

S  
14.GS:  
CIR 335  
c. 1

ILLINOIS GEOLOGICAL  
SURVEY LIBRARY

STATE OF ILLINOIS  
DEPARTMENT OF REGISTRATION AND EDUCATION




# SILICA BRICK FROM NORTHERN ILLINOIS SILICA SAND

D. L. Deadmore  
J. S. Machin

ILLINOIS STATE GEOLOGICAL SURVEY  
URBANA

CIRCULAR 335

1962



Digitized by the Internet Archive  
in 2012 with funding from  
University of Illinois Urbana-Champaign

<http://archive.org/details/silicabrickfromn335dead>

# SILICA BRICK FROM NORTHERN ILLINOIS SILICA SAND

D. L. Deadmore and J. S. Machin

## ABSTRACT

This investigation was made to determine whether or not the fine-grained, high-purity (St. Peter) silica sand of northern Illinois could be made into a satisfactory silica brick refractory.

To this end, various bonding materials were tried, the best of which proved to be phosphates of calcium and aluminum. Certain lime binders were somewhat less promising. The results indicate that it may be feasible to use St. Peter sand to make a satisfactory silica refractory suitable for use in some furnace applications.

## PART I — PROPERTIES OF EXPLORATORY COMPOSITIONS

### Introduction

This work explored the possibilities of finding a refractory bonding material that could be used to produce a fine-grained silica refractory from the St. Peter sand of Northern Illinois. Various possible bonding agents were chosen for trial after an extensive review of the literature on this subject.

In the first phase of the work, test bars were prepared from a variety of mixtures and heat-treated in various ways. Some of their physical properties were then determined. In the second phase, the compositions showing the greatest promise were re-examined, and the results are presented in the second part of this report. Several compositions were found that produced what appeared to be satisfactory bricks from the standpoint of the tests given them and on the basis of information from the literature.

### Materials

The quartz sand used in all compositions came from a commercial silica sand plant near Ottawa, Illinois. Two size fractions were used; the "sand" was washed sand as mined, and the "silica flour" was a commercially ground material.

TABLE 1 - PARTICLE SIZE DISTRIBUTION OF SILICA

Sand	Percent	Silica flour	Percent
on 20 Mesh	0.1	on 100 Mesh	0.0
-20 + 35 Mesh	32.5	-100 + 200 Mesh	5.9
-35 + 48 Mesh	27.9	-200 + 250 Mesh	3.0
-48 + 80 Mesh	22.6	-250 + 270 Mesh	1.2
-80 + 100 Mesh	9.6	-270 + 325 Mesh	8.7
-100 + 200 Mesh	7.0	-325 Mesh	81.2
-200 Mesh	0.3		
	100.0		100.0

TABLE 2 - PACKING OF UNHEATED SAND AND SILICA FLOUR MIXTURES

Composition weight percent	Bulk density	Percent of true density	Void space percent
100 Sand	1.75	66	34
85 Sand + 15 Flour	1.84	70	29
75 Sand + 25 Flour	2.04	77	23
70 Sand + 30 Flour	1.98	75	25
65 Sand + 35 Flour	1.91	72	28
60 Sand + 40 Flour	1.89	71	29
50 Sand + 50 Flour	1.83	69	31
25 Sand + 75 Flour	1.55	59	41
100 Flour	1.51	57	43

Table 1 gives some size distribution data. Both materials are highly crystalline and 99.8 to 99.9 percent  $\text{SiO}_2$ .

The additives shown in the tables in symbolic form as  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$ , etc., were all high-purity materials of known composition. Most of the other additives were not of high purity and were not analyzed. Examples are the ilmenite, magnetite, siderite, talc, dunite, glauconite, mica, and Georgia kaolin, all of which are natural minerals and of uncertain composition. For example, the glauconite used was approximately 30 percent glauconite and 70 percent sand.

Refractory Binder No. 32 was prepared from a description given by Bechtel and Ploss (1960). First, 168 grams of  $\text{Al}(\text{OH})_3$  was added slowly to 796 grams of 85 percent  $\text{H}_3\text{PO}_4$ . After the initial reaction subsided, a small amount of water was added and the mixture was digested on the steam bath for about 8 hours. This solution was diluted to 1-liter with water and stored in glass until needed. This mixture is roughly 3.2 moles of  $\text{H}_3\text{PO}_4$  to 1 mole of  $\text{Al}(\text{OH})_3$ .

The calcium phosphate compositions (13 and 14, table 3) were obtained from a patent by West and Veale (1959).

#### Preparation of Samples

The sand and silica flour were proportioned; then the desired amount of additive was introduced and mixed mechanically; then sufficient water was mixed in by hand to bring the total liquid content to 10 to 12 percent by weight of the sand. No temporary binder was used. The mixture was molded into bars by hand tamping into a 1" x 1" x 2" steel die. The bars were dried at room temperature for several days, then at 110° C for several more days. All the bars possessed sufficient dry strength for easy handling in the laboratory. The compositions that contained No. 32 Binder were particularly hard.

The dried bars were heated in a Globar furnace in laboratory air. The temperature was increased to 600° C over a period of 5 hours, held at 600° C for 2 hours, then raised to the maximum desired temperature over a period of 12 hours. The maximum temperature was maintained for the desired time, then the power to the furnace was turned off. After three days the temperature was down to less than 100° C and the bars were removed from the furnace.

#### Testing

The bulk properties, as apparent porosity and bulk density, of the heated bars were determined by the usual procedure of water saturation (Andrews, 1928).

A part of each bar was ground up and the true density determined by the pycnometer method, using xylene as the displacement liquid. All true densities were determined at 35° C. The density of the xylene was measured at this temperature frequently and was constant.

X-ray powder diffraction patterns were made of each composition after each heat treatment. A General Electric XRD-3 x-ray spectrogoniometer and copper K  $\alpha$  radiation was employed.

In order to arrive at some mixture near the optimum packing of the quartz sand and silica flour, some packing tests were made. The silica flour and sand were proportioned by weight and vibrated in a graduated tube; from the volume and weight of the mixture the bulk density was estimated. From this the volume percentages of quartz and void space can be calculated. Table 2 shows that the maximum bulk density is near a mixture of 75 percent quartz sand and 25 percent silica flour.

## Discussion of Results

The bulk density, apparent porosity, and true density of the variously heat-treated compositions are given in tables 3, 4, 5, and 6. From these values, along with the diffraction patterns and a visual examination of each bar, some tentative conclusions about the influence of the additive or binder can be drawn.

Before discussing the mineralogical compositions of the mixtures, it may be well to discuss the physical appearance of the bars after firing. Compositions 2 and 3 (table 3) containing no additive were so friable as to be easily crumbled between the fingers. There was considerable crack formation and swelling, especially in the bars heated at 1500° C. Compositions 6, 7, and 8 containing No. 32 Binder exhibited very good strength with no cracking and very little swelling. Compositions 13 and 14 containing calcium phosphates were the best compositions investigated; the bars were very strong with no crack formation or swelling. All compositions shown in table 3 other than 6, 7, 8, 13, and 14 were very poor, had low strength, and cracked and swelled.

As shown in table 4, compositions 17 and 18 contained only CaO as additive. Bars heated at 1200° C had good strength, but after heating at 1420° and 1500° C they were soft. Compositions 19, 20, and 21 containing alkali were very soft and cracked badly at all temperatures. Compositions 24, 25, and 26 containing CaO and Fe<sub>2</sub>O<sub>3</sub> were all strong and showed no cracking or swelling as did compositions 30 and 31. Compositions 32 and 33 were the best of all the mixtures shown in table 4; they appeared very strong with no cracking or swelling. Portland cement, glauconite, and kaolin in compositions 36, 37, 38, and 42 produced a moderate amount of bonding. All the other compositions shown in table 4 produced very poor bars.

The bars of compositions 46, 47, 48, and 49, as shown in table 5, were either completely disintegrated to a powder after heating or were badly swelled and cracked, with very low strength. Bars of compositions 50 and 51 showed good strength when fired at 1200°, 1350°, and 1420° C, but both had low strength and cracked badly at 1500° C. All the other compositions in table 5 produced very poor bars.

Table 6 shows the data on mixtures heated for various lengths of time. The physical condition of the bars usually changed very little with increased heating time at 1420° C; if they were of high integrity after 24 hours they were also high after 100 hours.

It will be noted that the true density of the unmolded coarse fraction containing no additive decreased much more slowly than the corresponding fine fraction. The influence of particle size on the rate of conversion of quartz has been studied in some detail and will be reported elsewhere.

An inspection of the tables shows that the best bars, from the standpoint of physical integrity, had the lowest porosity and highest bulk density. It is believed, from information in the literature and the tabulated results, that some of these mixtures would produce a satisfactory silica refractory. However, refractoriness under load would have to be measured to check this.

After the molded bars listed in tables 3 to 7 were fired, they were ground and then studied by x-ray diffraction.

The mineralogical composition of some of the mixtures can be inferred from an examination of the diffraction patterns given in figures 1, 2, 3, 4, and 5. Figure 1 shows that after 24 hours at 1420° C the mixture containing no additives is only slightly converted to cristobalite, but at 1500° C no quartz remains. At

TABLE 3 - PHYSICAL PROPERTIES OF PHOSPHATE-BONDED, HAND-MOLDED QUARTZ SAND BARS AFTER HEATING 24 HRS. AT INDICATED TEMPERATURE

Composi- tion number	Quartz sand weight percent		Additives weight percent	1200° C			1350° C			1420° C			1500° C		
	*Coarse	**Fine		Apparent porosity Percent	Bulk density	True density	Apparent porosity Percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density
1	100	0	0 (unmolded, loose silica)	-	-	2.64	-	-	2.64	-	-	2.59	-	-	2.37
2	75	25	0	18.1	1.91	2.64	-	-	2.64	-	-	2.47	18.7	1.78	2.47
3	60	40	0	23.7	1.83	2.64	24.2	1.81	2.60	34.2	1.43	2.38	30.5	1.46	2.33
4	0	100	0 (unmolded, loose silica)	-	-	2.64	-	-	2.53	-	-	2.39	-	-	2.33
5	75	25	3.6 No. 32 Binder	15.8	1.97	2.59	15.1	1.90	2.54	14.8	1.84	2.48	24.7	1.48	2.30
6	75	25	7.2 No. 32 Binder	15.2	1.96	2.58	13.1	1.90	2.52	14.0	1.81	2.46	18.2	1.60	2.34
7	75	25	10.8 No. 32 Binder	14.7	1.98	2.58	14.5	1.90	2.50	15.4	1.82	2.46	14.6	1.67	2.34
8	75	25	14.4 No. 32 Binder	11.9	2.00	2.57	9.4	1.93	2.49	6.3	1.87	2.45	7.2	1.68	2.33
9	60	40	10.8 No. 32 Binder	12.3	2.03	2.58	10.9	1.97	2.48	9.1	1.90	2.44	10.0	1.79	2.33
10	75	25	10.8 No. 32 Binder + 1.0 K <sub>2</sub> CO <sub>3</sub>	13.8	1.97	2.57	16.0	1.90	2.49	15.9	1.80	2.44	23.1	1.51	2.32
11	75	25	10.8 No. 32 Binder + 2.0 CaO	26.9	1.76	2.63	29.6	1.66	2.56	26.0	1.71	2.52	29.5	1.52	2.36
12	75	25	10.8 No. 32 Binder + 1.0 Na <sub>2</sub> CO <sub>3</sub>	17.3	1.91	2.56	-	-	-	21.4	1.68	2.40	31.2	1.40	2.30
13	75	25	3.0 CaHPO <sub>4</sub> + 6.0 H <sub>3</sub> PO <sub>4</sub> (85%)	-	-	-	-	-	-	10.5	1.89	2.48	7.2	1.86	2.38
14	75	25	2.0 Ca <sub>3</sub> PO <sub>4</sub> + 6.0 H <sub>3</sub> PO <sub>4</sub> (85%)	-	-	-	-	-	-	6.6	1.92	2.47	6.4	1.82	2.38
15	75	25	1.5 BPO <sub>4</sub>	19.5	1.91	2.59	16.6	1.85	2.55	-	-	-	24.1	1.50	2.34
16	75	25	4.5 BPO <sub>4</sub>	14.9	1.99	2.54	10.5	2.00	2.46	-	-	-	6.3	1.79	2.32

\* Coarse = sand; Fine = silica flour.

TABLE 4 - PHYSICAL PROPERTIES OF LIME-BONDED, HAND-MOLDED QUARTZ SAND BARS AFTER HEATING 24 HRS. AT INDICATED TEMPERATURE

Composi- tion number	Quartz sand weight percent		Additives weight percent	1200° C			1420° C			1500° C		
	*Coarse	*Fine		Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density
17	75	25	2.0 CaO	17.0	1.95	2.64	17.6	1.72	2.37	25.5	1.56	2.34
18	60	40	2.0 CaO	20.3	1.88	2.61	19.4	1.70	2.34	24.2	1.58	2.34
19	75	25	2.0 CaO + 0.5 K <sub>2</sub> CO <sub>3</sub>	24.3	1.68	2.53	30.0	1.43	2.32	35.9	1.36	2.32
20	75	25	2.0 CaO + 1.2 K <sub>2</sub> CO <sub>3</sub>	24.1	1.60	2.44	33.2	1.36	2.31	36.8	1.33	2.32
21	75	25	2.0 CaO + 1.0 NaF	18.6	1.76	2.42	24.6	1.54	2.32	26.0	1.54	2.34
22	75	25	2.0 CaO + 0.5 Al <sub>2</sub> O <sub>3</sub>	17.8	1.93	2.63	16.3	1.73	2.36	23.9	1.58	2.35
24	75	25	0.5 CaO + 1.5 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	15.2	1.82	2.40	21.2	1.64	2.34
25	75	25	1.5 CaO + 0.5 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	15.0	1.85	2.41	18.3	1.71	2.34
26	60	40	0.5 CaO + 1.5 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	16.1	1.81	2.46	19.1	1.71	2.36
27	75	25	1.5 CaO + 0.5 Cr <sub>2</sub> O <sub>3</sub>	-	-	-	16.3	1.81	2.41	20.6	1.67	2.34
28	75	25	1.5 CaO + 0.5 TiO <sub>2</sub>	-	-	-	16.1	1.76	2.38	20.9	1.64	2.35
29	60	40	1.5 CaO + 1.5 ZrO <sub>2</sub>	-	-	-	19.5	1.73	2.40	20.9	1.66	2.37
30	75	25	1.5 CaO + 0.5 Ilmenite	-	-	-	15.7	1.86	2.46	19.3	1.69	2.34
31	75	25	1.5 CaO + 0.5 Magnetite	-	-	-	15.2	1.88	2.47	17.7	1.73	2.35
32	75	25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	13.6	1.85	2.42	17.7	1.71	2.35
33	60	40	0.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 1.0 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	15.7	1.82	2.48	17.7	1.73	2.35



34	75	25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub> + 1.5 K <sub>2</sub> CO <sub>3</sub>	-	-	14.4	1.81	2.35	20.5	1.65	2.36
35	75	25	2.0 CaO + 0.5 Al <sub>2</sub> O <sub>3</sub> + 0.5 K <sub>2</sub> CO <sub>3</sub>	20.9	1.78	24.6	1.54	2.32	26.0	1.54	2.34
36	75	25	2.0 Portland Cement	-	-	14.2	1.82	2.41	20.2	1.63	2.34
37	60	40	1.5 Portland Cement	-	-	16.9	1.75	2.41	22.8	1.58	2.34
38	75	25	1.5 CaO + 0.5 Kaolin	-	-	15.9	1.79	2.39	20.3	1.68	2.34
39	75	25	0.3 CaO + 1.0 Kaolin + 0.1 K <sub>2</sub> CO <sub>3</sub>	-	-	15.5	1.86	2.48	32.6	1.37	2.33
40	75	25	1.0 CaO + 1.5 Mica + 2.0 Fe <sub>2</sub> O <sub>3</sub>	-	-	19.7	1.70	2.37	29.9	1.48	2.35
41	75	25	1.5 CaO + 0.5 Kaolin + 0.2 Siderite	-	-	15.4	1.84	2.43	20.2	1.68	2.34
42	60	40	1.0 CaO + 2.0 Glauconitic Sandstone	-	-	19.6	1.69	2.35	23.6	1.58	2.34
43	60	40	0.2 CaO + 0.8 Siderite + 0.2 K <sub>2</sub> CO <sub>3</sub>	-	-	19.9	1.66	2.35	24.6	1.55	2.34
44	75	25	1.0 CaO + 1.0 Talc + 0.3 Fe <sub>2</sub> O <sub>3</sub> + 1.0 Cr <sub>2</sub> O <sub>3</sub>	-	-	15.6	1.87	2.40	20.4	1.68	2.35
45	60	40	2.0 Calcium Zirconium Silicate	-	-	20.7	1.66	2.39	26.7	1.51	2.35

\* Coarse = sand; fine = silica flour.

TABLE 5 - PHYSICAL PROPERTIES OF QUARTZ SAND BARS BONDED WITH MISCELLANEOUS MATERIALS, HAND MOLDDED AND HEATED 24 HOURS

Composi- tion number	Quartz sand weight percent		Additives weight percent	1200° C			1350° C			1420° C			1500° C		
	Coarse	Fine		Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density
46	75	25	0.5 K <sub>2</sub> CO <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-	2.82
47	75	25	1.0 K <sub>2</sub> CO <sub>3</sub>	-	-	-	-	-	-	-	-	-	-	-	2.81
48	75	25	2.0 K <sub>2</sub> CO <sub>3</sub>	39.2	1.19	2.27	41.6	1.13	2.28	44.3	1.09	2.28	49.7	1.10	2.28
49	75	25	2.0 Na <sub>2</sub> WO <sub>4</sub>	16.5	1.94	2.61	-	-	2.40	-	-	2.31	-	-	2.30
50	75	25	2.0 CaF <sub>2</sub>	16.0	1.93	2.63	15.8	1.92	2.56	16.5	1.74	2.37	22.2	1.57	2.88
51	75	25	5.0 BaS <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	-	-	-	-	-	-	21.3	1.64	2.39	24.9	1.56	2.38
52	75	25	0.5 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	16.3	1.79	2.46	22.5	1.84	2.81
53	75	25	2.0 Talc	-	-	-	-	-	-	22.6	1.66	2.40	29.4	1.50	2.83
54	75	25	1.0 Talc + 0.5 Cr <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	19.8	1.76	2.46	28.5	1.48	2.83
55	60	40	1.0 Talc + 0.3 Sid- erite + 0.2 Cr <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	20.4	1.70	2.42	24.5	1.55	2.83
56	75	25	1.0 Dunite	-	-	-	-	-	-	21.5	1.60	2.36	25.6	1.51	2.84
57	75	25	1.0 Dunite + 0.3 Siderite	-	-	-	-	-	-	17.5	1.77	2.44	23.0	1.57	2.84
58	75	25	2.0 MgO + 0.5 Fe <sub>2</sub> O <sub>3</sub>	-	-	-	-	-	-	22.0	1.64	2.39	26.6	1.54	2.85

\* Coarse = sand; fine = silica flour

TABLE 6 - INFLUENCE OF HEATING TIME AT 1420° C ON THE PHYSICAL PROPERTIES OF HAND-MOLDED QUARTZ SAND BARS

Quartz sand weight percent		Additives weight percent	12 Hrs.			24 Hrs.			50 Hrs.			100 Hrs.		
coarse	fine		Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density	Apparent porosity percent	Bulk density	True density
100	0	0 (Unmolded, loose)	-	-	2.62	-	-	2.59	-	-	2.51	-	-	2.45
75	25	0	19.6	1.80	2.56	18.7	1.78	2.47	18.9	1.74	2.42	20.1	1.69	2.42
60	40	0	27.7	1.70	2.53	34.2	1.43	2.38	27.1	1.63	2.38	27.5	1.61	2.38
0	100	0 (Unmolded, loose)	-	-	2.50	-	-	2.39	-	-	2.35	-	-	2.34
75	25	3.6 No. 32 binder	-	-	-	14.8	1.84	2.48	16.7	1.76	2.44	17.5	1.71	2.39
75	25	7.2 No. 32 binder	-	-	-	14.0	1.81	2.46	15.7	1.75	2.43	16.2	1.70	2.39
75	25	10.8 No. 32 binder	-	-	-	15.4	1.82	2.46	14.3	1.80	2.42	15.4	1.74	2.38
75	25	14.4 No. 32 binder	-	-	-	6.3	1.87	2.45	11.7	1.77	2.41	11.7	1.70	2.39
60	40	10.8 No. 32 binder	10.9	1.94	2.48	9.1	1.90	2.44	10.9	1.87	2.40	11.3	1.82	2.38
75	25	10.8 No. 32 binder + 2.0 CaO	28.5	1.69	2.55	26.0	1.71	2.52	28.2	1.63	2.46	29.8	1.57	2.45
75	25	10.8 No. 32 binder + 1.0 K <sub>2</sub> CO <sub>3</sub>	15.9	1.88	2.51	15.9	1.80	2.44	17.8	1.71	2.38	19.8	1.64	2.35
75	25	2.0 CaO	17.4	1.81	2.44	17.6	1.72	2.37	19.8	1.66	2.33	20.5	1.64	2.33
60	40	2.0 CaO	20.8	1.70	2.38	19.4	1.70	2.34	20.3	1.67	2.34	21.3	1.65	2.34
75	25	2.0 CaF <sub>2</sub>	17.1	1.77	2.44	16.5	1.74	2.37	19.0	1.66	2.34	20.9	1.62	2.34
75	25	2.0 K <sub>2</sub> CO <sub>3</sub>	44.4	1.09	2.28	44.3	1.09	2.28	43.3	1.12	2.27	43.8	1.11	2.27

\* Coarse = sand; fine = silica flour.

TABLE 7 - PROPERTIES OF PRESSED QUAKIL SAND COMPOSITIONS AFTER 24 HOURS AT THE INDICATED TEMPERATURE

Quartz sand weight percent *Coarse *Fine	Additives weight percent	Forming pressure psi	Firing temperature °C	Fired apparent porosity percent	Fired bulk density	Fired true density	Firing linear expansion percent	Firing volume expansion percent	Room temp. modulus of rupture psi	Room temp. compressive strength psi	Unfired bulk density
75 25	0	2500	1420	24.7	1.72	2.48	2.4	7.2	35	-	1.84
75 25	0	5000	1420	23.0	1.80	-	1.9	5.5	54	-	1.90
75 25	0	5000	1500	25.5	1.51	2.34	7.3	20.3	<20	-	1.90
75 25	2.0 CaO	2500	1420	20.4	1.73	-	4.0	11.4	360	-	1.97
75 25	2.0 CaO	5000	1420	19.7	1.81	-	3.7	10.6	420	-	2.01
75 25	2.0 CaO	5000	1500	23.0	1.64	-	6.4	18.1	130	-	2.01
75 25	1.5 CaO + 0.5 Fe <sub>2</sub> O <sub>3</sub>	2500	1420	22.5	1.78	-	3.1	8.9	440	3900	1.98
75 25	1.5 CaO + 0.5 Fe <sub>2</sub> O <sub>3</sub>	5000	1420	18.7	1.80	-	3.5	10.0	430	5000	2.02
75 25	1.5 CaO + 0.5 Fe <sub>2</sub> O <sub>3</sub>	5000	1500	22.1	1.66	-	5.8	16.4	150	2500	2.02
60 40	0.5 CaO + 1.5 Fe <sub>2</sub> O <sub>3</sub>	2500	1420	21.3	1.81	2.47	2.4	7.0	330	-	1.97
60 40	0.5 CaO + 1.5 Fe <sub>2</sub> O <sub>3</sub>	5000	1420	19.8	1.84	2.45	3.0	8.8	380	-	2.02
60 40	0.5 CaO + 1.5 Fe <sub>2</sub> O <sub>3</sub>	5000	1500	22.5	1.74	-	4.4	12.7	200	-	2.02
75 25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub>	2500	1420	20.4	1.80	2.45	2.5	7.3	430	5000	1.98
75 25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub>	5000	1420	19.8	1.83	2.44	2.9	8.5	470	5700	2.01
75 25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub>	10,000	1420	15.9	1.90	2.45	2.8	8.1	520	5300	2.09
75 25	1.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 0.4 Fe <sub>2</sub> O <sub>3</sub>	5000	1500	22.1	1.69	-	5.5	15.6	150	2400	2.01
60 40	0.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 1.0 Fe <sub>2</sub> O <sub>3</sub>	2500	1420	20.2	1.81	2.48	2.1	6.3	330	-	1.95
60 40	0.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 1.0 Fe <sub>2</sub> O <sub>3</sub>	5000	1420	17.5	1.84	2.47	2.7	7.8	290	-	2.02

60	40	0.5 CaO + 0.3 Al <sub>2</sub> O <sub>3</sub> + 1.0 Fe <sub>2</sub> O <sub>3</sub>	5000	1500	21.8	1.74	-	4.3	12.5	280	-	2.02
75	25	3 CaHPO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	2500	1420	16.2	1.81	2.49	2.0	5.9	310	-	1.96
75	25	3 CaHPO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	5000	1420	12.0	1.84	2.48	2.5	7.2	330	-	2.03
75	25	3 CaHPO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	5000	1500	5.9	1.84	2.39	3.2	9.2	590	6100	2.03
75	25	2 Ca <sub>3</sub> PO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	2500	1420	13.6	1.84	2.50	1.9	5.5	360	-	1.96
75	25	2 Ca <sub>3</sub> PO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	5000	1420	10.5	1.87	2.48	2.1	6.1	370	-	2.01
75	25	2 Ca <sub>3</sub> PO <sub>4</sub> + 6 H <sub>3</sub> PO <sub>4</sub> (85%)	5000	1500	5.2	1.82	2.37	3.6	10.4	870	5900	2.01
75	25	10.8 No. 32 Binder	2500	1420	13.8	1.81	-	1.7	5.1	240	-	1.92
75	25	10.8 No. 32 Binder	5000	1420	15.6	1.84	-	2.0	5.8	180	-	1.97
75	25	10.8 No. 32 Binder	5000	1500	11.8	1.74	2.40	4.1	11.8	470	-	1.97
75	25	7.2 No. 32 Binder	2500	1420	23.4	1.73	-	2.3	6.9	140	-	1.87
75	25	7.2 No. 32 Binder	5000	1420	18.2	1.80	-	2.5	7.4	220	-	1.98
75	25	7.2 No. 32 Binder	5000	1500	23.3	1.66	-	4.9	14.0	220	-	1.98
67	33	10.8 No. 32 Binder	2500	1420	21.0	1.82	-	2.4	7.1	160	-	1.95
67	33	10.8 No. 32 Binder	5000	1420	13.4	1.87	-	1.9	5.3	280	-	2.01
67	33	10.8 No. 32 Binder	5000	1500	13.4	1.80	-	3.2	9.2	450	-	2.01
60	40	10.8 No. 32 Binder	2500	1420	17.7	1.81	2.47	2.3	6.7	320	-	1.95
60	40	10.8 No. 32 Binder	5000	1420	18.7	1.87	2.48	2.1	6.1	270	-	2.00
60	40	10.8 No. 32 Binder	5000	1500	14.9	1.82	2.40	2.9	8.5	610	2400	2.00

\* Coarse = sand; fine = silica flour.

1500° C a broad, ragged line at approximately  $20.8^\circ$  in  $2\theta$  is present. According to Flörke (1955) this is produced by disorder in the cristobalite structure. When 2 percent CaO is added, there is nearly complete conversion of the quartz to cristobalite at 1420° C in 24 hours, with a very slight amount of tridymite. At 1500° C, however, the only component is cristobalite, which has less disorder than the pure quartz. When  $Al_2O_3$  and  $K_2CO_3$  are added along with CaO, considerable amounts of tridymite are also present.

The absence of tridymite in the fired pure sand, but its presence when  $Al_2O_3$  and  $K_2CO_3$  are present, agrees with the findings of Flörke (1956, 1961), Holmquist (1958), and unpublished work done in this laboratory. Flörke and Holmquist concluded that tridymite is not a crystalline phase of pure silica which is stable under normal (atmospheric) pressure, but is formed only when certain other ions are present, particularly the alkali ions. Buerger (1954) points out that tridymite is a stuffed derivative.

The CaO- $Fe_2O_3$  mixtures (fig. 2) show considerable amounts of quartz at 1420° C; however, at 1500° C only cristobalite is present. The sample containing only  $Fe_2O_3$  shows three or four times as much quartz present as the CaO-containing mixtures. Composition 32 containing  $Al_2O_3$ , as well as CaO and  $Fe_2O_3$ , shows about the same relative mineral composition as the CaO- $Fe_2O_3$  mixtures at the same temperature with the exception that some tridymite is present at 1420° C when the  $Al_2O_3$  is present.

Figures 2 and 3 show that at 1420° C after 24 hours considerable quartz is present in mixtures containing Portland cement, Kaolin,  $Cr_2O_3$ , and  $TiO_2$ , but at 1500° C only cristobalite is present and there is no appreciable amount of tridymite in any of them.  $BaS_2O_3 \cdot H_2O$  and MgO- $Fe_2O_3$  mixtures at 1420° C produce almost as good conversion of quartz as does CaO alone.

Figure 4 is a study of the influence of  $K_2CO_3$  additions on the conversion of quartz. At all levels of addition and at all temperatures and times of heating there is no unconverted quartz. However, there are considerable differences in the ratios of cristobalite to tridymite. The amount of tridymite present after 24 hours at 1420° C increases as the  $K_2CO_3$  content rises. Also the tridymite increases after 24 hours at temperatures from 1200° to 1420° C, but then decreases slightly at 1500° C. Increased time of heating at 1420° C seems to have little influence on the tridymite content. It was noticed that the strong tridymite line at  $23.3^\circ$  in  $2\theta$  had associated with it a poorly resolved line of lower intensity at  $22.9^\circ$  in  $2\theta$ . According to Hill and Roy (1958) this additional line at  $22.9^\circ$  characterizes this tridymite as the S-tridymite or stable variety. The low intensity line at  $24.3^\circ$  in  $2\theta$  ( $3.64\text{\AA}$ ) is not given in most x-ray data for tridymite, but Flörke (1961) shows this line in his data for a "potassium-tridymite."

Figure 5 shows that in general the conversion of quartz to cristobalite in the presence of the additives used is quite poor even at 1500° C and that no tridymite is formed. All these mixtures contain phosphate, which indicates that phosphates are not particularly good conversion agents.

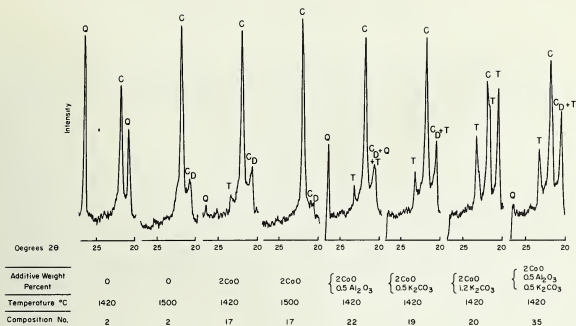


Fig. 1 - X-ray powder diffraction patterns of quartz sand compositions after 24 hours at indicated temperature.

C = cristobalite, Q = quartz, T = tridymite, C<sub>D</sub> = disordered cristobalite

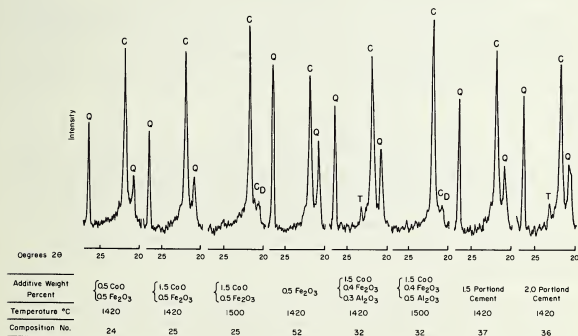


Fig. 2 - X-ray powder diffraction patterns of quartz sand compositions after 24 hours at indicated temperature.

C = cristobalite, Q = quartz, T = tridymite, C<sub>D</sub> = disordered cristobalite

## PART II — PROPERTIES OF SILICA BARS

## Introduction

Compositions which looked promising in the first examinations were re-examined. Bars measuring 1" x 1" x 6" were mechanically pressed in a steel die at various pressures, then after heat treatment some physical properties were determined, particularly strength at room temperature.

## Sample Preparation

The materials used and the mixing were the same as previously described. However, 0.4 weight percent of gum arabic was added to each mixture as a temporary binder. These mixtures were pressed at 2500, 5000, and in one case at 10,000 psi in the form of 1" x 1" x 6" test bars. Most compositions had adequate green strength, and after drying for several days at room temperature and for several more days at 110° C, were very strong.

The dried bars were heated and cooled in a Globar furnace on the same schedule described in part I. All bars were held for 24 hours at the maximum temperature.

## Testing

The bulk density of the unheated and heated bars was determined from the weight and external dimensions of the bars. The linear and volume expansion caused by firing was determined from the change in length of the bars. The apparent porosity was measured by the water saturation method.

Modulus of rupture measurements were made on a Tinius-Olsen testing machine, using supports at 3-inch centers. The compressive strengths were determined on 1" x 1" x 2 1/2" bars applying the load parallel to the long dimension. The loading rate was 2000 pounds per minute.

Some true density determinations were also made using the pycnometer method previously described.

## Discussion of Results

The results are all summarized in table 7. It can be seen that a mixture of quartz sand and silica flour alone, with no additives, is very weak, and that all the additives tried gave strengths considerably in excess of this blank. The best samples, from the standpoint of strength, bulk density, and porosity, are the mixtures containing calcium phosphate heated at 1500° C. It was noticed that in general the phosphate-bonded mixtures increased in strength with increased firing temperature, whereas the lime-bonded mixtures decreased in strength. This may be related to the greater amount of firing expansion of the lime mixtures.

The compressive strengths of the mixtures tested were rather high, in fact, much higher than expected from the rather low modulus of rupture values. In general, both the compressive strength and modulus of rupture increased with a decrease in the apparent porosity, but as different functions, as shown in figure 6.

Parmelee and Harman (1946), in their study of the production of silica refractories from southern Illinois novaculite, also found that the modulus of



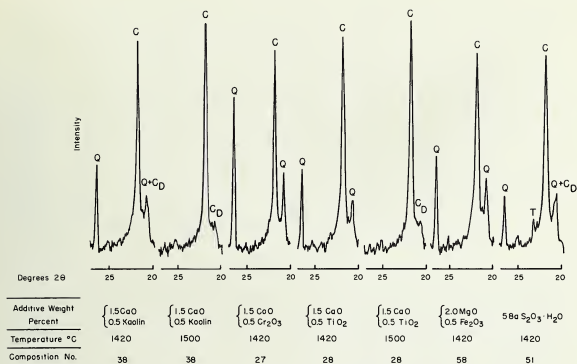


Fig. 3 - X-ray powder diffraction patterns of quartz sand compositions after 24 hours at indicated temperature.

C = cristobalite, Q = quartz, T = tridymite, C<sub>D</sub> = disordered cristobalite

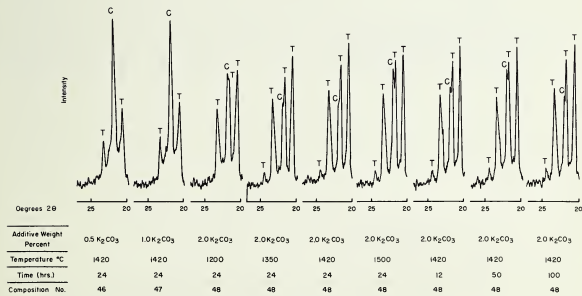
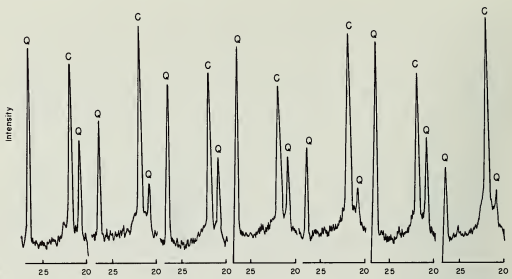


Fig. 4 - X-ray powder diffraction patterns of quartz sand compositions after indicated heat treatment.

C = cristobalite, T = tridymite



Additive Weight Percent	{ 3 Co HPO <sub>4</sub> + 6-85% H <sub>3</sub> PO <sub>4</sub>	{ 3 Co HPO <sub>4</sub> + 6-85% H <sub>3</sub> PO <sub>4</sub>	{ 2 Co <sub>3</sub> PO <sub>4</sub> + 6-85% H <sub>3</sub> PO <sub>4</sub>	{ 10.8 No. 32 Binder	{ 10.8 No. 32 Binder	{ 7.2 No. 32 Binder	{ 7.2 No. 32 Binder
Temperature °C	1420	1500	1420	1420	1500	1420	1500
Composition No.	13	13	14	7	7	6	6

Fig. 5 - X-ray powder diffraction patterns of quartz sand compositions after 24 hours at indicated temperature.  
C = cristobalite, Q = quartz, T = tridymite

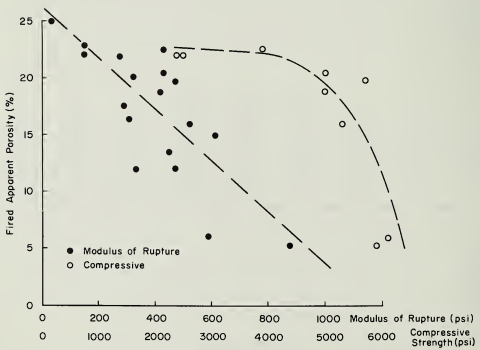


Fig. 6 - Relationship between porosity and strength of quartz sand bars after heating.

rupture was roughly proportional to the porosity. They also state that the strength of fired silica bricks depends largely on the manner in which the brick is made, such as grain size distribution, firing schedule, etc.

The No. 32 refractory binder, upon dehydration and calcination, produces  $AlPO_4$ , so the bonding in the mixtures containing No. 32 Binder is due to  $AlPO_4$  after firing. Obst and Trömel (1955) have studied in some detail the use of  $AlPO_4$  as a bond in silica refractories. They found it to be a satisfactory binder, but warn that in reducing conditions much  $P_2O_5$  may be lost, leaving  $Al_2O_3$  which is detrimental to the refractoriness of silica brick.

No. 32 Binder in amounts of 5 to 10 percent would give 0.4 to 0.8 percent of  $Al_2O_3$  if all the  $P_2O_5$  were lost. Inasmuch as a maximum of 0.5 percent  $Al_2O_3$  is all that can be tolerated in high-heat duty brick, it would be necessary to keep the amount of No. 32 Binder at or below 6 to 7 percent, especially if reducing conditions exist in the furnace.

### CONCLUSIONS

The conversion of the quartz to cristobalite or tridymite, or a mixture of the two, is associated with a large volume change. It seems that the paramount problem is to find a binder that will not lower the inherent refractoriness of the silica and yet at the same time will decrease the large silica volume change so that a coherent, low-porosity, and high-strength product results.

It was observed that the bars with the lowest expansion and porosity and highest bulk density were the best. Additives producing these results to the greatest degree were the calcium and aluminum phosphates (No. 32 Binder). It is believed that by further development along the lines of particle size distribution, firing schedule, forming procedures, and others, that some of the lime bonds might also produce a satisfactory product.

It was observed that heating this high-purity sand alone with no additives produced only cristobalite and that the production of tridymite required the presence of impurities, particularly potassium. The presence of potassium however, produced a poor bar of low strength and high expansion after heating on the schedule used here.

## REFERENCES

- Andrews, A. I., 1928, Ceramic tests and calculations: New York, John Wiley and Sons, Inc., 172 p.
- Bechtel, Von H., and Ploss, G., 1960, Binding of ceramic raw materials with monoaluminum phosphate solution: Ber. Deut. Keram. Gesell., v. 37, no. 8, p. 362-367.
- Buerger, M. J., 1954, The stuffed derivatives of the silica structures: Am. Mineralogist, v. 39, nos. 7, 8, p. 600-614.
- Flörke, O. W., 1955, Structural anomalies in tridymite and cristobalite: Ber. Deut. Keram. Gesell., v. 32, no. 12, p. 369-381. Reprinted in Am. Ceramic Soc. Bull., v. 36, no. 4, p. 142-148, 1957.
- Flörke, O. W., 1956, The unicomponent system  $\text{SiO}_2$ : Naturw., v. 43, p. 419-420.
- Flörke, O. W., 1961, The crystallization of  $\text{SiO}_2$  and its transformation behavior: Ber. Deut. Keram. Gesell., v. 38, no. 3, p. 89-97.
- Hill, V. G., and Roy, Rustum, 1958, Silica structure studies, VI - On tridymites: Brit. Ceramic Soc. Trans., v. 57, no. 8, p. 496-510.
- Holmquist, S. B., 1958, Sluggish silica transformations: Zeitschr. Krist., v. 111, p. 71-76.
- Obst, K. H., and Trömel, G., 1955, Possibility of binding silica with  $\text{AlPO}_4$ : Tonindustrie-Zeitung, v. 79, nos. 13, 14, p. 195-205.
- Parmelee, C. W., Harman, C. G., 1946, Southern Illinois novaculite and novaculite gravel for making silica refractories: Illinois Geol. Survey Rept. Inv. 117, 55p.
- West, H. F., and Veale, J. H., 1959, Chemically bonded silica brick: Brit. Patent No. 825792, Dec. 23.

Illinois State Geological Survey Circular 335  
18 p., 6 figs., 7 tables, 1962

Printed by Authority of State of Illinois, Ch. 127, IRS, Par. 58.25.



CIRCULAR 335

**ILLINOIS STATE GEOLOGICAL SURVEY**

URBANA