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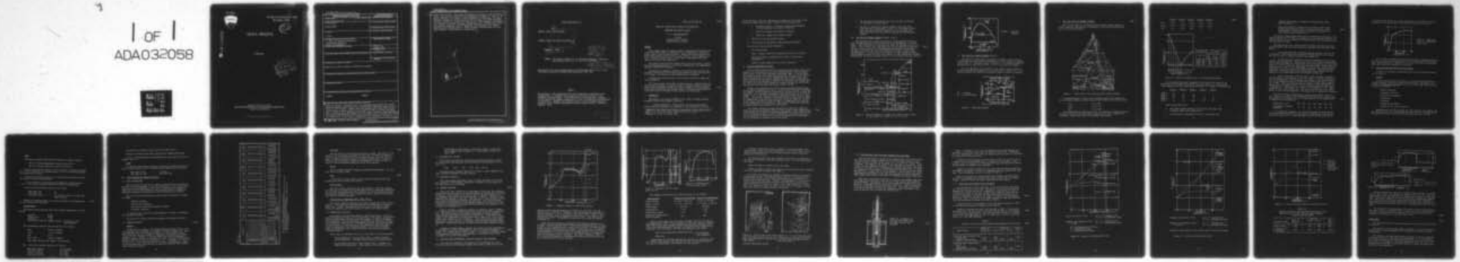

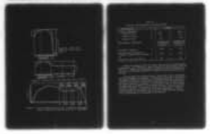

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SILICA GROUTS

J. Baron

CORPS OF ENGINEERS, U.S. ARMY
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY
HANOVER, NEW HAMPSHIRE

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Until recent years, the grouts used for cementing silica bricks had a quite different chemical composition and a mineralogical composition quite close to those of silica bricks. Indeed, they were prepared from baked finely ground silica bricks to which plastic clay was added in order to provide the grout with a certain ease in employment and allow ceramic setting at high temperature. The ternary SiO_2-Al_2O_3-CaO diagram shows that these types of grouts have limiting temperatures of utilization incompatible with temperatures reached in →

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cont. modern coke furnaces. The grouts are therefore developed in the direction of purity (decrease in contents of CaO and Al_2O_3) and fineness in order for the ceramic setting to be reached at high temperature by sintering. The specifications relating to silica grouts are few in number and rather disparate. The tests carried out on about 20 silica grouts: mineralogical and particle-size analyses, pyroscopic strength, thermal expansion, settling tests under differential charge and creep on "sandwich" test specimens have allowed specifying the limiting values of these different characteristics and can allow estimate of the quality of a given grout.

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TECHNICAL ASSOCIATION OF FRENCH IRON METALLURGY

COMMITTEE FOR COKING PLANTS**

C. 72. Silica Grouts***

J. Baron
(Laboratories of Refractories and Ores, Nancy)

SUMMARY

Until recent years, the grouts used for cementing silica bricks had a quite different chemical composition and a mineralogical composition quite close to those of silica bricks. Indeed, they were prepared from baked finely ground silica bricks to which plastic clay was added in order to provide the grout with a certain ease in employment and allow ceramic setting at high temperature.

The ternary SiO_2-Al_2O_3-CaO diagram shows that these types of grouts have limiting temperatures of utilization incompatible with temperatures reached in modern coke furnaces.

The grouts are therefore developed in the direction of purity (decrease in contents of CaO and Al_2O_3) and fineness in order for the ceramic setting to be replaced at high temperature by sintering.

The specifications relating to silica grouts are few in number and rather disparate.

The tests carried out on about 20 silica grouts: mineralogical and particle-size analyses, pyroscopic strength, thermal expansion, settling tests under differential charge and creep on "sandwich" test specimens /2580 have allowed specifying the limiting values of these different characteristics and can allow estimate of the quality of a given grout.

I. DEFINITION

According to the document AFNOR FD B No. 40014, unformed prepared materials include three types of products:

1. *Grouting materials:* Finely ground refractory compositions which, generally moistened, are intended for the placement of grouting

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*Numbers in the right margin indicate pagination in the original text.

**Circ. Inf. Techn. Cent. Doc. Sider, Vol. 31 (12), 1974.

***Meeting of 23 and 24 January 1974.

bricks and whose refractory components correspond to the quality of the bricks with which they are used: We make a distinction between:

a. Refractory grouts: refractory compositions hardening at high temperature by ceramic connection,

b. Refractory cements with hydraulic setting,

c. Refractory cements with chemical binder.

2. Refractory coats and surface covers.

3. The mixtures for monolithic constructions and repairs.

The refractory grouts should therefore:

Be finely ground,

Have a chemical composition compatible with that of bricks,

Have some degree of workability in order to allow their employment,

Harden at high temperature by ceramic connection.

II. SPECIAL PROPERTIES OF SILICA

In the construction of refractory masonries using silica clay or clay products, the characteristics of the grouting materials used correspond quite closely to the four requirements mentioned above. In many cases, the alumina content of the grout is even greater than that of the bricks. This is the special case of the regenerating coke furnaces built with bricks having 20-22% of alumina cemented with grout with 32-33% alumina. The clay grouts are composed of a mixture of refractory clay (baked clay) and coarse clay, this latter giving the required workability and providing the grout with the high temperature ceramic setting.

However, the preparations of silica grouts presents problems owing to the special properties of silica. A silica grout obtained by grinding, for example, silica bricks has no plasticity and does not set at high temperatures. It is therefore necessary to add a plasticizer to this silica powder. Clay is also added in variable proportions which can go as high as 20%. In this way, a product is obtained which no longer has the chemical composition of the brick but which will easily be spread by a trowel on the bricks and ensure ceramic setting at a temperature less than the service temperature of the masonry. This ceramic setting will therefore be reached during the heating up of the battery.

This simple solution has been satisfactorily used for a number of years so long as the masonries have not been raised to high temperatures. /2581
Nevertheless, with increase in operating temperatures, this formula turned out to be inadequate and, in order to understand the reasons for this, it is now necessary to examine the equilibrium diagrams with, furthermore, all the cautions for use which are of two types:

1. The theoretical equilibriums are rarely reached in practice or only after very long times;

2. The role of impurities, meaning elements other than SiO_2, Al_2O_3 and CaO is disregarded. Still, it is necessary to note that the impurities have a harmful role in the sense that they lower still more the eutectic temperatures between pure bodies.

III. THE SiO_2-CaO BINARY DIAGRAM (Figures 1 and 2)

The SiO_2-CaO binary diagram shows that at high temperatures and for lime contents going up to about 26%, there is no miscibility. In other words, a small proportion of lime does not lower the melting point of the silica. Let us recall that lime added into the raw materials during manufacture of silica bricks is a transformation mineralizer of the quartz /2582 and that its presence is absolutely necessary in order to ensure this transformation. A silica lime mixture with a low lime content therefore has advantageous properties from the viewpoint of high temperature strength. Nevertheless, as we have already stated, it is not plastic and will not set.

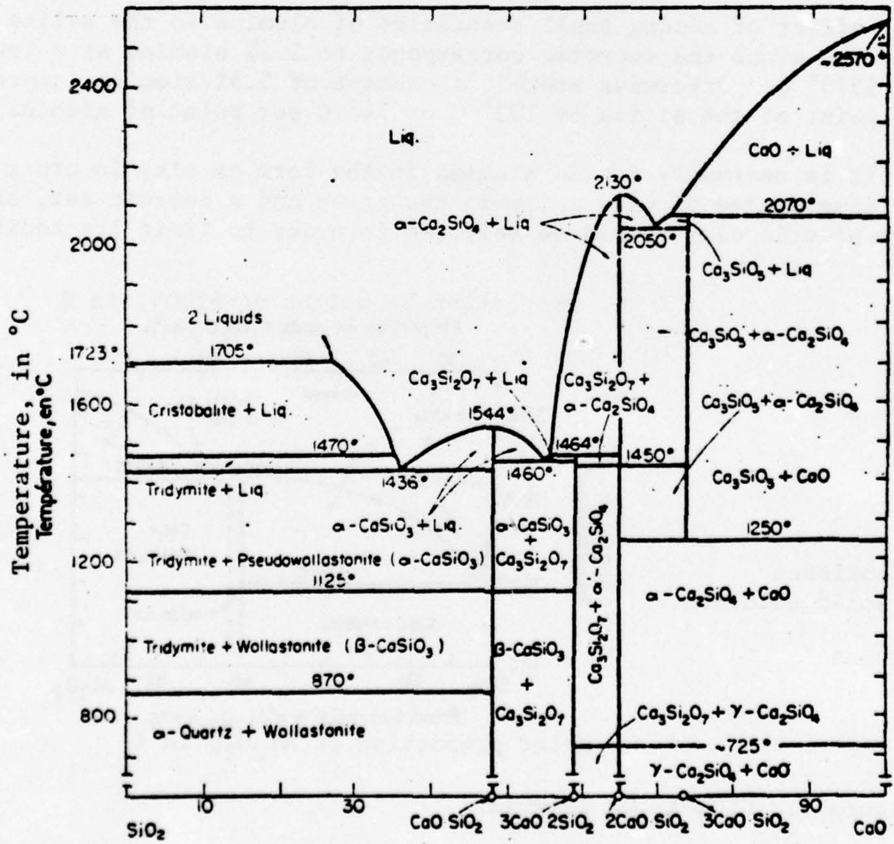


Figure 1. SiO_2-CaO diagram, according to B. Phillips and A. Muan (J. Am. Ceram. Soc., 1959, 42, No. 9, p. 414).

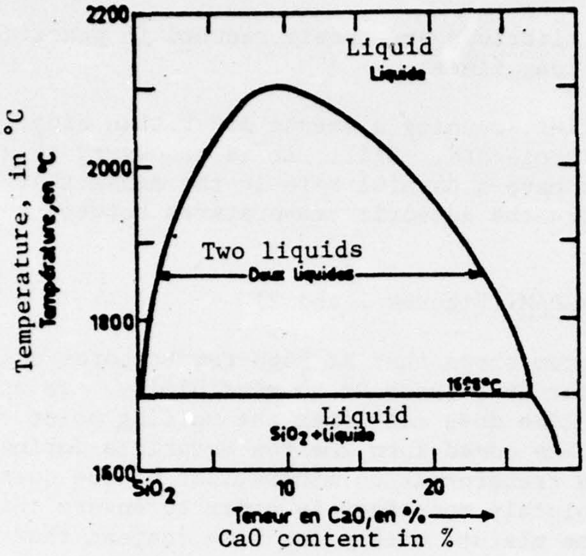


Figure 2. SiO_2-CaO diagram.

IV. THE SiO_2-Al_2O_3 BINARY DIAGRAM (Figure 3)

The effect of adding small quantities of alumina to the silica is considerable since the eutectic corresponds to 5.5% alumina at a temperature of 1595° C. Otherwise stated, a content of 5.5% alumina lowers the melting point of the silica by 133° C or 24° C per point of alumina.

If it is necessary to add alumina in the form of clay in order to produce some degree of plasticity in the grout and a ceramic set, an especially plastic clay should be selected in order to limit its addition.

Cor. = corindon
ss = solid solution

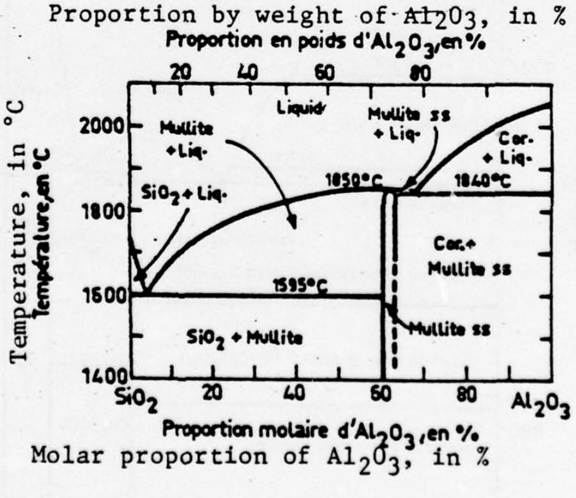


Figure 3. SiO_2-Al_2O_3 diagram.

V. THE SiO_2-Al_2O_3-CaO TERNARY DIAGRAM

/2583

The "silica" angle of the SiO_2-Al_2O_3-CaO ternary diagram (Figure 4) allows explaining the behavior in operation of the various silica grouts used in the past and present.

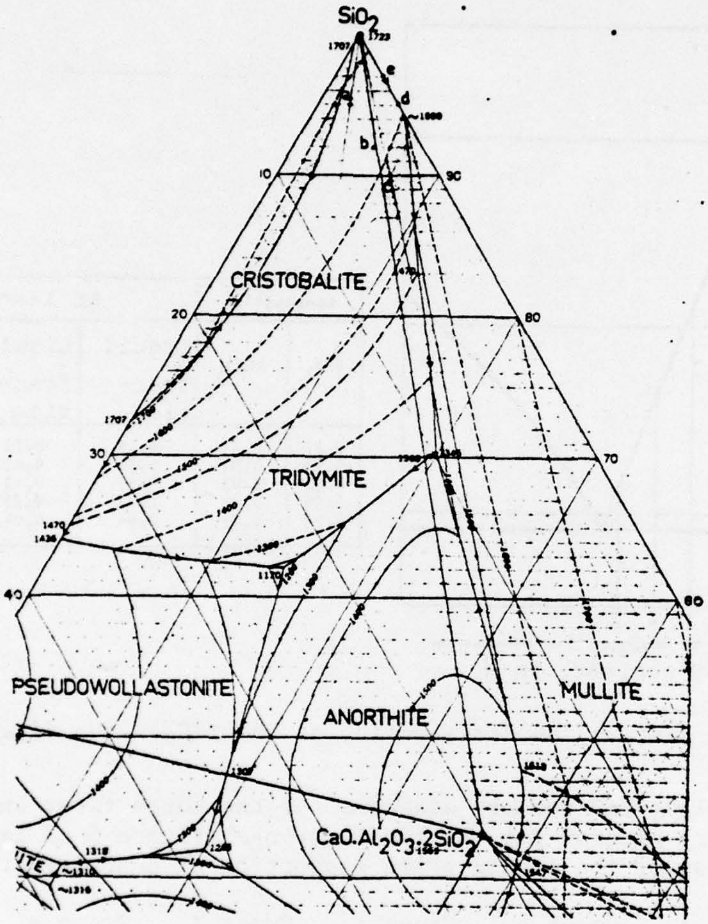


Figure 4. "SiO_2" angle of the SiO_2-Al_2O_3-CaO ternary diagram.

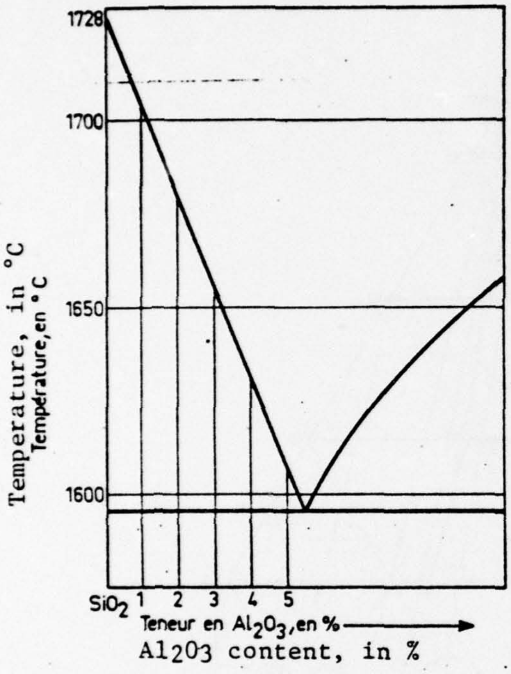
The approximately 20 silica grouts examined during this study have quite different chemical compositions and vary within the following limits:

SiO_2	86 to 98%
Al_2O_3	0.2 to 7.7%
CaO	0 to 4.9%

By disregarding the impurities which, by formation of complex eutectics, increase still more the liquid phase proportion, we shall consider five "synthetic" grouts which have the following compositions:

/2584

	Grout a	Grout b	Grout c	Grout d	Grout e
SiO_2	0.95	0.92	0.90	0.95	0.97
Al_2O_3	0.02	0.05	0.07	0.05	0.03
CaO	0.03	0.03	0.03	0	0



Composition		At 1600°C		
SiO_2	Al_2O_3	Liquid fraction	Liquid fraction	Ratio liquid/solid
0,99	0,01	0,19	0,81	1/4,3
0,98	0,02	0,38	0,62	2/3,3
0,97	0,03	0,57	0,43	3/2,3
0,96	0,04	0,75	0,25	4/1,3
0,95	0,05	0,94	0,06	5/0,3

Figure 5. Portion, on large scale, of the SiO_2-Al_2O_3 diagram.

The SiO_2-Al_2O_3-CaO ternary diagrams for the three first ones and the SiO_2-Al_2O_3 binary diagram for the two last ones (Figure 5 on large scale) allow computation of the liquid phase proportion at a number of temperatures:

	Grout a	Grout b	Grout c	Grout d	Grout e
1300° C	14				
1400° C	16	31	42		
1500° C	20	45	67	0	0
1590° C				0	0
1600° C	31	78	100	94	57

These figures show that:

1. The liquid phase proportion of the grouts containing lime increases rapidly with temperature;

2. The progressive replacement of silica, by alumina with

constant lime content, considerably increases the liquid phase proportion;

3. The grouts having no lime at all are solid at 1590° C but display starting with 1600° C a high proportion of liquid phase having a viscosity which increases in proportion as the alumina content becomes less. /2585

The ternary diagram again shows that the compositions included in the angle formed by the two 1600° C isotherms are to be rejected and that, as lime has turned out to be harmful, we should finally turn to products practically devoid of lime.

Although there are no clear boundaries between the different silica grouts studied, they can nevertheless be classified into three main categories:

1. Grout simultaneously containing lime and alumina. This is the old formula: these grouts were produced by mixing ground silica bricks and clay in order to ensure plasticity and ceramic set.

2. Grouts practically devoid of lime but including a clay in a relatively large proportion. These grouts can only be natural raw materials, silica sands enclosing on a natural basis some clay generally of an illitic nature, or silica products to which clay has been added. These grouts are therefore made up as a first approximation by quartz and clay for there is practically no natural silica other than the quartz. These grouts have, therefore, the characteristics of untransformed silica bricks, but the addition of clay makes them plastic and ensures ceramic set.

3. Clays containing no lime but with a small quantity of alumina. By decreasing the clay content to very low values, or without addition of clay at the same time only considering the alumina of the natural materials, it is possible to arrive at pure products with high silica contents (up to 98%). Since the products are not plastic, several thousandths of plasticizers are added to them in order to provide them with some degree of workability. Furthermore, as a result of the absence of clay, these grouts will not have ceramic set. They will therefore have to be finely ground so that at high temperature the ceramic set is replaced by sintering.

The initial setting temperature of silica grouts should not be too low. Owing to its nature, the transformed silica brick has a rather special expansion curve (Figure 6) for it expands mainly at low temperatures as shown by the following data: /2586

Temperature, in °C	100	200	300	400	500	600	700
Percentage of maximum expansion	22	60	80	85	89	93	96

It is therefore essential, in a construction made of silica bricks, for the setting of the grout to take place at temperatures in which the bricks are practically no longer expanded, that is to say above 700° C.

If the grout was setting at a lower temperature, the stresses caused by expansion of the bricks would cause the dislocation of the joints.

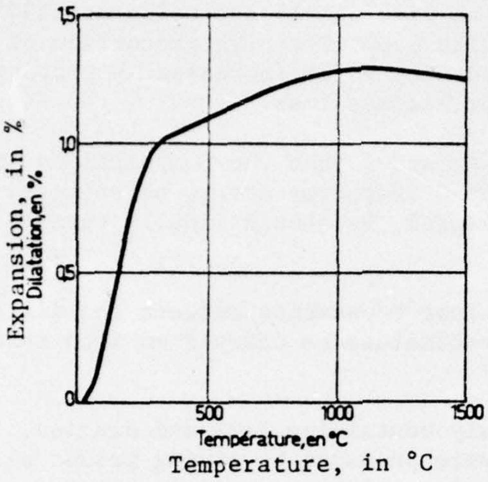


Figure 6. Expansion curve of a transformed silica brick.

All of these considerations show the difficulty of defining the quality of silica grouts which should have rather uncontroversial properties, hence characteristics of compromise as is quite often the case, furthermore, when refractory products are concerned.

VI. SPECIFICATIONS AND TESTS OF SILICA GROUTS

A number of standards and specifications have been published abroad on this subject.

Germany

In the study entitled "The Control of Siliceous Grouting Products of Coke Furnaces" by Mueller, Neugluck and Konopicky, published in the periodical Tonindustrie Zeitung, 87, No. 14, of July 1963, some tests are pointed out, such as:

Chemical analysis

Pyroscopic stability

Particle-size analysis

Workability

Polishing

Adherence when heated

Capability for water retention.

Specifications for silica grouts are also found as, for example, the two following ones: the one showing that the pyroscopic stability should be greater than 1680° C and the other one gives the value of 1695° C.

USSR

The Russian Standard GOST 5338-60 considers two types of grouts:

MA-1 for working temperatures greater than 1500° C,

MA-2 for working temperatures less than 1500° C.

The MA-1 grout should contain 4 to 6% of plastic refractory clay and 96 to 94% of a mixture in the proportion of 2.6 to 1 of natural quartzite and crushed silica bricks.

The MA-2 grout should contain 10 to 12% plastic refractory clay and 90 to 88% of the same siliceous mix.

A small proportion of plasticizers are added into the two grouts: 0.07 to 0.15% of soda carbonate and 0.05 to 0.10% of lignosulfite.

The particle-size analysis should be as follows:

More than 2 mm	0
More than 1 mm	3%
Less than 0.2 mm	65 to 80% of which 45 to 60% less than 0.080 mm.

Methods for measuring capacity for water retention and binding capacity of the grout are described. /2587

United States

The American specifications show the following composition of silica grouts:

Quartzite	88.8%
Plastic clay	10.0%
Bentonite	1.2%

Silica fines with low alumina content: 10% added to the above mixture.

The corresponding chemical analysis should be as follows:

SiO_2	93.5% at minimum
Al_2O_3	3.5% at maximum
CaO	0.7%
$Na_2O + K_2O$	0.25% at maximum

TiO_2, MgO, FeO and other fluxes: less than 2%.

The particle-size analysis should be as follows:

More than 1.168 mm	1% at maximum
1.168 to 0.295 mm	20 to 40%
0.295 to 0.074 mm	25 to 35%
Less than 0.074 mm	35 to 50%.

The pyroscopic stability should not be less than 1670° C.

Testing of plasticity and water retention are likewise described.

A test of refractoriness with checkerworks is also given and will be examined later on.

Japan

One Japanese specification provides a pyroscopic stability of 1710° C with a silica content of 92%. The particle-size analysis is as follows:

More than 0.3 mm	. . . .	7 to 13%
Less than 0.07 mm	. . . .	more than 55%.

VII. TESTS CARRIED OUT DURING THIS STUDY

7.1 TESTS ACCOMPLISHED

Faced with the multiplicity of tests and specifications collected in one part of the bibliography, it has not been possible to set up a specific plan from the very beginning of this study. However, since a number of varieties of grouts were available, this study has mainly a comparative character involving characteristics of these different silica grouts.

Some of the tests considered as essential were carried out in almost all cases:

Chemical analysis,

Particle-size analysis,

Qualitative radiocrystallographic analysis,

Pyroscopic stability.

In certain cases, testing involved expansion, settling on a sandwich test specimen and creep.

The results of testing the grouts examined are provided in Table I.

7.2 CHEMICAL ANALYSIS /2588

Alumina

Alumina has two origins: The intracrystalline alumina from the siliceous raw material and chiefly the alumina from added binding clay. Using the hypothesis that the binding clay added is of the kaolinite $Al_2O_3 \cdot 2 SiO_2 \cdot 2 H_2O$ type, the clay content is obtained by multiplying the alumina content by 2.53. However, in the case where this clay has undergone a thermal treatment leading to the departure of the 2 H_2O from the kaolinite molecule, this factor will be corrected to 2.18. In summary, the clay content is by 2.2 to 2.5 times the content of Al_2O_3. Nevertheless, a number of silica sands used for production of grouts often enclose illite with a poorly specified formula.

TABLE I -
SILICA GROUTS

CHARACTERISTIC		GROUT			GROUT							
		16 965 E	16 345 C-1	16 835 Ka	17 268 D-K	17 288 (02)	17 332 ATH-1	16 611 0-1	16 798 G-R	17 266 B-3	16 452 V-1	16 419 G-C-1
Chemical Analysis:												
- Fire loss	%	2,44	1,58	1,80	1,35	1,80	1,30	1,23	1,00	0,80	1,52	0,38
- SiO_2	%	85,85	87,65	91,88	91,72	91,57	92,81	93,66	95,07	96,32	96,45	98,04
- Al_2O_3	%	7,73	6,69	5,19	4,97	4,32	3,52	3,39	2,72	1,92	0,77	0,63
- TiO_2	%	0,42	0,55	0,20	0,86	0,36	0,93	0,29	0,16	0,28	0,10	0,13
- Fe_2O_3	%	0,92	0,81	0,37	0,37	1,20	0,30	0,76	0,30	0,25	0,55	0,50
- P_2O_5	%	0,07	0,05	0,06	0,04	0,04	0,02	0,04		0,03		0,02
- CaO	%	1,79	1,87	0,17	0,12	0,09	0,22	0,12	0,14	0,12	0,12	0,03
- MgO	%	0,12	0,04	0,07	0,12	0,06	0,15	0,06	0,10	0,10	0,04	0,03
- Na_2O	%	0,04	0,05	0,01	0,05	0,03	0,05	0,03	0,05	0,05	0,12	0,03
- K_2O	%	0,32	0,46	0,20	0,50	0,32	0,44	0,32	0,26	0,25	0,10	0,08
Pyroscopic Stability	°C	1 580	1 640	1 690	1 670	1 660	1 670	1 670	1 710	1 710	1 700	1 720
Differential settling under load (2 %) (*)	°C	1 480	1 470	1 590	1 510	1 530	1 530	1 530	1 575		1 580	1 630
Particle-size Analysis (**)												
> 1 mm	%	2,5	3,5	0,4	0,3	1,1	0	0,6	0	0	0	0,4
< 1 mm	%	19,8 97,5	26,2 96,5	3,2 99,6	2,9 99,7	4,7 98,8	3,1 99,9	3,0 99,4	2,9 100	0,7 99,9	1,1 100	0,8 99,5
< 0,50 mm	%	19,9 77,7	23,1 70,3	22,5 96,4	10,8 96,8	39,1 94,1	25,4 96,8	36,3 96,4	21,3 97,1	24,4 99,2	17,2 98,9	3,0 98,7
< 0,25 mm	%	19,1 57,8	15,3 47,2	38,2 73,9	22,7 86,0	15,9 55,0	35,2 71,4	17,9 60,1	21,6 75,8	46,5 74,8	15,0 81,7	28,9 95,7
< 0,125 mm	%	15,9 38,7	12,4 31,9	18,6 35,7	25,7 63,3	11,3 39,1	13,0 36,2	10,7 42,2	10,0 54,2	7,9 28,3	16,6 66,7	29,6 66,8
< 0,063 mm	%	22,8 22,8	19,5 19,5	17,1 17,1	37,6 37,6	27,8 27,8	23,2 23,2	31,5 31,5	44,2 44,2	20,4 20,4	50,1 50,1	37,2 37,2
Radiocrystallographic (+) Analysis	-	quartz α f cristobalite F tridymite F	quartz α f cristobalite F tridymite F	quartz α TF				quartz α TF	quartz α TF		quartz α TF	quartz α TF

(*) Test with sandwich test specimen with 6 mm grout joint.

(**) The first column of results corresponds to the screened material by screen and the *second one to the cumulative screened materials.*

(+) Radiocrystallographic analysis: f = low intensity; F = high intensity; TF = very high intensity.

Fire Loss /2589

The fire loss of silica grouts has several origins: The water of constitution of the binding clay added (in this case, it should correspond to 0.35% of Al_2O_3 when the clay is of the kaolinite type), and also the organic or organic-inorganic plasticizers added intentionally. A number of producers are occasionally limited to determination of the fire loss in order to confirm production constancy of the silica grouts.

Silica

This is clearly the basic component ensuring refractoriness. Its content can be as high as 98%.

Lime /2590

A lime content in the vicinity of 2% shows that the grout has been prepared from raw or baked silica bricks.

Ferrous Oxide

This is a natural impurity of the raw materials. The iron, however, can also have its origin in particles coming from the pulverized substances. It is clearly advantageous for this content to be as low as possible since the reducing atmosphere of coke furnaces can lead to formation of fayalite $SiO_2 \cdot FeO$ with low melting point.

Titanium Oxide, Magnesium Oxide, Soda, Potash

These minor elements constitute the natural impurities of the raw substances. The titanium content increases with the proportion of alumina, hence clay, content. One exception to this rule is the case of South African raw materials in which titanium is found in the silica system.

7.3 MINERALOGICAL ANALYSIS

This analysis has only been made on a qualitative basis. It has allowed discerning the origin of the raw materials. The natural raw materials provide intense quartz lines and the total absence of lines of tridymite and cristobalite. On the other hand, the presence of lines from tridymite and cristobalite shows that the raw materials are made up from bricks made of baked silica. In this case, it is also possible to find weak quartz lines corresponding to this component present in clay added as binder. These low intensities quartz lines could also come from an incompletely transformed silica.

Three cases can therefore occur as to the origin of the raw materials:

Natural Materials: Strong quartz lines -- neither tridymite nor cristobalite -- low lime contents except for special cases;

Bricks Made of Raw Silica: Heavy quartz lines -- neither tridymite nor crystobalite -- lime contents in the vicinity of 2%;

Bricks Made of Baked Silica: Weak quartz lines -- heavy lines from tridymite and cristobalite -- lime contents in the vicinity of 2%.

7.4 PARTICLE-SIZE ANALYSIS

The rational particle-size analyses were carried out using a series of screens whose mesh apertures were in geometrical progression at an 0.5 rate, i.e.:

1000 500 250 125 and 63 μm.

The results were likewise cumulative in order to allow comparison between different specimens of grouts studied.

7.5 PYROSCOPIC STABILITY

This conventional measurement leads to values expressed in °C, which are a function of the chemical composition (contents of SiO_2, Al_2O_3, CaO and impurities) and the fineness.

7.6 THERMAL EXPANSION /2591

These tests were carried out on specimens of pure grout with approximately 8% water added and which had been prepared by molding with a pressure of 200 bar. After drying in the oven at 110° C, they were subjected to the expansion test with a low load amounting to 0.08 bar. The rate of temperature rise amounted to 180° C/h. The first part of the expansion curves also allows differentiating between raw materials. The grouts prepared from natural raw materials have an expansion slightly less than 1% at 500° C whereas those prepared from baked silica bricks have an expansion in the vicinity of 1% towards 250° C.

Figure 7 provides a number of examples of expansion curves. However, it is the second part of the expansion curve which is the most interesting one. The grouts prepared from natural raw materials provide expansion curves having large rises starting from 1250-1300° C. These rises correspond to the transformation of the quartz with a density of 2.65 in cristobalite with a density of 2.32 (Figure 8). The grouts prepared from baked bricks lead, on the contrary, to expansion curves having a maximum towards 900-1000° C beyond which we find a rather large settling phenomenon (Figure 9).

A number of German authors consider the initial and final temperatures of settling to be those corresponding to the two successive changes of /2592 slope, i.e., towards 600 and 1100 to 1300° C. In reality, the second change of slope should correspond to the beginning of sintering and the later rise point to the end of sintering.

7.7 SETTLING UNDER DIFFERENTIAL LOAD WITH SANDWICH TEST SPECIMEN /2593

This test was inspired by the American "refractoriness pier test". This test consists in cementing together eight silica bricks of the "coke

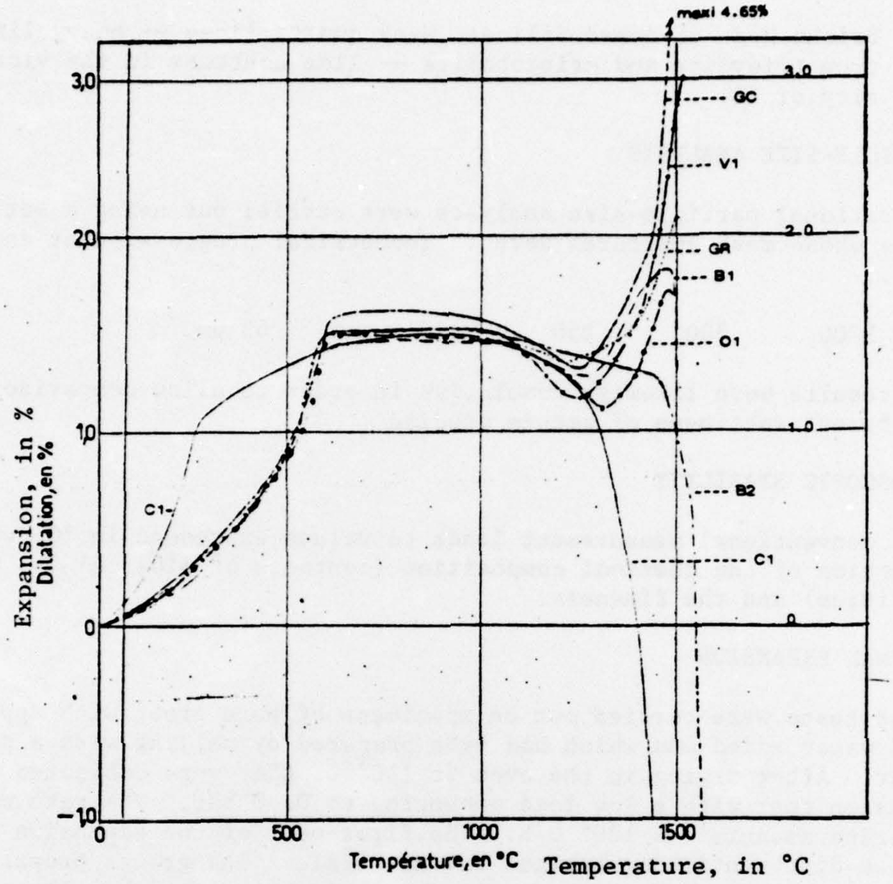


Figure 7. Expansion curves of a few silica grouts.

furnace" quality having dimensions of 228.60 mm x 114.30 mm x 25.4 mm with joints of 4.7625 mm in thickness. This checkerwork is then dried out and then loaded to 1.75 bar followed by heating to 2900° F (1539° C) at a uniform rate which does not damage the silica bricks. The stage at this temperature is 10 h. The maximum deformation after cooling down should not exceed 4%.

Since this test cannot be accomplished with European resources (it requires a furnace with sufficient volume enabling maintaining for 10 hours at 1600° C the checkerwork under a total load of 450 kg), the BCRA (British Ceramic Research Association) has designed a simplified test by preparing a double sandwich test specimen made up of three portions of silica bricks with dimensions 44.5 mm x 44.5 mm x 19.1 mm between which are formed two joints of grouting 4.7 mm in thickness. The time of holding at 1590° C is 4 h and the deformation is simultaneously measured during the test and after cooling down on the test specimen.

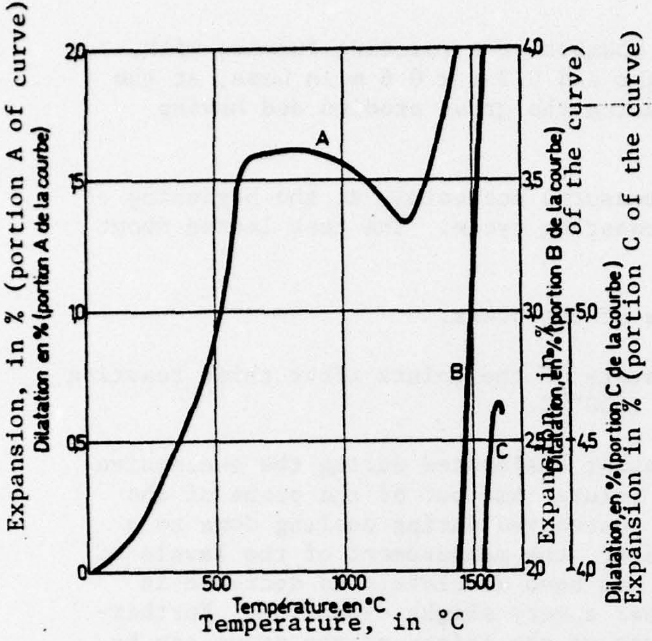


Figure 8. Expansion curve of silica grout 16 419.

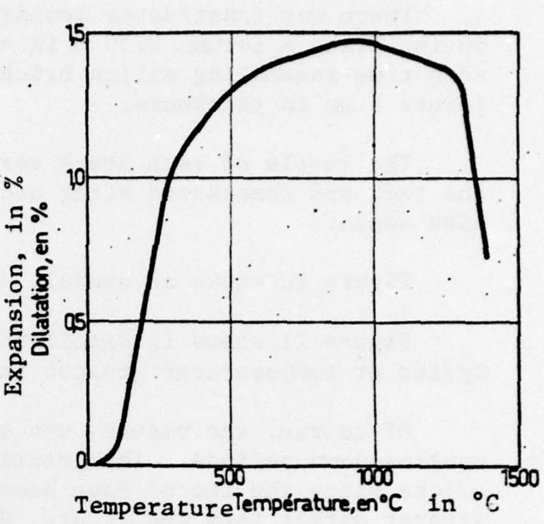


Figure 9. Expansion curve of silica grout 16 965.

The compared specifications of these two tests are as follows:

Specification	Standard US Checkerwork	Modified GB Checkerwork
Type of bricks	8 x 25.4 = 203.2 mm	3 x 19.1 = 57.3 mm
Height of grout	7 x 4.76 = 33.34 mm	2 x 4.7625 = 9.525 mm
Total height	236.5 mm	66.8 mm
Grout/total %	14.1%	14.3%
Deformation allowed	4%	4%
Equivalent deformation of joints of grout	28.4	28.0

Both of these tests were criticized in France, first of all owing to the temperature of 1590° C which appeared too high and, above all, because these tests always give favorable resutls when the grout includes quartz. All of the grouts prepared from natural raw materials would therefore be consistent. For this reason, the test was replaced by two others:

Test of settling under differential load	with sandwich test specimens
Creep test	

Nevertheless, one European manufacturer carried out a stability test on a rather large masonry. The test had the goal of confirming absence of creep of a high quality silica grout for coke furnaces.

There was constructed inside a chamber of a roasting furnace with moving flame a column 2.30 m in height and 0.3 m x 0.6 m in base, at the same time assembling silica bricks using the grout studied and having joints 6 mm in thickness.

The levels of each stack were measured accurately at the beginning of the test and remeasured after each roasting cycle. The test lasted about nine weeks.

Figure 10 shows an overall view of the stack.

Figure 11 shows in detail the state of the joints after three roasting cycles at temperatures greater than 1500° C.

Of course, the masonry was somewhat dislocated during the successive cooling-down periods. The grouting joints come out of the plane of the bricks since the latter have become contracted during cooling down to a greater extent than the grout. However, the measurement of the levels of the various stacks shows that there has been absolutely no decrease in height (therefore no creep) but rather a very slight expansion. Furthermore, the clearness of the live crests of the joints of the grout can be seen which shows the complete absence of melting.

Figure 10. Overall view of the stack 2.30 m in height and 0.3 m x 0.6 m in base, used for stability testing on a large masonry.

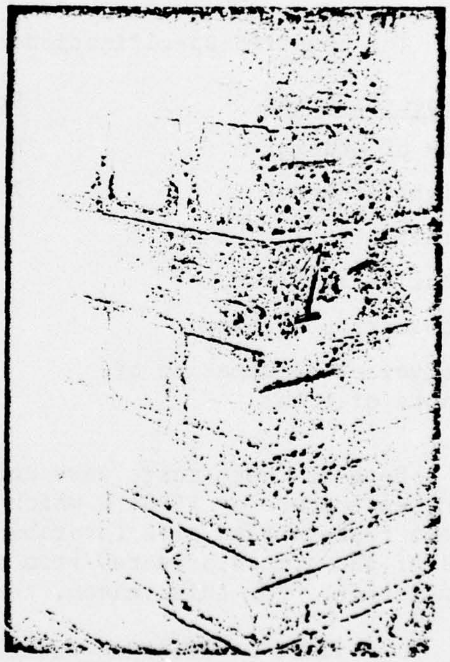


Figure 11. State of the joints with silica grout of the stack of Figure 10 after three roasting cycles at more than 1500° C.

ORIGINAL PHOTOGRAPHS UNCLEAR

7.7.1 Settling Test Under Load with Sandwich Test Specimens

The test specimens are formed by two semicylinders with 35 mm in diameter and 22 mm in height between which there has been inserted a layer of grout having a suitable water content so as to produce a joint 6 mm in thickness. The height of the sandwich test specimen is thus 50 mm. After drying, the test specimen is subject to the settling test under load using a load of 2 bar with a rate of temperature increase amounting to 5° C/min, the temperature being measured at the geometrical center of the test specimen pierced by an axial hole 10 mm in diameter. The equipment used allows simultaneously performing on the same test specimen the test of settling under normal load as well as the test of differential settling (Figure 12).

This test, previously carried out on a silica clay sandwich test specimen using silica clay grout, has led to settling curves under standard and differential, the behavior of the brick alone and the behavior of the sandwich. These behaviors are practically identical. There is therefore an excellent agreement between brick and grout. Since under this load of 2 bar the silica does not settle at temperatures less than 1600° C, the settling measured only concerns the grouting joint.

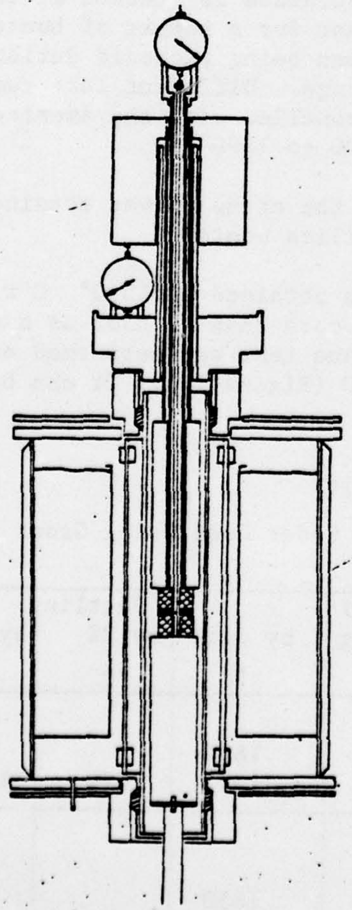


Figure 12. Equipment for settling tests under loading using sandwich test specimens. /2595

Thus, a settling of 1%, or 0.5 mm, measured on the test specimen corresponds to a settling of the joint of (0.5/6) x 100 = 8.33%. Conventionally, the temperature at which the test specimen settles by 2% (or a settling by 16.66% of the joint) is noted.

A number of settling under load tests were carried out first of all on a complete silica test specimen and on a sandwich test specimen. Subsequently, since the behavior of the silica was known, the tests were carried out exclusively on sandwich test specimens.

Figure 14 provides an example of the curves obtained with standard and differential settling on a silica test specimen and on a sandwich test specimen. The corresponding results are listed in Table II.

Figure 15 provides the curves obtaned with standard and differential settling on a sandwich test specimen only using a grout with low alumina content. Table III gives the values recorded with this figure.

7.7.2 <u>Creep Test with Sandwich Test Specimens</u>

The test specimen used is identical to the one previously described for the settling test on the load. The load of 2 bar is applied from the beginning of the test and the test temperature is reached at the rate of 5° C/min after which it was kept constant for a number of hours with the variations in height of the test specimen being recorded during the increase in temperature and during the stage. Different test temperatures /2596 were used: 1590° C (in order to be reconciled with the American prescription) and temperatures ranging from 1200 to 1500° C.

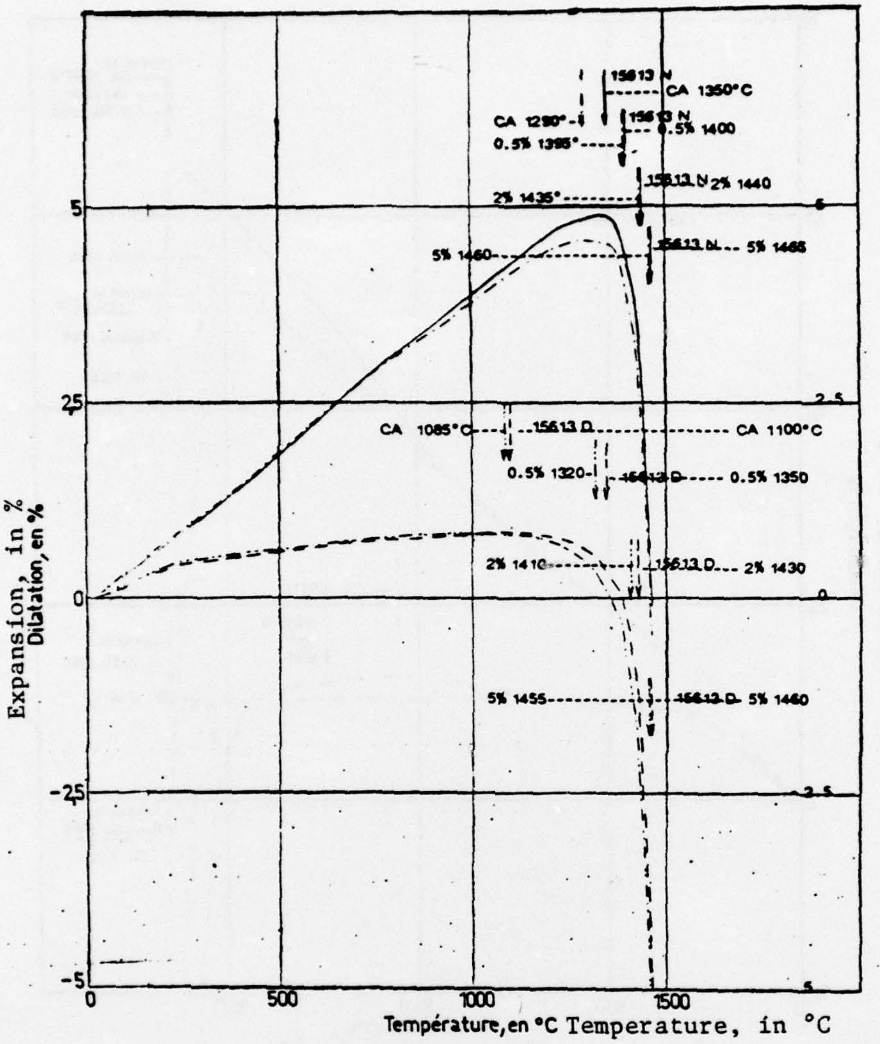
Figures 16 and 17 are relative to the creep curves obtained at 1590° C with the grouts having the highest silica content.

Figure 18 provides the creep curve obtained at 1590° C with a grout including lime. The test did not last more than an hour as a consequence /2599 of the large settling observed. The same test was performed on a similar grout but at the temperature of 1350° C (Figure 19). It can be seen that, after 24 h, the creep continues.

TABLE II

Results of Tests of Settling Under Load Using Grout 15 342 (B1) /2598

Specification	Start of Settling °C	Settling by 0.5% °C	by 2% °C	by 5% °C	Rupture °C
Settling under standard load:					
Silica alone	1640	1650			1655
Sandwich test specimen	1440	1535	1570	1625	
Settling under differential load:					
Silica alone	1240	1650			1655
Sandwich test specimen	1055	1460	1540	1595	

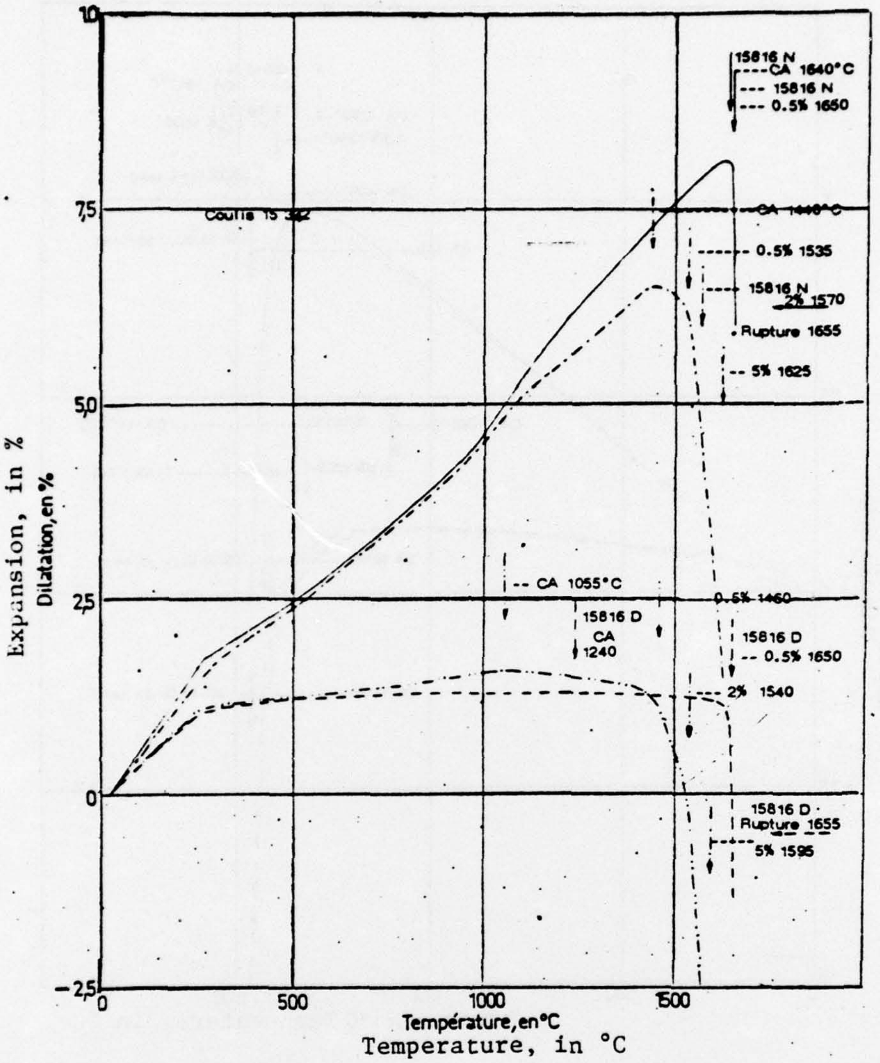


Silica clay brick 15 613 { ———— Standard curve
{ -------- Differential curve

Sandwich test specimen 15 613 + 15 820 { —·—·—· Standard curve
{ —·—·· Differential curve

CA = The beginning of settling
N = Standard settling
D = Differential settling

Figure 13. Curves of settling under load.



Standard silica brick 15 816 { ——— Standard curve
------ Differential curve

Sandwich test specimen 15 816 + 15 342 (*) { —·—·— Standard curve
—··—·· Differential curve

*Standard silica brick 15 816 + silica grout 15 342 (6 mm joint).

Figure 14. Curves of settling under load.

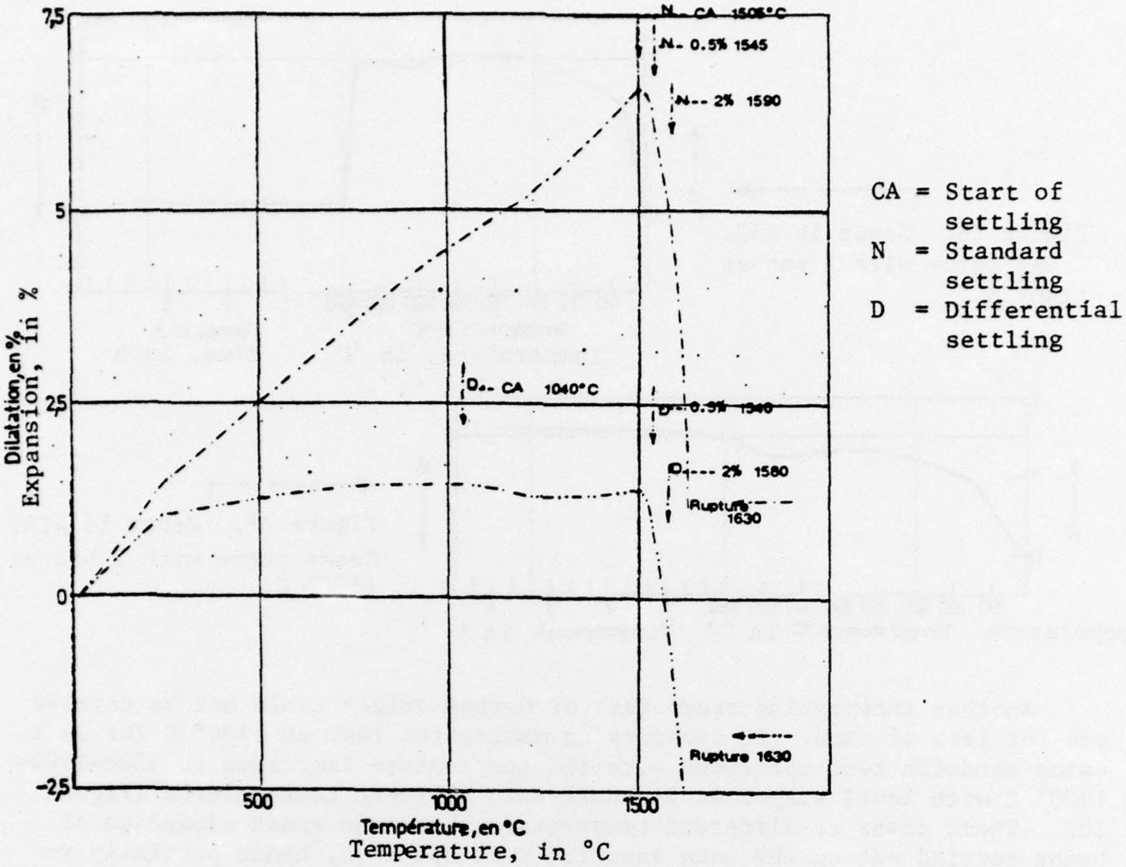


Figure 15. Curves of settling under load of grout 16 452.

Table III

Results of Tests of Settling Under Differential Load Using Grout 16 452 (V1) with Low Alumina Content (Sandwich Test Specimen)

Specification	Start of Settling °C	Settling by 0.5% °C	by 2% °C	Rupture °C
Silica alone	1505	1545	1590	1630
Sandwich test specimen	1040	1540	1580	1630

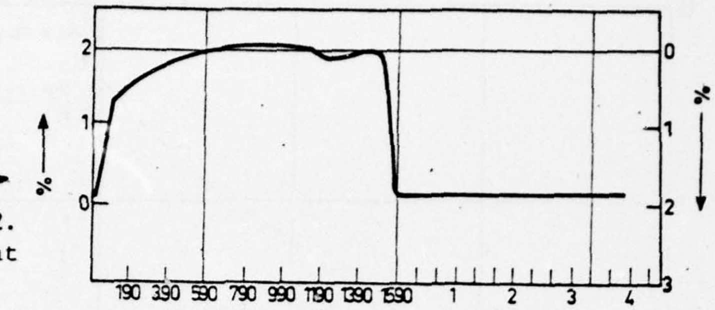


Figure 16. Grout 16 452. Creep curve with 2 bar at 1590° C.

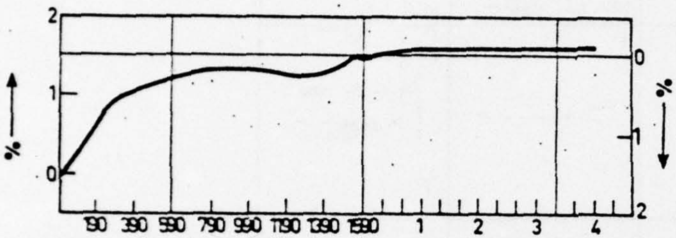


Figure 17. Grout 16 419. Creep curve with 2 bar at 1590° C.

Another interesting creep test of German origin could not be carried out for lack of time. It consists in making the test at 1200° C for 24 h using sandwich test specimens with the temperature increased to 1300-1400-1500° C with level stages of 24 hours each at these temperatures (Figure 20). These tests at different temperatures have the great advantage of being carried out on the same sandwich test specimen, hence partially removing the factors relating to the difficult preparation of the test specimen.

The creep curve of one grouting joint cannot have the same meaning as the creep curve of a refractory brick. Indeed, the creep is obligatorily limited to a certain value which should be on the order of half of the thickness of the joint, i.e., on the order of 6%. /2600

CONCLUSIONS /2601

The specifications of the grouts examined vary within the limits given in Table IV.

The values of the left-hand column correspond to old grouts whose performances have become incompatible with temperatures attained in modern coke furnaces.

The values of the right-hand column correspond to the most elaborate recent grouts used for high operating temperatures. It is nevertheless not always necessary to have these high characteristics when the furnaces do not have to be brought to very high temperature since the setting of these grouts is produced by sintering (and not by ceramic setting) which requires a high temperature.

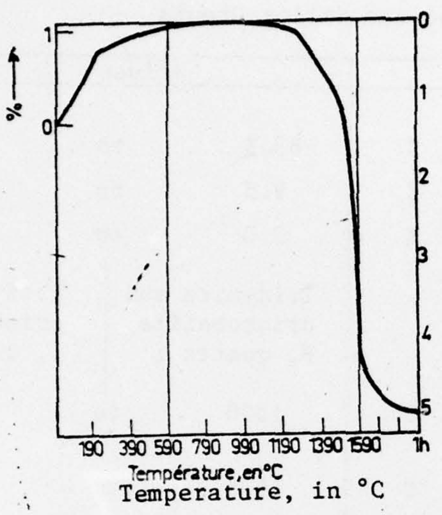


Figure 18. Grout 16 414. Creep curve with 2 bar at 1590° C.

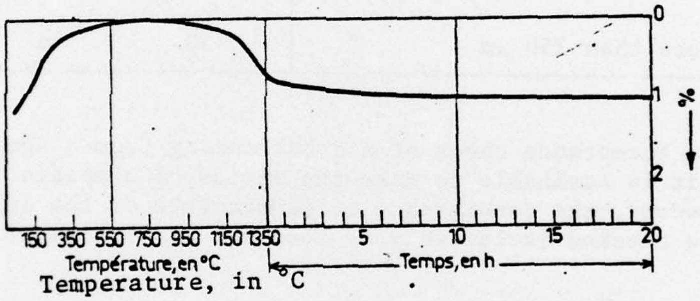


Figure 19. Grout 16 140. Creep curve with 2 bar at 1350° C.

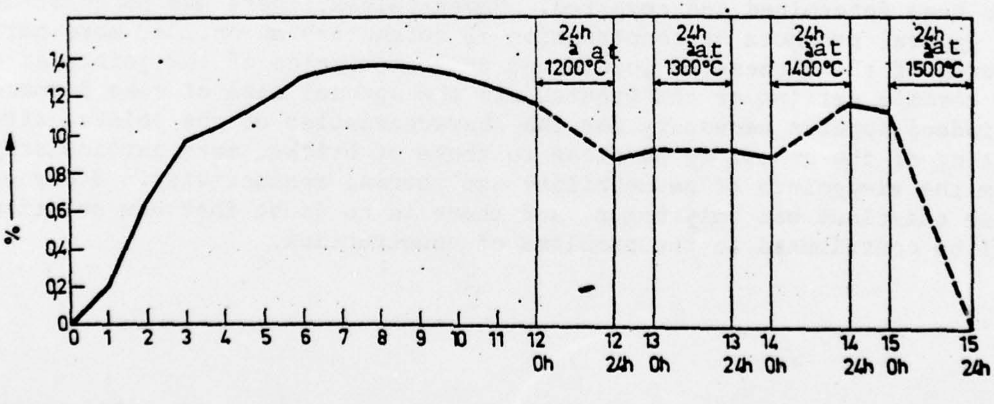


Figure 20. Curve of creep test with 2 bar at different temperatures. Curve reported by Dr. Overkott of the Dr. C. Otto GmbH.

Table IV

Principal Specifications of the Silica Grouts

Specification		Values		
Chemical composition:				
Content of SiO_2	%	83.5	to	98.0
Content of Al_2O_3	%	9.5	to	0.6
Content of CaO	%	2.0	to	0.03
Mineralogical composition	-	Tridymite and cristobalite F, quartz f		Tridymite and cristobalite f, quartz F
Pyroscopic stability	°C	1530	to	1720
Settling with differential charge on sandwich test specimen: t_2	°C	1475	to	1630
Fraction of less than 250 μm	%	50	to	96

During the acceptance check of a grout coming from a specific manufacturing plant, it is advisable to make the series of complete tests with the first lot. However, the consistency of manufacture of the following lots will have to be checked exclusively by chemical as well as particle-size analysis.

In this study, the characteristics of the grouts found on the market have been determined and compared. Nevertheless, there was no question of the general products of construction of refractory masonries, more particularly of the fitness of joints and characteristics of the joints after the ceramic setting of the grouts. In the special case of coke furnaces, it indeed appears necessary for the characteristics of the joints, after setting of the grout, to be close to those of bricks, more particularly from the viewpoints of permeability and thermal conductivity. Study of these questions has only begun, and there is no doubt that new solutions will be contributed to the problems of construction.