 1500 pounds per square inch in order to obtain brick of smooth finish and uniform size.

The porosity of a finished silica brick depends primarily upon the porosity of the unburned mix. However, in so far as the burning does affect their porosity, the lowest porosity will probably be obtained by not allowing the temperature of the kiln to rise above  $1350^{\circ}\text{C}$  until a large percentage of the quartz has had time to be converted to the lower specific-gravity forms. Rapid heating of a silica brick to temperatures above  $1350^{\circ}\text{C}$ , while a large proportion of the silica is still present as quartz, invariably produces a friable (punky) brick. To obtain a brick of comparatively low specific gravity, however, the temperature should eventually be slowly raised to a maximum corresponding to cones 18–20.

The strength of a brick of slight or medium burn (gauged by present practice) is probably due to the glassy bond formed by the interaction of the basic fluxes with the silica, while in well burned brick it appears that the strength is greatly augmented by the formation of interlocking crystals of the low specific-gravity forms of silica. As a general rule, it has been found that silica brick, made from quartzite giving entire satisfaction in other ways, usually meet the strength requirements of service.

#### **Inspection of Ware Based on the Above Observations.**

Some of the properties of a finished brick which may be used in judging its probable value in use are as follows: Chemical composition, specific gravity, porosity, cold cross-breaking strength, behavior in the load test, the hot crushing strength

(at the temperature at which bricks are to be used), and the amount of interlocking crystals—determined by viewing thin sections of the brick under the microscope—and the softening temperature of the brick. For the best quality brick these properties, based on available data, approximate the following:

The silica content should not be much under 94 per cent. Bricks containing lower percentages of silica are less refractory. The alkalis should not exceed 0.5 per cent. Greater percentages reduce the refractoriness in direct proportion to their amount. The limit of iron oxide was previously assumed to be 0.5 per cent. However, greater percentages, up to 1.6 per cent, do not appear to materially affect the refractoriness of the brick. The limit for lime is usually set at 2.0 per cent, although larger amounts of lime (up to several per cent) do not greatly lower the softening temperatures. However, in commercial practice, more than 2.0 per cent of lime is considered undesirable.

The average specific gravity for brick made from Medina quartzite, as shown in Table 3, is 2.357 and, for brick made from Baraboo quartzite, it is 2.399. Hence, bricks made from similar materials may be considered as having received a medium burn if their specific gravities correspond to these figures.

The practical limits of porosity which first quality silica brick are apt to have are, Medina 22.80 to 31.52 per cent, and Baraboo 23.45 to 25.66 per cent. However, porosities lower than these might be desirable.

The cold cross-breaking tests, as shown in Table 4 and from other data, should not show an average modulus of rupture much below 500 pounds per square inch. The reliability of this figure is considerably impaired by the comparatively small amount of data upon which it is based.

After having been tested under a load of 25 pounds per square inch at 1500° C, a brick should have neither expanded (linearly) more than two per cent (preferably 1.0 per cent), nor contracted more than one per cent. If desired, the load test furnace may be arranged so that the specimen can be crushed hot at the completion of the test. It would seem desirable to conduct this test at the temperature at which the bricks are to be used.

A micro-examination of a thin section of a brick will detect the amounts of interlocking crystals of the low specific-gravity forms which are present, and thus indicate the degree of burning which the brick received in manufacture.

First quality brick should not have a fusion temperature much below that of cone 31.<sup>1</sup> Cones of the most refractory silica brick bend over at cone 32<sup>1/2</sup>.

### Summary.

In summing up, we may say that the bulk of all silica bricks are made from the quartzites of early geologic age, and that, as a rule, the quartzites most suitable for the manufacture of silica brick are those which range from the slightly porous to the highly metamorphosed impervious rocks—having tightly interlocking grains. These may be distinguished in thin section under the microscope, by the fact that the interstitial impurities (such as hydrated iron oxide) appear as sharply defined lines between the tightly interlocking quartz grains, while in material which has been but slightly metamorphosed the interstitial material appears in translucent, cloudy areas between the harder quartz grains. Those quartzites which crush largely by a breaking through of the original grains are apt to yield silica brick of lower porosity than those in which the breaking is largely through the interstitial material between the built up grains, or those in which the original grains break free from the interstitial material.

In special cases, to obtain greater uniformity of product, it may be advisable to control the grind by unusual manipulation—so that the percentages of various-sized particles in the mix will remain constant at all times—and to then mold the brick by machine.

The porosity of a finished silica brick depends primarily upon the porosity of the unburned mix. However, the heating of brick, which contain large percentages of unchanged quartz, to temperatures above 1350°C causes undue expansion—resulting in a punky product. On the other hand, maintaining the tempera-

<sup>1</sup> When ground to pass through a 60-mesh screen and made into cones similar to the standard cones used for comparison.

ture of the kiln at from 1250° C to 1350° C, until a large percentage of the quartz in the bricks has been transformed to the low specific-gravity forms, and then slowly proceeding to the higher temperatures, should result in a low porosity brick of low specific gravity.

The specific gravity of a silica brick, as determined by the wet, dry and suspended weight method, answers as a quick means of determining the degree to which the quartz originally present has been transformed to the lower specific-gravity forms of silica. But to obtain a comprehensive idea of the qualities of any variety of silica bricks, the other properties, such as porosity, cold cross-breaking strength, softening temperature, behavior in the load test, and appearance in thin section under the microscope should also be determined.

#### COMMUNICATED DISCUSSIONS.

R. M. HOWE: Mr. Ross mentions a great many interesting points arising in the field of silica brick manufacture and gives considerable valuable information.

An interesting point is in connection with his screen analyses as applied to "sand rock." A typical sand-rock analysis follows:

				Per cent.
Retained on	14-mesh sieve	.....		0.73
" "	20 " "	.....		2.02
" "	40 " "	.....		42.55
" "	60 " "	.....		46.30
" "	80 " "	.....		7.12
" "	100 " "	.....		0.92
" "	150 " "	.....		0.39
" "	230 " "	.....		0.21
Through	230-mesh sieve	.....		0.20
Total				100.44

He also mentions the rapidly growing importance of the "specific-gravity" test. Its value is recognized at the present time to such an extent that one company finishes all kilns by means of it. The draw trials are taken from the kilns at intervals and when they have a specific gravity of 2.40 the firing is stopped.

As the kiln is held the brick undergo further transformation—the specific gravities of the brick when drawn being below 2.38. Records are carefully kept, and the firing of each particular kiln may be controlled by this means after sufficient data has been collected.

Mr. Ross, however, makes some statements regarding chemical analysis which are evidently not justified by the work completed to the present time. There is no evidence on record which proves that certain impurities cannot be tolerated. Some materials are high in one particular impurity, but are correspondingly low in other impurities. In view of this and of the necessary incriminating evidence, one cannot justly say as to what percentage of each individual impurity may or may not be tolerated.

As a rule, however, the total percentages of impurities in good grades of silica brick are similar. These generally run between 4.0 and 6.5 per cent. If, then, the total of silica averages in the vicinity of 94.0 per cent or more, about all has been done which can be done. A silica content of 94.0 per cent excludes any superabundance of impurity and yet does not unjustly discriminate against any particular combination of the same. It appears that suitable material can be secured on a silica basis alone. In so doing, the usual exceptions encountered when specifying ceramic materials on the analytical basis will be avoided.

The tests recommended by Mr. Ross have the same general aim. They all tend to develop a well-made, well-burned brick. It is surprising to note how well these same features can be determined instantly by one familiar with a particular brand of silica brick. Two bricks when tapped together show by their ring nearly as much as can be learned by tests. This may be explained by the fact that the raw material is practically the same—the lime bond being kept within narrow limits and most silica brick being sufficiently refractory. The “ring” test determines the variable qualities—the burn and structure. The specific-gravity test, however, goes beyond the scope of the “ring” test in that it is accurate in discriminating between different brands. Some raw materials burn to form a product of good “ring” at low



temperatures. Such materials are quickly detected because of their high specific gravities. This is found to be particularly true when checked by the re-heating (expansion) test.

D. W. Ross: With reference to Mr. Howe's remarks on the above paper, it is of interest to note that in his screen analysis, in determining the size of grain in sandrock (presumably either Homewood sandstone or Oriskany sandstone) large percentages were retained on the 40- and 60-mesh sieves. This apparently checks the results of our own screen analyses.

It is gratifying to know that in so short a time the specific-gravity test for silica brick has been applied in so many useful ways, not the least of which is the method for control of the burning as set forth by Mr. Howe.

Mr. Howe strongly emphasizes the point brought out in the paper, that silica brick, as manufactured in the United States, usually fail on account of their physical properties and not on account of their chemical composition. In our opinion, entirely too much importance has, in the past, been placed on the chemical composition. With this in mind, no presentation of data and detailed discussion has been given in reference to chemical composition. Instead, the merest statement of the results obtained by ourselves and others, and of the usual practice as we understand it, have been set forth. This has been done in order to place on record information which we hope may be of assistance to future investigators in this complex and interesting field—the effects of fluxes, etc., on the properties of silica brick.