A survey of refractories used in glass tank furnaces

A Report of the Refractories Committee of the Society of Glass Technology

Introduction

The glass industry consumes probably less than 5% of the refractories produced in this country. To quote an example of a major user, the steel industry consumes approximately 60–65% of the production. These proportions, plus a certain basic similarity in process, have meant that the glassmaker has had a wide choice between the many varieties of silica, fireclay, high-alumina, and basic refractories developed to withstand the generally more arduous conditions in steel-melting furnaces. Thus, the provision of refractories for roof, breastwalls, ports, regenerator chambers, and fillings has simply been a question of choosing between the numerous qualities available subject to the cost.

Refractories which are to be in contact with glass are, however, quite special to the glass industry. The steelworks practice of melting on a thick rammed lining which can be repaired between melts is obviously not applicable to conventional glass melting operations where the quality of the glass is affected by reaction with the container. From a very early stage in the development of glass tank furnaces, ready fired and shaped tank blocks have been used for lining. The branch of the studies of refractories where appreciable development has taken place specially for the glass industry is restricted to the composition and manufacture of tank blocks and other glass-contact refractories, such as the various forehearth and feeder refractories.

The development of tank blocks and associated products has proceeded along rather narrow lines, there being only a few manufacturers concerned. This is in contrast to the many more suppliers and wider development of varieties of refractories available for other locations in the furnace.

The primary intention of this survey is to give a true picture of the present situation; before going on to consider the available materials under appropriate headings, a study of the following tables indicates the relative proportions used of the various types of materials.

Table I

Data supplied by a firm of furnace designers and builders

<table>
<thead>
<tr>
<th>Furnace output</th>
<th>40 tons per day</th>
<th>50 tons per day</th>
<th>60 tons per day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superstructure and ports</td>
<td>1460 ft³ = 18%</td>
<td>2800 ft³ = 25%</td>
<td>2200 ft³ = 19%</td>
</tr>
<tr>
<td>Tank blocks</td>
<td>1080 ft³ = 13%</td>
<td>1360 ft³ = 12%</td>
<td>1625 ft³ = 14%</td>
</tr>
<tr>
<td>Regenerator chambers and fillings</td>
<td>5600 ft³ = 69%</td>
<td>7000 ft³ = 63%</td>
<td>7900 ft³ = 67%</td>
</tr>
<tr>
<td>(Insulating brick)</td>
<td>1600 ft³</td>
<td>2000 ft³</td>
<td>3000 ft³</td>
</tr>
</tbody>
</table>

* This survey will be completed by a consideration of tank blocks which will be published shortly.
TABLE II

Data supplied by a glass manufacturer having a producer gas fired, regenerative furnace of 50 tons per day capacity

<table>
<thead>
<tr>
<th>Crown</th>
<th>840 ft³</th>
<th>11%</th>
</tr>
</thead>
<tbody>
<tr>
<td>End and side walls above glass, bridge covers and shadow wall</td>
<td>790 ft³</td>
<td>8%</td>
</tr>
<tr>
<td>Tank blocks</td>
<td>1170 ft³</td>
<td>6%</td>
</tr>
<tr>
<td>Uptakes and ports</td>
<td>910 ft³</td>
<td>6%</td>
</tr>
<tr>
<td>Regenerators and fillings</td>
<td>11,000 ft³</td>
<td>75%</td>
</tr>
</tbody>
</table>

These data are not intended to give a complete and comprehensive idea of the general position but the figures given seem to warrant the following general comments.

(a) The glassmaker who supplied the figures in Table II admitted that he was very considerably surprised to discover how small a proportion of the whole furnace structure consists of tank blocks, and how little consideration he had previously given to the largest item, the regenerator chambers and checker bricks. Others have expressed similar views.

(b) The tank blocks did undoubtedly at one time provide the most vital and pressing problem, as a failure can cause a drastic and sudden stop to production, and the tank blocks as a rule have more influence than any other refractories on the quality of glass produced. But failures have been known to occur in other parts of the furnace than the bath, and at the present time the quality of refractories available, or in actual use, in the burner ports and in the regenerators are in fact keeping the production rate of some furnaces well below that which the combustion design and the tank blocks themselves would allow.

SILICA REFRactories

Qualities of silica brick available and in use

Many different brands and qualities of silica brick are available to industry in general, but comparatively few brands have been used in the glass industry, and so far there has been no concerted attempt by the glass industry as a whole to effect any sort of standardization. It is almost certainly true to say that silica bricks have presented the glassmaker with fewer troubles and problems than any other type of refractory he has to use. Furnace crowns give trouble-free lives of 5 to 20 years or more, side walls and tuckstones have rarely been known to limit the life of a properly designed furnace.

Within the last few years several manufacturers have attempted to meet the severer demands of the steel-making industry by providing an improved quality known as ‘Super Duty’. The chief measurable characteristic of this type is the higher refraCTORiness under load which is associated with lower contents of alumina and of the alkali oxides which is shown in column B of Table III. It is well known that calcium oxide, up to perhaps 3%, has no significant harmful effect on the refraCTORiness of silica bricks, and in fact it has such beneficial effects in facilitating the proper controlled ‘growth’ of cristobalite and tridymite, the two high-temperature crystal forms of silica,
that practically all the calcium oxide present in commercial brick is deliberately added for that purpose. Magnesia is a minor natural impurity which has similar effects to those of lime. Iron oxide is potentially dangerous but in practice it never is, chiefly because so much of it occurs in 'iron spots' which do not appear to diffuse into the body of the brick. Titania appears not to be dangerous provided that sufficient calcium oxide is present, and indeed it has been claimed that the presence of 1 to 2% of titania in some brands is of positive advantage in conferring what might be called high temperature 'toughness' rather than rigidity. Alumina, soda, and potash reduce refractoriness and general durability without any compensating or even mitigating factors whatsoever; if it were possible to find silica rock of suitable physical character completely free from these impurities, brick of considerably improved performance in some conditions could undoubtedly be made.

**TABLE III**

*Chemical and physical properties of typical silica bricks*

<table>
<thead>
<tr>
<th>Brand</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>SiO₂</td>
<td>96-27</td>
<td>95-98</td>
<td>94-5/95</td>
<td>95-8/96-2</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃</td>
<td>0-69</td>
<td>0-36</td>
<td>1-2/1-3</td>
<td>0-6/0-8</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>0-80</td>
<td>0-82</td>
<td>0-6/0-7</td>
<td>0-5/0-7</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>0-09</td>
<td>0-05</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>1-75</td>
<td>2-50</td>
<td>1-7/1-9</td>
<td>1-6/1-8</td>
</tr>
<tr>
<td></td>
<td>MgO</td>
<td>0-08</td>
<td>0-07</td>
<td>0-1</td>
<td>0-1</td>
</tr>
<tr>
<td></td>
<td>K₂O</td>
<td>0-22</td>
<td>0-09</td>
<td>0-2/0-3</td>
<td>0-1/0-15</td>
</tr>
<tr>
<td></td>
<td>Na₂O</td>
<td>0-06</td>
<td>0-04</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>27</td>
<td>22</td>
<td>26/28</td>
<td>20/23</td>
<td>18-5/19</td>
</tr>
<tr>
<td>Bulk density</td>
<td>1-66</td>
<td>1-75</td>
<td>1-68</td>
<td>1-78</td>
<td>1-84</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2-33</td>
<td>2-34</td>
<td>2-34/2-36</td>
<td>2-34/2-36</td>
<td>2-30</td>
</tr>
<tr>
<td>Temperature of failure under 50 lb/in.²°(C)</td>
<td>1675</td>
<td>1710</td>
<td>1650</td>
<td>1680/1690</td>
<td>1740</td>
</tr>
</tbody>
</table>

Reference is made here to these Super Duty types because increasing demands are being made on the furnace as a whole with higher temperatures and faster throughput. Twenty years ago it was almost always the tank block which failed first, but in several cases today it is the regenerative system and the superstructure which are setting a limit to the useful 'campaign' life of a furnace and even limiting the production speed at which it can be worked. If it becomes necessary to use furnace temperatures constantly higher than, say, 1650°C it will obviously become equally necessary to use some material other than silica for the furnace crown. In the open hearth steel furnace, where experience has shown that Super Duty silica can remain completely unaffected at temperatures at which normal good quality silica actually drips at the exposed face, the advantages of being able to work at higher temperature, coupled with secondary advantages, has led to very considerable large-scale replacement of silica by bricks made from different proportions of magnesite and chromite. A large measure of success has been achieved over the last four years, but the
technical and economic difficulties are such that it is by no means certain that the steel melter will not finally accept the limitations of silica as the most reliable and economic material for furnace crowns. Basic bricks are well established in other parts of the steel furnace structure.

If silica proves unsatisfactory in any type of glass-melting furnace the obvious step is to turn to alumina–silica refractories of 60% Al₂O₃ content or more. It seems pertinent to point out to glassmakers that the better quality silica bricks are in fact available, in order that they may give them due consideration before departing from silica altogether. At the time of writing there is not sufficient works experience to indicate whether or not Super Duty silica is in fact capable of showing to as much advantage in a glass-melting furnace as it undoubtedly does in some steel furnaces.

**Properties of silica brick**

*Refractoriness*

Silica brick consists of a very high proportion of crystal silica (in the form of tridymite and cristobalite) with the minimum amount of inter-spersed glass and it is permissible for practical purposes to speak of a high melting point rather than to be academically correct and speak of its softening range or to use the convenient American term Pyrometric Cone Equivalent (P.C.E.).

It is a very fortunate circumstance that the lime–silica glass used as bond in silica brick does not lower the P.C.E. by more than about 10°C; and while pure silica melts sharply at about 1710°C good commercial silica brick containing about 2½% of calcium oxide can be taken up to 1700°C in the crown of steel-melting furnaces before it begins to "drip" or "run". In addition these bricks can bear a mechanical load or stress without collapsing at very high temperature. In the refractoriness under load test carried out according to British Standard 1902 : 1952, a good quality silica brick will bear a load of 50 lb/in.² up to about 1670°C before collapsing.

Only one end of the brick will reach the highest temperature and there is no danger in normal glass furnace work of a silica roof sagging or collapsing due to load and temperature. This is the chief reason for preferring a silica crown to a crown built of first quality fireclay brick of the 40% alumina type. The latter brick may have a Pyrometric Cone Equivalent (P.C.E.) of 34–35—corresponding to 1750°C—but in the standard refractoriness under load test it shows 5% deformation at about 1575°C. The standard test occupies a matter of a very few minutes at the highest temperature; with long exposures to load progressive softening occurs. Consequently the use of fireclay brick in furnace arches and crowns is limited to a face temperature of about 1450°C, and its choice for such cases is governed by its better resistance to very dirty atmospheres and to temperature changes—such as are found in reverberatory reheating furnaces in the iron and steel industry.
**Spalling**

Silica brick is relatively poor in resistance to spalling, but as the thermal expansion between 0 and 400°C is approximately 1·0%, while a further temperature rise up to 1400°C only produces a further expansion of 0·2%, the tendency to spalling is practically negligible above red heat. Thus while a silica roof demands very careful treatment during heating up from the cold state, it is admirably suited to the conditions in modern continuous glass tanks and it is in fact very rare to encounter spalling.

**Corrosion**

If the equilibrium diagrams are studied it seems obvious that silica should be very much less resistant to corrosion by alkalis and other basic materials than are fireclay refractories in which a good development of mullite has been achieved, and this is true provided that the reactions leading to the formation of low-melting eutectics actually take place. In fact, silica crowns have been known to last 20 years and even more in glass tank furnaces without any significant loss of thickness: the working face seems to have grown outwards due to the formation of new crystals, producing a granulated porous layer up to $\frac{1}{8}$ in. in thickness. It seems therefore that good silica brick can withstand the attack of alkali vapour and dust with very little reaction provided the conditions (temperature, impact of flame or gases and amount of soda present) do not become too severe. Another factor, which becomes more evident in steel-melting practice, is that a well-made silica brick possesses such a mechanically stable structure of interlocking crystals that it is capable of absorbing large amounts of silicate glasses in the pores and still maintaining its rigidity at temperatures at which the silicates are liquid. A P.C.E. test cone cut from the face of a silica brick which has absorbed considerable amounts of iron and calcium oxides will deform at a temperature very little lower than that of the original brick, but if a test piece is crushed and ground to a fine intimately mixed powder and the powder moulded into a test cone by the aid of an adhesive that cone will deform at a temperature lower possibly by 200°C.

Any material entering the glass from a superstructure of silica, whether entry is brought about by mechanical damage or by chemical and solvent attack, is comparatively readily incorporated in the melt. The displacement of firebrick roofs by silica in some works was determined by the fact that ‘droppers’ from a firebrick roof were such a nuisance, before temperature conditions altered sufficiently to make the greater high-temperature rigidity of silica the decisive factor that it is today. As mentioned above, fireclay brick roofs are still used in furnaces producing glasses which are later to be dissolved in water; here physical homogeneity of the glass is of little importance.

**Applications of silica brick**

**Crowns**

Thirty years ago it was fairly common to find crowns built of siliceous clay brick (approximately 70% silica) and even today there are a very few
small furnaces in which a normal good quality fireclay brick is found to be more durable than silica. These exceptional furnaces are used in the production of sodium silicate and potassium silicate and it is found that the severe attack by alkali vapour and dust is the crucial factor. Prior to the advent of modern bottle-making machines with the consequent very great increase in furnace output and the demand for continuous working under steady temperature melting conditions, the crown had to withstand much greater changes of temperature than could be tolerated today. In those days the raw materials were sometimes charged in separately, without any previous mixing, at intervals of several hours. Under such conditions the crown was subject to severe spalling stresses and to uncontrolled corrosive attack by alkali vapours and dust, and a fireclay brick could compete with the silica brick then available.

Today practically all glass tank furnace crowns are built of silica brick and only a few special glasses needing exceptionally high temperatures make it necessary to consider any other material.

*Side walls, etc.*

The same considerations which make silica an ideal material, for the construction of tank furnace crowns, obviously make it suitable for tuckstones, side and end walls between the tank blocks and crown, for burners, ports and uptakes. In all these situations, where, except in the most severe conditions, fireclay bricks of high alumina content are found to be physically stable under the mechanical loads imposed, and may be fully as durable as silica, silica is generally favoured because any material entering the glass is more readily incorporated in the melt. With side walls, tuckstones, and port mouths the superiority of silica is much more evident to the eye than in the crown. Owing to the fact that silica bricks usually contain less than 1% of iron oxide, and the fact that alkali attack is greater at this level, it is noticeable that silica shows none of the discoloured streaks running down into the glass that are apparent from even the best fireclay bricks. In these conditions, if silica fails, as it sometimes does under severe stress of temperature and corrosive influences, it is necessary to pass over the range of alumina-silica proportions found in natural clays and to use refractories containing 50% alumina or over, based on the use of kyanite, sillimanite or andalusite.

*Regenerators*

In the regenerator chambers themselves there does not appear to be much demand for anything other than fireclay brick. Regenerator arches seem to offer more scope for silica, but here again highly aluminous fireclay bricks appear capable of giving satisfactory service. It may be of interest to note that in the more severe conditions of open-hearth steel-melting furnaces, silica arches for regenerator chambers are generally being replaced by good quality fireclay brick. The very curious reason is that while the individual bricks do not suffer any damage, the arch itself, nearly always semicircular in section, suffers distortion. It 'peaks up' to a Gothic type of arch
in course of time, and as the bricks are of course tapered to fit the semi-
circle the whole structure may become mechanically unsafe.

Whatever form of construction is used, if the temperature at that point is
high enough to give rise to any fear of sagging in fireclay blocks or relieving
arch silica brick will be preferred. First quality fireclay brick should be
quite satisfactory unless the temperature exceeds 1350°C.

Bricks used as checkers or fillings in the regenerator chambers will be
considered almost solely from the point of view of durability. In this
application silica of course would withstand the temperature and load
indefinitely. The destructive agents are the dust and vapour carried over by
the outgoing gases, the alkali compounds being of course the most
destructive constituents. The temperature is lower than those to which the
tank crown and superstructure are subjected so that the intrinsic intensity
of the attack is less in the checkers. But, as the checkers depend for their
thermal effectiveness on securing the maximum intimacy of contact
between gas and refractory solid, the resultant effect of the corrosive attack
is many times greater. The function of the checker bricks is to 'scrub out'
the maximum possible amount of heat from the gases before they reach the
flues, and it seems reasonably obvious that in the same way they are also
very likely to 'scrub out' the maximum possible amount of entrained dust
and of vapour capable of entering into chemical combination with the
solid material. Moreover, the checker system offers the first opportunity
the dust-laden gases have of depositing their burden on a horizontal
surface, although some checkerwork layout designs, and designs of
individual bricks, are intended to reduce to a minimum the extent of
horizontal surface presented.

It is thus commonly found that silica bricks used in the checkers are
corroded away to a very much greater degree than in the crown and side
walls, and if durability alone were to be considered silica checkers would
rarely be used. But durability of the brick itself is a relatively small matter
compared to the durability of the whole furnace as measured by the length
of time between shut-downs for necessary repairs, and silica offers one
important advantage over many types of fireclay brick in this respect. Just
as silica dissolving in the glass bath causes few production troubles, so
silica dissolved by the alkalis brought over runs cleanly away, to be
absorbed by the lower courses without seriously constricting the area
through which the gases have to pass. In other words, the upper courses of
silica checkerwork may disappear comparatively quickly, thus leading to
some loss of thermal efficiency of the furnace, but they may not choke up
the passages; and choking the passages can not only cause loss of thermal
efficiency but can also enforce a shut-down.

_Silica cement_

Silica is almost completely devoid of the property of forming plastic
mixtures with water, and the manufacturer of silica bricks is to some
extent dependent on the slight plasticizing and binding effect of the lime
added, effectively as calcium hydroxide, for the purpose of facilitating
recrystallization on firing. To an even greater extent, modern moulding methods tend to rely on organic plasticizers and binders which make it easier to shape the bricks and give them greater mechanical strength at all stages between moulding and transfer to the kiln. But the plasticity of all mixtures used for the shaping of bricks falls a long way short of what is necessary or convenient for use as a cement. There is thus a very natural tendency for the furnace brick setter, and for the supplier of silica cements, to improve the 'workability' of the plastic mixture by the addition of plastic clay. This is a tendency which must be kept very severely in check. It is foolish to insist on the best available quality of silica bricks in a furnace crown and to joint them with a material which owing to the presence of 2% or more of alumina may actually melt in the form of very troublesome 'droppers'.

In the more general aspect the term 'cement' as applied to silica materials is really a misnomer. It is true that silica jointing material, like fireclay, does play a useful part in holding the bricks together during construction and drying; indeed the lubricating and adhesive effect of good jointing materials will help to allow bricks to be set more tightly together than without it. But once the temperature has been raised sufficiently to drive off water and any organic plasticizer used the jointing material loses all cement-like properties. True refractory cements are available, the addition of plasticizers, air-setting materials, and vitrifying agents making them adhere to the brick throughout the complete range of temperature from setting to softening. Such cements are of very great value when used in the right conditions as they weld the brickwork into a solid mass in which the joints do not present any physical weakness towards corrosive attack, and if the cement is of suitable chemical composition it may be at least equal to the brick itself in resisting chemical attack. The danger is in fact that it is very easy to make the joint stronger than the brick itself so that the brick itself may crack while the joint remains sound. This can be an advantage in some cases, but it is obviously dangerous in such places as furnace crowns and walls which are exposed to the furnace atmosphere and not protected by the glass as in the bath. Such vitrifying cements are rarely if ever used with silica brickwork, but they are frequently misused in fireclay brickwork. It seems legitimate and sound advice to the furnace builder always to consult the manufacturer of the brick itself before deciding on what cement to use.

In jointing silica brickwork, the jointing material should be regarded as a stopping rather than as a true cement; its purpose being to permit the brickwork to be set more tightly than if set dry, and to act as a true cement during the stage in which the structure is heated up for work.

When silica jointing material is used, it is often the practice to set a tank crown dry and to apply the 'cement' in the form of a liquid grout poured on from the outside and possibly brushed into the joints. This again is a controversial matter. On the one hand it can be said that with skilled setting of accurately shaped bricks there should never be any openings on the outside big enough for slurry to be poured into them. There is much to
be said in favour of making the joints even closer on the outside (cool) surface than on the inside, so that when the crown is first heated the expansion of the heated inside face, being greater of course than at the outer face, will tend to squeeze the brick faces into close and even contact. With jointing material already present such expansion adjustment can occur quite easily, excess material being squeezed out. It is much more difficult to obtain such an effect with grouting poured on from the outside. The advocates of grouting are probably largely influenced by the fact that experience has caused them to be suspicious of any silica jointing material which is sufficiently plastic or ‘creamy’ to be usable in dipping or trowelling consistency as readily as fireclay materials: they suspect that clay is in fact responsible for this workability and are rightly afraid of the consequences. But at the present time that suspicion should not be allowed to rule out without further consideration and investigation the materials now available which can bear scrutiny in this respect, both in the laboratory and in works experience.

**Bonded Alumina-Silica Refractories**

In sharp contrast to the comparatively simple and narrow range of silica materials, the field covered by fireclay and alumina-silica products in general is very wide and complex and classification is a matter of some difficulty. In considering how to classify what are most commonly described, quite simply, as firebricks, it may be simplest to consider two fundamental facts.

First, the essential constituent of all fireclays can be thought of as a clay mineral such as kaolinite, which on calcination has the approximate composition 46% alumina, 54% silica. It is, of course, true that even china clays, the purest forms of kaolinite commercially available, contain some impurities. It is also true that some clays consist of minerals other than kaolinite, having the same ratio of alumina to silica, but differing from it in crystal form and in combined water content, and that clay minerals of different alumina: silica ratio are well known. But these variations, while they are very interesting to the mineralogist, and indeed to the manufacturer of refractories, are not of great importance to the user and it is not necessary to consider them in a simple classification of the finished products.

Second, while the addition of between say 3% and 8% of alumina to a silica material, combined with the other impurities unavoidably present, would make it completely useless as a refractory, a mixture of 30% kaolinite (calculated on the calcined basis) and 70% silica would give 86% silica, and bricks of this silica content under the obviously unscientific description ‘semi-silica’ give very good service under suitable conditions. The term ‘semi-silica’ may first have been applied to a 50/50 mixture of silica and siliceous clay of about 75% SiO₂.

The term ‘aluminous’, applied to fireclay products containing 30% or more of alumina, is even more unsound scientifically, and now that
refractory materials containing between 50% and 95% alumina are finding application in quite large quantities (measurable in thousands of tons annually) the use of the word ‘aluminous’ is becoming positively inconvenient.

One attempt at a workable classification is shown in Fig. 1 superimposed on the Bowen & Greig phase-rule diagram.

![Fig. 1](image)

**TABLE IV**

*A suggested classification of alumina–silica refractories*  

<table>
<thead>
<tr>
<th>Type</th>
<th>Silica bricks</th>
<th>Semi-silica bricks</th>
<th>Siliceous firebricks</th>
<th>Aluminous firebricks</th>
<th>High alumina firebricks</th>
<th>Special high alumina materials: sillimanite, kyanite, andalusite, bauxite, diaspore, corundum, mullite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>above 94% silica</td>
<td>80–90% silica</td>
<td>18–30% alumina</td>
<td>30–40% alumina</td>
<td>40–45% alumina</td>
<td>45–99% alumina</td>
</tr>
</tbody>
</table>

It has recently been reported (*Berlin Deut. Keram. Ges.*, 1957, 34, 397) that mullite can show congruent melting, and that a eutectic exists between mullite and corundum. This may be of importance in the future.

In using Fig. 1 and Table IV the following points should be remembered. The impurities inevitably present in commercial products have a marked effect in lowering the softening temperatures with different impurities having different effects at different points on the curve. For example, calcium and iron oxides have little effect on silica bricks but alkali oxides are a very serious impurity, whereas iron and calcium oxides can be much more deleterious than alkalis in bodies of higher alumina content. Whilst a body of 40% alumina content has a softening point markedly higher than...
that of silica bricks, the 40\% alumina body contains a much higher proportion of eutectic liquid and in consequence is much more liable to deformation under load. With impure commercial materials the eutectic temperatures should be very considerably lower than suggested in Fig. 1. In general, it is not safe to allow a high alumina firebrick (type E) to be heated throughout to 1400\ºC in any part of a structure in which it has to bear any significant load. Where, as is most frequently the case, only one side or end of the brick is exposed to the full furnace temperature and the structural stresses are taken by the supporting steel frame, type E bricks can be used at 1450\ºC or even a little more and have an economical life. It is true of course that at such temperatures the exposed face of the brick will be plastic or ‘soft’, but that is not necessarily a defect; indeed it may be an advantage in at least two respects. A brick which is plastic at the face at working temperatures can under some conditions be much less liable to cracking during temperature changes than a better quality brick which is more rigid. Further, paradoxical though it may seem, a brick which is softened at working temperature may resist both abrasion and corrosion better than another whose chemical and physical properties would lead one to expect it to show clear superiority. The paradox is merely superficial, of course. A softened brick face may ‘flow’ under abrasion, and be worn away slowly in thin layers, while a more rigid surface may be fretted away by the detachment of comparatively large fragments, the roughened surface becoming immediately more liable to further attack. Similarly, the effect of corrosive solvent attack often produces, under the glazed surface, a layer of newly formed corundum or mullite crystals embedded in glass, a layer which appears to prevent further penetration by the corroding solvent and to slow down the rate of corrosion very considerably. The means of obtaining the texture which will best lend itself to the formation of such a layer is a major problem. These protective layers can under some conditions be more easily and effectively formed on refractories containing only 20–30\% of alumina than on those containing 40–45\%, while it is often impossible to form one at all on refractories of the 45–99\% alumina range. There are many conditions under which no evidence of any protective layer formation can be found, but in such conditions also it is very frequently true that a more refractory material, judging by its place in the phase-rule diagram, is not merely no more serviceable than one of lower refactoriness but actually less serviceable. This aspect will be considered more fully later.

One great merit of the method of classification in Fig. 1 is that it reveals and emphasizes the continuity of the whole range of silica–alumina bodies and reveals and stresses the fact that there is no special or unique place for clay, as such, when considering the properties of the fired, finished, and usable product. The curve passes smoothly through the composition of pure kaolinite, between the two kinks showing the formation of the silica–alumina eutectic and the temperature at which mullite breaks up into corundum and glass.

Fireclays have of course been established for many years, even centuries,
longer than the higher alumina materials, the introduction of which on a commercial scale is well within living memory. They have the advantage of relative cheapness, being found in Britain in large and easily worked deposits, and they have a very great advantage in lending themselves to forming and firing into the desired shape by very simple means. During the last fifty years or so, however, so much progress has been made in manufacturing technique that fireclay has lost its uniqueness in this respect, and, in particular, manufacturers have been impelled to pay so much attention to texture, determined by proportioning of the body, shaping and kiln treatment, that there is now no perceptible break in continuity between products containing approximately 35, 40, 55, 60, and up to 85% of alumina. Several manufacturers do in fact list a complete range of such materials and nobody without specialized experience could say by mere inspection which was a ‘natural’ fireclay brick. The one factor that does remain is that all the materials needed to increase the alumina content of refractories above 43% in the case of fireclays or 45% in the case of china clay, have to be imported: these materials—kyanite, sillimanite, andalusite, bauxite, and corundum—are all very expensive by the time they reach the manufacturer, and their preparation before they can be incorporated in a brick-making batch is also very costly. The result is that to increase the alumina content of a firebrick from 43% to 50% involves increasing the cost to the user approximately twofold. In general, furnace lives are so long and refractory costs per unit of product are so low in the glass industry in comparison with many others, that these ‘artificial’ high alumina refractories have been adopted by the glassmaker far more readily than by most other users of refractories.

Neglecting other impurities for the moment, and speaking broadly, any firebrick with less than 46% alumina is a mixture of clay mineral with silica, any with more is a mixture of clay mineral with some form of alumina. It is now possible to prepare bricks of sillimanite, even to use bricks and shapes cut from natural rock sillimanite, and to bond, shape, and fire high-alumina materials without the use of any clay at all. It is also possible, of course, to melt any desired mixture of silica and alumina and to cast it into usable and useful refractory shapes—a practice which seems likely to increase.

Where speed and a high degree of precision are required special shapes are now being made from sillimanate bonded with ethyl silicate. Shapes made in this way, however, tend to have a rather high porosity.

**Choice of materials**

The following notes on the different general types of alumina-silica refractories offer some guidance as to the main principles on which the choice of materials to meet particular applications may be made. However, many relevant factors have had to be omitted. For example, the methods used in preparing the body, in giving it the desired shape, and in firing, all exert a considerable influence on the properties of the refractory. It is probably not realized by the majority of users that in many cases the
manufacturer has very little choice in the matter: a very plastic and fine-grained clay which slakes very readily to its finest natural state of division demands very different treatment at all stages from another (possibly of almost identical composition) which is naturally coarse in grain, very slow to imbibe water and in consequence very poor in plasticity.

Type B: ‘Semi-silica’ bricks, 80–90% silica

The phase-rule diagram indicates that type B bricks will be less refractory, as measured by P.C.E., than those of types D and E, but in practice it is found that well-made ‘semi-silica’ bricks can compete successfully with even type E (40–45% Al₂O₃) under specific conditions. There are many factors responsible for this.

One factor is that raw materials for type B can be found in large quantities, showing relatively very small amounts of iron oxide and other fluxing impurities. In consequence the P.C.E. approaches more nearly to the curve laid down for pure materials than it does with more aluminous material which, in general, is more contaminated with iron oxide. A secondary consequence of this is that a good ‘semi-silica’ brick is very little affected by even strongly reducing conditions; to match this quality in the more aluminous materials it is sometimes necessary to use minerals of the sillimanite group.

Another important factor is that materials of these compositions show very little contraction during firing, and in consequence it is possible to fire them for long periods in the kiln to a temperature of 1400 to 1450°C, which means in turn that the finished product can be used at such temperatures even under load, without showing any tendency to contract or to sag. Up to a temperature limit of possibly 1450–1500°C a good ‘semi-silica’ material can withstand load at high temperature in a way comparable with silica brick, with the added advantage that, by virtue of its low thermal expansion, ‘semi-silica’ shows very little tendency towards spalling even under comparatively severe treatment.

Finally, ‘semi-silica’ material of type B, while naturally subject to greater corrosion by alkali and basic fluxes generally than is material richer in alumina, is actually more resistant to some specific slags. In particular, fuel ashes may often be of an acid siliceous type, with iron oxide as a major flux, and their attack on ‘semi-silica’ may be less destructive than on bricks even of type E. There is one flux which is often forgotten or ignored, namely, sulphur in the form of sulphur dioxide and sulphur trioxide in the furnace atmosphere. It is probable that these gases dissolve in the glassy constituent of the refractory, giving it a much enhanced fluidity. Whether that is the explanation or not it is a fact of observation that sulphur oxides in the kiln atmosphere, emanating from the fuel, have a very marked effect in increasing the vitrification of refractories containing more than 35% of alumina, often to a very dangerous extent, without exerting any measurable influence on ‘semi-silica’ material in the same kiln.

It is thus evident that there are many fields of service in which this type of brick can give very good service, and it may well be that it has not
received sufficient consideration in the glass industry. One reason for this is probably the wide and apparent difference in physical texture between different products within this range, differences which are conditioned by the nature of the raw material and the kiln treatment applied. At approximately 75% silica one material is a fine grained and plastic clay which can be used to bond at least its own weight of grog well enough to permit shaping into covered glass-pots and into tank blocks, or it may be a harsh ganister of such low plasticity and bonding power that it can only be used as jointing or patching material, any bricks produced from it being of a texture which cannot be modified for any particular application. The materials made up at 85% silica may be artificial mixtures of quite coarse silica grog or natural rock with a selected clay, or they may be natural mixtures in which the silica constituent is either coarse or fine in grading. The firing treatment given to them is largely conditioned by the history of their development, and some products would certainly deserve consideration for much wider applications than they receive if they were fired to high temperatures and with more regularity.

Types C and D: Siliceous and aluminous firebricks, 18–40% alumina

It is unnecessary to devote much attention to types C and D with alumina contents ranging between about 18% and 40%. It is true that good tank blocks can be, and have been, produced in this range and that they have given excellent service, but the qualities required in the tank blocks are highly specialized. In general it is within this range of alumina contents that the plastic range, in practice at least, is greatest, so that the bricks soften in use much below their P.C.E. They are more resistant to most types of slag attack than 'semi-silica' types but the differences in this respect between different brands are greater than can be accounted for by chemical composition. All told, fireclay bricks of 25–40% alumina are probably sold in greater numbers than any others, and they give entirely adequate service as a 'general purpose' brick; in fact, as is so often the case with refractory materials they often give much better service than bricks of better quality. But in glass tank furnaces they cannot compete with silica or more siliceous material or more aluminous material, and in general their use is confined to those parts of the structure, such as the lower parts of regenerator chambers and fillings, gas-flues, etc., where conditions are comparatively easy and their lower price makes them attractive.

Type E: High alumina firebricks, 40–45% alumina

Type E, 40–45% alumina, is that most widely used wherever a fireclay product can meet the conditions in glass tank furnace work, and the development of this type within the last 25 years or so has played an important part in keeping up with increasing demands from the glassmaker. As in other cases the higher alumina content has a twofold effect: directly, it increases P.C.E. and resistance to most types of corrosion; indirectly, it allows the brick to be fired to much higher temperatures and it is only if this much harder firing treatment is actually given that the full
benefits are realized. With hard firing the brick becomes dense and hard, very resistant to corrosive and abrasive dusts and vapours, and it retains full size and shape, under normal constructional practice, up to about 1450°C for long periods, though as already stated it cannot compete with silica where any considerable mechanical stress is applied at that temperature. At the present time, wherever fireclay bricks can meet glass tank furnace and regenerator conditions successfully, bricks of 40–45% alumina content are most widely used.

The upper limit of 45% is not reached in commercial products available in any considerable quantity. Natural fireclays have been found, with an admixture of diaspore or bauxite which may increase the alumina content even beyond 46%, the limit set by the composition of pure kaolinite, but they contain such large and variable quantities of iron oxide, titania, and other impurities that they show no advantage over the more regular and purer deposits in which 43% is the average. Within the last twenty years considerable developments have been made in the application of Cornish china clay. This material has of course been used for a very long time in the preparation of pottery and other types of porcelain, but comparatively recently it has become possible to consider its application as a firebrick in commercial competition with the much cheaper fireclays. The reason for the difference in cost is that while fireclays are ready for use immediately after mining, needing only to be crushed to a suitable grading and mixed with a suitable proportion of grog (prepared by firing the same clay) before being ready for shaping, Cornish china clay deposits, though occurring in extremely large and easily accessible deposits, are mixed with large amounts of silica and mica so that the clay constituent must be separated first.

When the chemical compositions of fireclay and this refractory grade of china clay are compared the china clay seems to have the advantage as the following figures (on the calcined basis) show:

<table>
<thead>
<tr>
<th></th>
<th>Fireclay</th>
<th>China clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO</td>
<td>51%</td>
<td>53.5%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>43%</td>
<td>43.0%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3%</td>
<td>1.0%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1%</td>
<td>trace</td>
</tr>
<tr>
<td>CaO</td>
<td>0.5%</td>
<td>trace</td>
</tr>
<tr>
<td>MgO</td>
<td>0.5%</td>
<td>—</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.5%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>trace</td>
<td>—</td>
</tr>
</tbody>
</table>

Figures have been ‘rounded off’ to the nearest 0.5%, which is sufficiently accurate in view of the unavoidable variations in both materials. One feature that the analysis does not reveal is that while iron impurities occur as segregations in the fireclay, leading to ‘iron spots’ which can be a source of trouble in some conditions, such segregations are practically completely absent from china clay.
From the chemical compositions given it would be expected that the refractoriness or P.C.E., would be slightly but significantly higher in the case of china clay, but determinations by an independent laboratory give the same figure (cone 35, 1770°C) for both. The explanation is twofold. By its intrinsic nature, assisted by the settling out of coarser grains during purification, china clay is not only of finer grain size than the fireclay but breaks down to that size when mixed with water for shaping and, as is well known, finely grained material fuses at a slightly lower temperature than the same material in coarser grains. Secondly, while the fireclay has a higher content of total fluxes these fluxes do not reduce the P.C.E. to any greater extent than the potash which is the chief and unavoidable fluxing impurity in china clay. Moreover, this potash, present as very finely divided mica, is disseminated very evenly throughout the mass and apparently is more effective in reducing refractoriness on that account.

The consequences of the naturally fine grain size of china clay and of the presence of mica in it, cause the raw material to exhibit a slow shrinkage, continued for a very long time, when held at temperatures of about 1350°C or over. For this reason it is necessary to calcine a large proportion of the china clay to a high temperature and to use it as grog with the minimum admixture of bonding clay before shaping and firing the actual brick or block; in the early days this precaution did not prove completely effective. Several glassmakers found that pots made from such a body, while giving excellent melts over a satisfactory life, continued to shrink over a long period. Work is being continued in the attempt to remove this tendency towards long-term contraction. With a shrinkage that proceeds steadily over a period of several months only tests in industrial furnaces working over similar periods can be relied on to give the final answer.

It can be seen that fireclay and china clay refractories of 43% alumina content have specific differences in behaviour in favour of china clay. The very low iron content means that china clay refractories are much less liable to be affected by reducing conditions during use, and the absence of 'iron spots' removes a possible source of localized corrosion with its effects on refractory life and contamination of materials in contact with it. The possible advantages of this in some parts of the glass furnace is obvious. As will be discussed later, the usefulness of an alumina-silica brick in regenerator fillings may depend on whether it 'flakes' and 'shells off' due to the formation of nepheline on the surface or acquires a glaze which slows up the rate of attack. What little experience has been gained so far suggests that the predominating influence of potash in the china clay body tends to favour glazing more than flaking.

Outside the glass industry, the complete absence of iron segregations has the effect, which is very important to some users, of reducing enormously the tendency towards what is called carbon monoxide disintegration. When carbon monoxide is in contact with refractories at temperatures of 450 to 550°C approximately it tends to break up according to the reaction

$$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$$
The elementary carbon is liberated in the pores of the brick and is capable of destroying its strength and cohesion completely. This reaction has received considerable study, and while it is not yet completely understood, many of the conditions which favour it or make it possible are well known. The temperature range over which the reaction occurs is comparatively small and is influenced by the concentration of carbon monoxide and the presence of other gases. The presence of catalysts within the refractory is a primary condition and of these catalysts the most prominent and most effective is segregated iron oxide. With almost all natural fireclays it is impossible to prevent the occurrence of these 'iron spots' but it has been found that by suitable preparation and hard firing in the kiln it is possible to reduce their catalytic effect to such an extent that carbon monoxide disintegration has ceased to be a danger in many furnaces in which at one time it was a major factor in determining the length of service.

So far as is known carbon monoxide disintegration of refractories has never been encountered on any significant scale outside the iron-making blast furnace and its immediate accessories. The phenomenon is not met with even in the heat exchanging 'Hot Blast Stoves', where blast furnace gas is burned to heat the checkers which in a second stage will heat the air blown into the blast furnace itself. In a glassworks the only parts of the plant where it is conceivable are in the gas producers, the mains conveying producer gas to the furnaces and in any regenerators used for preheating the gas. At some depth in the thickness of refractories the temperature must be at the optimum point to favour the reaction, but the composition of the gases themselves inhibit it.

*Type F: Special high alumina refractories*

The development on any large scale of refractories containing more than about 43% of alumina is comparatively recent. It has so far been in the hands of a comparatively small number of manufacturers, but active development is steadily proceeding in a number of different directions. Moreover, the various raw materials available show very decided and well-defined, if imperfectly understood, differences in behaviour; so great are these differences that more than one manufacturer produces 'pairs' of refractory materials having roughly identical alumina content, with differences in the proportion of minor constituents quite insufficient to account for any difference in behaviour. Yet, because different raw materials are involved, the individual members of the 'pair' show such marked differences in properties that their ranges of application are also widely separated. For these reasons it is at the present time impossible to give more than a mere outline of the types of material available. In order to follow up any material for any given application the refractory user must rely on his own testing and research workers to study the specific properties of interest to him, or approach individual refractory makers with the clearest possible statement of the conditions he wishes the material to withstand. Most refractory makers would probably agree that such approaches have been extremely rare in the past and would be very wel-
come in the future. On the other hand the refractory maker engaged in active research would also admit that research quite frequently yields quite unexpected results and that he has to rely considerably upon the co-operation of users to discover for what specific applications and conditions a refractory can be used to advantage.

An increase from 43% of alumina, as found in the most refractory fire-clays, to rather less than about 50% does not offer a sufficient increase in quality to be worth consideration; while 80% alumina is at present about the highest available in bricks made by normal bonding and firing methods on any considerable scale. Materials containing more than that amount are increasingly difficult to bond successfully, and in the special cases where 90–100% alumina is really called for, sintered or even fused bodies are available. Within this 50–80% alumina range, the first advantage offered by increasing alumina content is, as a glance at the equilibrium diagram indicates, an increase in ultimate refractoriness. Standardized tests made on commercial bricks show P.C.E. values ranging from cone 35–36 (1780°C) for approximately 50% Al₂O₃ to cone 38 (1850°C) for 72–80%. Such temperatures as these are, of course, much higher than are called for in normal glass melting, but the advantages of the large margins of safety are obvious. Also these higher P.C.E. values imply that the material will endure and benefit by much higher firing during the course of manufacture, and in fact all successful bricks of this type are fired to very high temperatures. The second advantage does not appear to be so generally recognized as the first. These high alumina materials can safely be used much nearer to their ultimate refractoriness than can normal fireclay bricks. As the composition proceeds farther away from the eutectic point (always given adequate preparation, chiefly heat treatment) the proportion of crystalline material increases, and the softening range of temperature decreases. With pure sintered or fused alumina one would expect the softening range to become a true fusion point, and while this can never be true when silica is present the 70–80% alumina bodies can in many practical cases be dealt with as if they had no softening range at all; the material remains rigid at the highest temperature called for in use. They can in fact be used at the same temperatures and loading conditions as the best silica. The temperature at which 5% deformation occurs varies as follows (rising temperature test, load 28 lb/in.²):

<table>
<thead>
<tr>
<th>First grade</th>
<th>42%</th>
<th>50–55%</th>
<th>72–80%</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica</td>
<td>1710°C*</td>
<td>1570°C</td>
<td>1600–1640°C</td>
</tr>
<tr>
<td>alumina</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is a valid objection to this test that it does not correspond sufficiently closely to conditions in industrial practice and can therefore be misleading. For materials of very high refractoriness some technologists prefer to quote figures for maintained load tests: a specimen is heated to an arbitrarily chosen temperature and maintained at that temperature under a

* In the case of silica, failure is so rapid that 5% deformation cannot be measured accurately and the temperature given is that of failure.
specified load. The results may be quoted either as the percentage deformation suffered in a specified time, or as the time necessary to produce a specified deformation, or illustrated by a graph.

It may be helpful to quote some results obtained with tests more closely resembling working conditions. In one test whole bricks (9 × 4½ × 3 in.) are heated to a controlled high temperature in a furnace large enough to ensure that the brick is heated throughout, and the bricks are so placed as to accentuate the tendency to deform, being supported only on half their length, a condition of stress which is more severe than any encountered in good furnace design. After maintaining a temperature of 1650°C for 3 hours it was found that

- approximately 35% Al₂O₃ fireclay sags completely
- approximately 42% Al₂O₃ fireclay sags 10%
- approximately 50% Al₂O₃ fireclay sags 5%
- approximately 60% Al₂O₃ (sillimanite) sags 2.5%
- approximately 72% Al₂O₃ (sillimanite) sags 1.5%.

It is evident from tests of this kind that highly aluminous material is now available which will remain as rigid as silica brick for all practical purposes. As the high alumina bodies are also much more resistant to spalling than silica (indeed, some of the branded varieties are extremely good in this respect) and in general are more resistant to many of the slagging agents commonly encountered, they offer many advantages in application where hitherto only silica, with its well-known limitations, has been worth consideration.

Although some of these special high alumina refractories, e.g. fusion-cast alumina, are fully capable of taking the place of silica in many industrial furnaces it is extremely unlikely that silica will ever be completely displaced.

**Raw materials.** It is desirable for the user to have some knowledge of the raw materials on which special high alumina refractories are based, because by their influence on the texture the raw materials exert a very profound influence on the properties and behaviour of the finished products.

Dealing first with those refractories which have so far been used in the largest quantities the two chief raw materials are:

(a) The sillimanite group, which includes sillimanite, kyanite and andalusite.

(See note on the nomenclature of these materials by the Refractories Committee, *J. Soc. Glass Tech.*, 1953, 37, 45 N.)

(b) Bauxite.

The sillimanite group consists of different mineral forms having the ideal composition Al₂O₃·SiO₂, with a theoretical content of approximately 63% alumina. Naturally occurring deposits contain, of course, various impurities, mostly fluxes, but occasionally significant amounts of corundum. Carefully selected material, however, is so good in this respect that impurities are of little importance in all save the most critical applications. All three materials in this group change to mullite (3 Al₂O₃·2 SiO₂) when
exposed to a sufficiently high temperature, the 'extra' silica going into a glass with the fluxing impurities present, together of course with the eutectic silica–alumina glass. The main difference between the three groups lies in the fact that sillimanite needs a higher temperature than does kyanite and andalusite and suffers a very small change in volume during the conversion to mullite plus glass. (See paper by C. F. Griffith, *J. Soc. Glass Tech.*, 1953, 37, 221–39.) This means that sillimanite need not be calcined before being bonded and fired, and, indeed, when sufficiently massive lumps of adequate purity and homogeneity are available they can be cut into usable blocks (the process would obviously be very costly for 9 × 4 1/2 × 3 in. standard bricks) and put to use without any further treatment.

Both kyanite and andalusite must be calcined to a temperature high enough to ensure full conversion to mullite plus glass, and this calcination naturally produces a considerable degree of cracking and fissuring. It is thus necessary to crush and grind the calcined material to a ‘grog’ of suitable grading, and to bond, shape, and fire this grog in the normal way. At the present time by far the greater portion of commercial refractories made in this way are bonded with the aid of carefully chosen clays, inevitably lowering the alumina content and the proportion of mullite, but for special purposes bonds such as organic silicates are used which have the advantage of involving less ‘dilution’ of the mullite content.

It will be obvious that the choice of graded grain sizes of the grog, of the bonding material, of the moulding processes and of the heat treatment, will all exert a very considerable influence on the texture of the final refractory product. Different deposits of bauxite ores vary widely in purity and for use in the manufacture of refractory materials it is essential to select material which (after driving off the combined water) contains 90% or more of alumina. It is a general feature of all bauxitic material that it needs prolonged calcination at a fairly high temperature in order to ensure complete shrinkage and it will be evident that this will be most conveniently carried out on the raw material; excessive shrinkage in firing the final moulding composition would make it very difficult to maintain the necessary accuracy in size and shape of the finished product. Thus, with less than 10% of fluxing impurities in the base material there is a smaller proportion of glassy material than is the case with the kyanite and andalusite grog, and the formation of mullite crystals proceeds to a smaller extent. The result is that not only is there a significant difference in the physical and chemical reactions between grog and bond in the two types, but in the bauxite type the formation of mullite crystals tends to be largely deferred until the second firing stage, namely, the final firing of the moulded body. In combination these two factors cause a marked difference in texture between the two types: in the bauxitic group the grog grains tend to lose their identity far more than in the kyanite–andalusite group, and the network of interlocking microscopic needles of mullite tends to be far more evenly distributed through the body. Differences in texture involve differences in behaviour, and in general it will be found that the ‘sillimanite’ type of refractory will be the better in resistance to load at high temperature and
also in resistance to spalling stresses. There seems good reason to suppose that there will be similar differences in resistance to solvent attack by corrosive materials, slags, glasses, vapours, and dusts. But while different manufacturers have made very considerable progress in controlling manufacture, hoping to meet specific conditions by a predetermined texture, it must be admitted that working tests occasionally give surprising and anomalous results. Experience is being accumulated steadily, but it is not at present possible to present a complete picture, and in this field the user will be very well advised to discuss his requirements with individual manufacturers before deciding on any large-scale trials.

**Fused and cast refractories**

Some reference should be made to refractories prepared by melting the raw materials and casting them into the desired shape. Such a process has, of course, been applied to silica and good results with tank blocks of fused silica have been reported from the Continent. The process can also be applied to any desired composition in the alumina-silica range, but the historical development of these fused materials has naturally tended so far to concentrate on the production of mullite and of fused alumina (which crystallizes as corundum or \( \beta \)-alumina) and of both mullite and corundum modified by the incorporation of zirconia or chromium oxide.

These fused and cast materials are naturally most economically produced in comparatively large sizes, the cost of producing normal \( 9 \times 4\frac{1}{4} \times 3 \) in. bricks being prohibitive. For a long time their use in the glass industry was largely confined to actual tank blocks. A fuller discussion of their properties will be found in a monograph, *Refractory blocks for glass tank furnaces*, by J. H. Partridge (1935) and the manufacturers' literature. During recent years such fused material has found increasing application in tank superstructures and with the general tendency to longer working lives they are serious competitors of the older, bonded and fired materials. Their two chief defects at present lie in their comparatively high thermal conductivity and the fact that so far the problem of controlling texture does not appear to have been completely solved.

**Jointing materials for alumina-silica materials**

It is often laid down as a general principle that firebricks should always be jointed or cemented with material of similar chemical composition. Although this seems a logical statement, further consideration will show that it is by no means conclusive or all-sufficient, and that it may be positively misleading. As already shown, the use of any significant amount of plastic clay in a jointing material used with silica brick is dangerous, the admixture of a little alumina having so large an effect on the refractoriness. But it is obvious from an inspection of the phase-rule diagram that the addition of a little silica to any of the fireclay materials on the alumina side of the eutectic point can have but a minor effect, especially when it is remembered that in practice no fireclay material can safely be used within
200–250°C of its P.C.E. It is also obvious that with materials containing more than about 55% alumina the effect of admixture of silica becomes more marked, and in fact it is best to use jointing material of special composition with these special high alumina refractories: they are in general only used where other materials fail and are often used at temperatures much nearer their temperature of failure than it is safe to use fireclay material.

The manufacturer of refractory material is occasionally distressed to find brick containing more than 70% alumina being given, in some metallurgical furnaces, the ‘additional protection’ of a thin layer of silica sand! He is apt to be equally distressed when he finds 42% alumina brick jointed with a plastic clay or artificial mixture containing 70–75% silica: but in this instance he is often confronted with quite convincing proof that in practice no harm is done. There is no selective wear at the joints, brick and cement wearing away at the same rate, and all his arguments fall to the ground. The solution to this apparent paradox is that neither material in such cases is being used dangerously close to its limit of endurance. If the temperature were increased sufficiently, or the structure exposed to more corrosive slagging attack, the siliceous material would certainly yield more easily and pronounced wear at the joints would occur. This has been borne out in practice, and in some furnaces a naturally plastic highly siliceous clay is used to joint 42% alumina brick in the walls and crown of the working chamber, while for the same brick in the combustion space, where the temperature is higher and slag attack more severe, a carefully selected high alumina cement is used.

Class 1: Natural clays

The bricksetter or mason, who is as a rule not concerned with chemical composition, desires chiefly a jointing material which will work well on the trowel, at whatever consistency he wishes to use. From time to time argument arises as to the relative merits of ‘dipped’ joints, obtained by dipping the brick into a slurry or slip, as against ‘trowelled’ joints. Provided the joints are reasonably thin and uniform it is the opinion of many good craftsmen that such arguments ought never to arise. When aiming at the thinnest possible joint it is obviously desirable to have the jointing material of such a consistency that it may be applied more conveniently by dipping the brick face in it than by applying with a trowel. But even if the brick is dipped, a good craftsman will always make sure of the slip wetting the brick face and spreading evenly over it by application of the trowel. Without that application quite large areas of the brick face may not retain any coating at all, while the trowel also helps to force the slip into all the minute irregularities which are to be found on the faces of the most accurately shaped bricks.

Numerous fireclays of very satisfactory plasticity and trowelling consistencies are available. The objection to most fireclays arises after the bricksetter has completed his task: fireclays shrink to some extent on drying off the water used in bringing them to working consistency, and show a
further shrinkage on firing. With really plastic clays of alumina content about 40% of these combined shrinkages may be sufficient to cause the jointing material to recede from the edges and to show numerous open fissures across the jointed faces. When this happens the jointing material fails to some extent in nearly all its functions. By shrinking away from the edges it exposes them to increased attack, by the formation of fissures it allows gases, vapours, and dusts to penetrate, and its diminished area of contact with the bricks does not allow it to hold them together.

In fact, all it does is to help to hold the bricks apart, so that they are free to move independently when expansion or contraction due to changes in temperature take place; and, of course, in vertical or inclined joints, as in arches, it may actually crumble and fall out thus losing even that function. For these reasons, of the approximately 40% alumina clays available only those which are comparatively deficient in plasticity should be used when a reasonably tight ‘stopping’ is desired: these non-plastic clays, while not so easy to work, do not shrink so extensively, so that what is lost during the setting process is regained during drying and heating up.

There are available natural fireclays of approximately 75% silica content which have plasticities almost comparable with ball clays and when made up to a jointing consistency are ideal from the bricksetter’s point of view. For all practical purposes these fireclays can be considered as consisting of 50% kaolinite and 50% of very finely divided silica in the form of quartz, the bulk of it finer than 100 mesh. In fact in some steelworks it is the successful practice to imitate these natural clays by wet-grinding used (and cleaned) silica bricks with a suitable proportion of a plastic fireclay, the grinding being continued long enough to achieve whatever degree of fine grading is desirable. These highly siliceous materials have the outstanding advantages that the shrinkages on drying and heating are very small, and that at temperatures above approximately 1350°C expansion takes place. Thus when used for jointing they form a continuous and compact lamina or ‘wafer’ between the bricks, protecting the brick edges completely, and offering much the same resistance to penetration by gas vapour and dust as the brick itself. In fact, until conditions become too severe for them there is little or no fault to be found with these highly siliceous materials, and the question of just when conditions do become too severe is one that can only be solved by experience.

**Class 2: Specially prepared non-vitrifying cements**

These materials are comparable with the natural highly siliceous clays (and with the artificially prepared mixtures of similar composition) in that an attempt is made to eliminate shrinkage as a harmful factor. This is very simply achieved by incorporating the largest possible proportion, consistent with good workability, of pre-fired and fully shrunken material of similar chemical composition to the brick. This pre-fired material may be high alumina fireclay grog for high alumina fireclay bricks, or it may be kyanite, sillimanite, andalusite, bauxite, or corundum for the special high alumina bricks. The choice of bonding material and the method of prepara-
tion designed to give the maximum degree of workability are still matters which the manufacturer keeps to himself, but there is an entirely adequate supply of such cements available. Their use is essential for refractories containing more than 50% alumina, and they are in general desirable for 40% alumina bricks: they have the obvious advantage of having the same working limits of temperature and corrosive attack, they form as complete and homogeneous a wafer as the highly siliceous materials, but exhibit no crystallographic changes which will cause them to expand at high temperatures. There are two chief considerations: conditions of use and cost (the natural highly siliceous clays are in general considerably cheaper).

Class 3: Vitrifying cements

For use where it is in fact desirable to cement bricks together, there are now available synthetic materials which will vitrify well before the working temperature is reached and yet retain an ample degree of rigidity at working temperatures, and, if necessary, have a P.C.E. at least equal to all but the most refractory brick. These vitrifying cements are made by taking a finely ground base substance of such high refractoriness that the addition of plasticizing and fluxing agents, sufficient to give the required degree of vitrification, cannot reduce the ultimate refractoriness sufficiently to cause danger at the designed limit of working temperature: moreover it is possible to achieve this without more than an insignificant amount of shrinkage in volume during heating. It is thus possible to obtain true cements which will vitrify as thoroughly at temperatures as low as about 850°C as to become practically impervious to gases, to unite firmly with the adjoining brick faces, and still to be rigid enough for practical purposes at temperatures as high as 1650°C. If the conditions of use make it desirable, it is also possible by the addition of air-setting agents to produce cements which give very strong adhesion on simple drying at normal temperature, an adhesion which increases steadily with increase of temperature so that there comes a point at which it is easier to break all but the very hardest brick than to break the cement. Very careful selection and compounding of these air-setting bodies is obviously necessary if the cement is not to be a direct cause of the formation of random cracks which will be at least as dangerous as the weak joints it is intended to prevent. Given such care it is possible to provide cements which produce completely 'tight' adhesion from within a few hours of laying, or from 850–1100°C upwards, and which at a sufficiently high temperature will unite the structure into a jointless monolith.

The first two classes considered have the common feature that they do not in fact cement the bricks together at high temperatures. (Some of the plastic fireclays of low refractoriness will of course soften sufficiently to do so, but such clays are ruled out in practice by their very high shrinkage.) These two types of material lose their cementing power once the combined water in the clay has been driven off, and the 'cement' then becomes a simple 'stopping' between the bricks, preventing undue access of gases, etc.
Nor must it be overlooked that the materials of classes 1 and 2 offer the positive benefit of *not* cementing the bricks together at high temperatures. Thus the bricks are left free to move slightly relative to each other when the wall or other structure expands and contracts with changes of temperature, and in many cases such freedom is very important. It will be obvious, of course, that materials of class 2 will vitrify if exposed to a sufficiently high temperature, but at such temperatures the brick itself will also vitrify and tend to lose shape, so that point is not of practical importance.

*Examples of the use of cements*

Perhaps two simple instances, not specifically related to the glass industry, will illustrate the general principles sufficiently.

First consider a working chamber at, say, 1450°C, of sufficient size to make thermal expansion a considerable factor, and subject to change of temperature during life. A vitrifying cement, particularly if it is strongly air-setting as well, will obviously tend to prevent the bricks from moving relative to each other, thus cracking and disruption are very likely to occur. For such a chamber a non-shrinking, non-vitrifying cement of class 2 is most satisfactory. But if there is a combustion zone or chamber anterior to the working space, fed by automatic stoker, oil or gas flame, and necessarily at a higher temperature and more subject to corrosive attack by fuel ash and the abrasive effect of the flame itself, then it may often be best to use a vitrifying cement in that portion of the structure in spite of the apparently increased tendency towards cracking in such conditions. The reason is that, unless a non-vitrifying cement which is more refractory than the brick is chosen—as for example, by using a ‘sillimanite’ or other very high alumina cement with a fireclay brick—the cement, when undergoing its first firing, cannot be as resistant to corrosive attack as the brick. In consequence the exposed brick faces or ends will tend to assume a ‘cobblestone’ appearance, similar to that already described when referring to the absence of jointing material with silica brick. In this case differential slag attack will reinforce the spalling effect. Slag attack causes vitrification to penetrate more deeply into the exposed joints, and as the thermal expansion of the vitrified portion is probably different, and the mechanical strength is certainly different from that of the unaltered brick, it can readily be imagined that spalling-off of the rounded ends will occur. This is confirmed in practice.

When a suitable vitrifying cement is used, the joint is attacked at approximately the same rate as the bricks, total slag penetration is less in depth through both brick and cement, and the total surface exposed to attack remains unchanged. It must be realized that in such conditions the whole exposed face of the refractory is in a plastic condition at top temperature: not plastic enough to deform under properly distributed structural stresses, but sufficient to yield and ‘flow’ with changes of size due to thermal expansion and contraction. It is even an advantage in some cases to brush vitrifying cement on to the working face of the brick. The effect appears to be to encourage the formation of a uniform plastic face, a semiviscous layer which encourages the formation of a protective mullite layer,
which in turn prevents the penetration of slag into deeper layers of the brick. Keeping the vitrified layer thinner naturally tends to minimize stresses due to temperature changes.

The second example is an unusual one and illustrates the use of vitrifying and non-vitrifying cements on one and the same structure. In a suspended furnace crown it was desired for various reasons to have the individual suspended blocks larger in size than was convenient for manufacture or even for handling when the blocks were set in position. They were therefore made in halves, joined along a vertical face in the setting, and it was essential that the two half-blocks should not move relative to one another once placed in position. On the other hand, with a large flat roof, suspended from rigid and immovable steelwork, it was necessary to make adequate provision for movement between adjacent pairs to cope with temperature changes. The simple and quite effective solution was to cement the half-blocks together with a vitrifying cement and to joint between the pairs with a non-vitrifying cement of class 2.

It must be emphasized again that these examples do not relate to glass furnaces, in fact the use of a vitrifying mortar in the superstructure of a glass tank furnace would be highly undesirable as it would tend to run out of the joints after a short exposure to the flux dust and vapour present. Non-vitrifying silica mortars are in general found satisfactory.

### Basic Refractories

Increasing interest is being displayed by the glass industry in the possibility of using basic materials, magnesite, magnesite allied with chromite, dolomite and serpentine. They are widely used in the metallurgical industries and have made possible considerable progress in technique and efficiency. With this very large demand from the metallurgist the refractory maker has not as yet had time to make any specialized study of the possible applications of basic materials in the glass industry, and there are so many factors to consider that glassmakers in this country have only recently been tempted to make working trials on any large scale. Accordingly a very brief outline of the materials available will suffice. The use of basic bricks in air regenerators is well established in many American glassworks, and appears to be increasing on the Continent.

#### Magnesite

There are no commercial sources of magnesium carbonate in Great Britain and until about twenty years ago all magnesite refractories were made from ‘dead burned’ magnesite rock imported chiefly from Austria. Magnesium oxide itself, while having a melting point of well over 2000°C, has a natural tendency to absorb water from the air to form magnesium hydroxide, and if it is to be of any use as a stable refractory, capable of withstanding storage and the effect of water vapour in the furnace, it is...
necessary to calcine it to a high temperature. This calcination is termed ‘dead burning’, i.e. calcination is carried on until the material becomes non-reactive or ‘dead’. Naturally, the presence of impurities, leading to the formation of compounds between magnesium oxide with other oxides present and even of glasses, has a considerable effect on the ease with which this non-reactive or dead burned condition can be achieved. It is the presence of impurities and the micro-texture of the rock which for long kept naturally occurring Austrian magnesite supreme in this respect. Much purer magnesites are available, but it is much more difficult to calcine them to the non-reactive condition, and there are further difficulties owing to shrinkage: the purer the magnesite the harder it is to ensure that all the shrinkage is achieved during manufacture. In fact, as with alumina, with a refractory approaching 100% MgO, the only practicable way of ensuring non-reactivity and volume stability is that of fusion, or of sintering just short of fusion.

During the last twenty years the position has been completely changed in Great Britain by the successful manufacture on a very large scale of magnesium oxide artificially prepared from native materials. Somewhat loosely described as ‘sea-water magnesite’, this material is produced by causing natural dolomite (mixed carbonates of lime and magnesia) occurring abundantly in this country, to react with magnesium chloride in the form of a solution obtained from sea-water. The final product may be metallic magnesium, magnesium oxide, or any desired compound of magnesium. The chemical purity of the products is almost entirely a matter of cost. For use in commercial refractories cost is a matter of great importance, and a high degree of purity is not necessary.

Naturally, during the early stages of developing into large-scale manufacture the product did not always attain the high standard aimed at. Variations in composition and physical quality occurred. In particular, calcium oxide derived from the dolomite was apt to be troublesome. Calcium oxide, unlike magnesium oxide, cannot be made resistant to attack by water by any heat treatment up to and including fusion, so that calcined dolomite, and magnesite containing too high a proportion of calcium oxide, require special care to guard against the possibility of hydration. The presence of excessive calcium oxides also leads to a decrease in refractoriness and in resistance to some forms of slag attack.

During the early stages of the Second World War, when the production of magnesite refractories (as well as of metallic magnesium and other magnesium compounds) exclusively from native resources was vitally needed, the products obtained were to some degree stop-gap substitutes. But before the war ended sea-water magnesite was firmly established as a refractory material capable of competing on equal terms with any similar material, natural or artificial, produced anywhere in the world. The steel industry, by far the largest user, has seen no advantage in resuming importation of basic refractories from Europe, and British manufacturers, using sea-water magnesite exclusively, are now exporting basic refractories to practically all parts of the world.
The composition of a typical British-made magnesite brick is:

- MgO 92.0%
- CaO 3.0%
- Fe₂O₃ 2.0%
- Al₂O₃ 1.5%
- SiO₂ 1.5%

with a variation of not more than ±0.2% on any constituent.

(The very low content of iron oxide is worthy of special notice by the glassmaker as natural magnesites from Europe as a rule contain much more than this.)

Other data include:

- Porosity 20%
- Bulk density 2.82% (176 lb/ft³)
- Refractoriness under load of 28 lb/m² 5% deformation at 1700°C
- Cold crushing strength 15,000 lb/in.²
- After contraction—2 h at 1600°C 0.45%

A material with these properties is evidently well adapted to resist the corrosive attack of other basic materials and thus offers the possibility of being useful in resisting corrosion by the alkalis used in making glass. A likely application would be in regenerator checkers. Unfortunately magnesite refractories have a thermal expansion even higher than that of silica (1.1% at 1400°C as against 1.4% for silica) and the expansion is continuous over the whole range instead of being almost entirely completed in the first 500°C as with silica. Coupled with the very high density this means that in spite of their great mechanical strength magnesite refractories are apt to suffer badly from spalling with changing temperature, and there is no 'safe' range of temperature in this respect. While a silica brick is reasonably secure against a rapid temperature change as long as the general temperature does not fall below 500°C, a magnesite brick is just as likely to spall through a sudden fall from, say, 1400°C to, say, 1100°C as it is through a similar change from 400°C to 100°C.

It is in this connection that certain claims are made in favour of magnesite bricks made from natural magnesite rock. With a natural rock, even after calcining and crushing, it is possible to make the body with a predetermined grading of grain sizes which, while still maintaining a low porosity and high bulk density, offers so many internal 'fissuring zones' that expansion and contraction can to some extent be accommodated or 'taken up' at innumerable places inside the brick without giving rise to a major disruption, crack, or spall. It is quite true that this is not so easy to arrange when sea-water magnesite is the raw material: the methods used in preparing the sea-water magnesite coupled with its comparatively very high purity and the fact that the high temperature form of magnesia (periclase) is spheroidal like quartz rather than needle-like or plate-like like mullite, tridymite, or corundum, makes it difficult to vary the texture from that very close and homogeneous evenness which is so valuable in resisting
basic slag attack. It may never be possible to produce a 'straight' magnesite (or silica) brick designed specifically to meet very severe spalling conditions, as can be done with special high alumina refractories, but it is already possible to produce straight magnesite bricks which will stand normal, careful usage in conditions where spalling can be a major factor.

In the United States periclase bricks with a magnesium oxide content of 95% are used considerably in glass furnace air regenerators.

**Chrome-magnesite**

The chromium-bearing constituent in chrome-magnesite bricks is not simply a commercially impure form of chromium oxide but a chrome ore: mineralogically it is a chromite of the type $R''O : R'''O_3$ in which $R''$ may be ferrous iron, manganese, calcium, manganese, etc. and $R'''$ chromium, alumina, etc. Chromites are thus very variable in composition and those highest in content of chromium are reserved for the preparation of metallic chromium, its alloys and compounds. Considerable investigation has been necessary in selecting the sources of chrome ores most suitable for refractory manufacture and the following approximate composition indicates the type of material in current use:

- $Cr_2O_3$ 40%
- $Fe_2O_3$ 15%
- $Al_2O_3$ 15%
- $CaO$ 1%
- $MgO$ 20%
- $SiO_2$ 7%

Odd as it may appear these considerable admixtures, of iron oxide in particular, which are too big to be called impurities, are of real advantage in chrome and chrome-magnesite bricks used in the steel industry, but they can hardly be expected to be of direct benefit to a refractory to be used in a glassmaking furnace. In fact the use of chrome ore blended with magnesite for the steel trade depends on two factors, only the second being applicable to the glass industry:

1. Chrome ore is more resistant than is magnesite to some of the slags encountered in metallurgical practice.
2. Admixture of chrome ore with magnesite confers a very enhanced degree of resistance to spalling. Not only can chrome-magnesite be used in the superstructure (that is above the metal line or slag line) where normal magnesite bricks have been found to spall too seriously to permit useful lives to be obtained, but they can actually be used for hot repairs.

To the glassmaker an important possible advantage offered by chrome-magnesite over magnesite is this significantly greater resistance to spalling, but it is doubtful if the advantage can ever offset the drawback of attack by glass constituents. Chromium oxide is even more deleterious as a glass colorant than is iron oxide, while the attack of alkali dust and vapour on chrome-bearing materials in the superstructure and substructure might be
expected to be very destructive, often causing the brick to swell in a sponge-like manner, to split, or to crumble and disintegrate completely and to produce highly insoluble stones. Nevertheless, it is known that basic bricks of this type have been used successfully in glass tank regenerators in the U.S.A.

**Dolomite**

There are ample native resources of dolomite, approximating to an equimolecular mixture $\text{CaCO}_3 \cdot \text{MgCO}_3$, sufficiently free from impurities to permit use as a refractory at temperatures much higher than are at present needed in glassworks. Unfortunately it suffers from the serious defect that the calcium oxide constituent cannot be made completely stable against hydration. Considerable quantities of highly calcined dolomite are in fact used in the steel industry both as a ramming or ‘fettling’ material and as bricks. In steel-melting practice it is possible to make special provisions to avoid dangerously long exposure to the risk of hydration, and once in the furnace the risks no longer apply. Any possible application in the glass industry, however, seems to depend on a considerable degree of ‘stabilization’ against the tendency to hydration. The only successful method so far achieved depends on converting all the lime present to calcium silicate, which is achieved by calcining dolomite mixed with a suitable proportion of serpentine (a native hydrated magnesium silicate with $\text{MgO} : \text{SiO}_2$ ratio approximately $3 : 2$) to a temperature of about $1600^\circ\text{C}$.

The composition of such stabilized dolomite bricks is approximately:

<table>
<thead>
<tr>
<th></th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>15</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>3.5</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>2</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>40</td>
</tr>
<tr>
<td>$\text{MgO}$</td>
<td>39.5</td>
</tr>
</tbody>
</table>

The refractoriness under load (failing under rising temperature test at $1650^\circ\text{C}$) is much lower than that of good magnesite or chrome-magnesite but can be adequate for many conditions. There is little information on the use of dolomite bricks in glass furnace applications.

**Forsterite**

The only other basic material to have been applied so far in any quantity is based on natural serpentine itself, serpentine being the name applied to a group of rocks of variable composition. Forsterite, $2 \text{MgO} \cdot \text{SiO}_2$ (42% $\text{MgO}$, 58% $\text{SiO}_2$), is highly refractory having a melting point of $1890^\circ\text{C}$, but unfortunately the refractoriness decreases very rapidly with increasing silica content, so that the serpentine materials, $3 \text{MgO} \cdot \text{SiO}_2$ or 50% $\text{MgO}$, 50% $\text{SiO}_2$ approximately, are not sufficiently refractory. The idea of mixing magnesite with serpentine in the right proportions to yield forsterite is attractive, but so far no commercial success has been claimed in this country. It is claimed, however, that forsterite bricks are being used successfully in regenerators in America and although they are now avail-
able in this country there is insufficient information to appraise their suitability for use in regenerators.

**ZIRCON REFRACTORIES**

Of the many, more uncommon, refractory materials outside the three main groups, silica, alumina silica, and basic materials which are of possible interest, only zircon is available in large enough quantities at a competitive price and able to compete in ordinary commercial usage. (See J. H. Partridge & O. Adams, ‘Glass Making at 2000° C’. *J. Soc. Glass Tech.*, 1944, 28, 105 t.) Zircon, being a compound of zirconia and silica, is sufficiently refractory and resistant to certain corrosive agents such as \( \text{B}_2\text{O}_3 \) to make an excellent refractory for use in glass furnaces. It has also a very low coefficient of thermal expansion which increases the spalling-resistance of bodies of suitable texture made from it. However, the only commercially available deposits so far known take the physical form of fine sands of uniform grading and almost spherical grains. Also it is so resistant to reaction with other ceramic materials that it is very difficult to find a bonding agent for it. Normal bonding agents will not take it into solution in order to help recrystallization and it is also so inert that heat treatment alone will not cause the crystalline spherulites to ‘grow’ together. While it is a very simple matter to make sound, and heavy (200 lb/ft\(^3\)), bricks and blocks from it by bonding with a very small proportion of clay, the finished product has a porosity of 30\% or more. The absence of any crystal intergrowth between the grains must weaken the resistance to load at high temperatures and offers little or no resistance to the penetration of slags and vapour. For these reasons, zircon refractories made by substituting zircon sand for normal grog in clay bonded refractories have so far shown very little improvement over alumina-silica materials. All-zircon refractories have been used successfully in superstructures of furnaces making certain types of glass, but difficulty can be experienced where there is a high concentration of alkali.

It is possible of course to overcome the physical defects to a large extent by grinding a portion of the sand to a very much finer state of division, 200 mesh or under, and to bond sufficiently to give the desired shape and to stand up to firing, by purely physical methods such as slip casting or by the use of organic silicates which ‘dilute’ the material to a negligible extent.

Small trials have indicated that even with these handicaps there is a strong possibility that zircon bricks could be used with advantage as checker bricks, but this work does not seem to have been followed up on any large scale.

**APPLICATION OF REFRACTORIES IN VARIOUS PARTS OF THE GLASS TANK FURNACES**

**Crown**

At present first-class silica, which should be capable of giving several years’ service at a steady temperature of 1600° C, is not only the most
economical but the most generally satisfactory for the furnace roof. Whenever conditions become too severe for silica special high alumina materials will probably be adopted which will be capable of maintaining a rigidity at 1650–1750°C and be more resistant than silica to the attack of alkali vapour. In the metallurgical industry there is already a very marked change-over from silica to chrome-magnesite for the roof, but it seems improbable that basic material will ever be adopted extensively for glass-melting furnaces: if conditions become so severe as to demand refactoriness greater than is obtainable with alumina–silica material, it is probable that materials such as fused alumina, stabilized zirconia, etc., which are already in use in laboratory-scale work, will be developed.

**Burner ports**

The conditions at burner ports are so severe that silica fails long before the rest of the furnace is worn out. So far the special high alumina bodies, both the bonded and fired and the fusion-cast types, have met all demands.

**Side walls and end walls**

The general tendency has been to concentrate on the silica and the very high alumina types, to the exclusion of the fireclay materials of between 30% and 43% alumina. The endurance of fireclay material has in some cases been entirely satisfactory, except in the hottest furnaces worked at the highest rates. But even when it gives a long enough life, it suffers from the defect that any material dissolved and washed down into the glass is very apt to produce discoloration and inhomogeneity.

In general, silica suffers very little loss by solvent attack, although silica in walls above glass level does naturally tend to become much more glazed on the surface than it does in the roof. Any material running down into the glass is quickly dispersed without causing streaks of bad colour or cord. When silica does fail (there should of course be no risk of spalling in these situations) it can sometimes be replaced quite successfully by material containing 60% alumina or more, but there is a possibility of cord formation due to contamination with material much higher in alumina than the glass.

A particularly vulnerable place is the superstructure over the dog-house or batch-feeding devices, and the replacement of silica by special high alumina, bonded or fusion-cast, is fairly general.

**Regenerator uptakes**

Silica bricks appear to be generally used in this application, but the use of special high alumina material offers several advantages in specific cases.

**Regenerator chambers**

The upper parts are usually built of 42% alumina brick. In the lower parts of the structure, normal good fireclay brick is amply good enough for the conditions.
Regenerator checkers

It is in the materials found necessary or desirable for checkering that the widest divergences are found, not only in the glass industry but in the essentially similar open-hearth furnaces used in steel melting. To the refractory maker it is more surprising that this is the case in the steel furnace than in the glass furnace, as temperatures of 1600°C to 1700°C are commonly encountered in steel melting. Yet it is found that among different works where conditions appear very similar, demanding similar refractory material for the furnaces themselves, one may find in cheap works ‘semi-silica’ quite satisfactory in checkers, a second may need silica, a third may have been obliged by short lives (and rapid loss of regenerating capacity—a factor often forgotten) to change from silica to 43% alumina, and a fourth has changed from firebrick to a special high alumina and is making trials with magnesite or chrome-magnesite.

Corrosion problems in steel furnaces and glass furnaces are different in character, but there is one destructive factor in common, namely, the temperature to which the regenerators and fillings are subjected, and very wide and indeed rather puzzling variations are encountered.

Where checker brick temperatures are determined it is a surprising fact that while some very efficient steel furnaces, with operating temperatures of 1650–1700°C, carry a temperature of not more than 1150–1200°C in the top row of checkers, others, working no more efficiently, or at least no more effectively, find it necessary to carry 1500–1550°C at the checker tops and to install ‘waste heat boilers’ between regenerator and chimney to keep down fuel consumption figures. There is room for conjecture as to whether very high checker temperatures are necessary or even advantageous; there may be an optimum checker temperature giving most efficient heat utilization to a furnace of given size working at a given temperature and duty. However, the fact that such very large differences in checker temperatures do exist explains, in part, why such widely different checker brick qualities are needed.

In glass-melting furnaces the corrosive agent is predominantly alkali and it causes considerable differences in the behaviour of different refractories.

With silica checkers, as already stated, the general effect is simple and straightforward. Sodium (and calcium) silicates are absorbed by the brick. At a certain concentration a fluid is formed which is absorbed by lower cooler courses which remain sufficiently rigid. The final stage is complete disappearance of the upper portions without the gas passages being unduly restricted.

When alumina–silica bricks are used, the first difference noted is that the slags formed by reaction with alkali are less fluid than when no alumina is present; they are not absorbed into the body of the brick, and the consequence is that the dust carried over is far more likely to accumulate on the horizontal surfaces. Thus it is common experience that while a fireclay brick may show less wear than silica, the checkerwork built up of fireclay brick is very much more liable to choke up, thereby impeding the working
of the furnace unless means can be provided for removing the obstruction at suitable intervals.

The corrosion of alumina–silica refractories by sodium oxide at comparatively low temperatures is by no means a simple process. The complexities are introduced by the possibility of forming nepheline, which has the molecular composition Na$_2$O.Al$_2$O$_3$.2 SiO$_2$. The reader who is familiar with the technique needed to interpret three-component phase-rule diagrams will be able to trace the course of events with any given brick composition at various temperatures, but others may find the following greatly simplified account helpful.

Consider a checker brick containing approximately 20 to 40% alumina subject to the attack of sodium oxide. Liquid slag can form at a temperature as low as 900°C, and at higher temperatures this slag will tend to be absorbed into the porous brick, to react with it and become more refractory by the solution of more alumina and silica. As the temperature will naturally decrease with distance from the surface, absorption of soda will tend to be confined to a relatively thin layer. If it were not for the formation of nepheline with its specific individual properties further reaction would present a simple picture: absorption of more soda would simply make this glazed layer more and more fluid until at a certain temperature it would flow down into the lower part of the checker. This happens with silica bricks, though with fireclay bricks the slag tends to choke up the openings rather than be absorbed.

The formation of nepheline is much more marked as soda concentration increases however and leads to solidification of the surface layer, since pure nepheline does not melt below about 1250°C; indeed the high temperature form carnegieite has a melting point greater than 1500°C. If that were all that is involved in the formation of this definite crystalline compound the only consequence would be a retardation in the rate at which the refractory material is slagged away. Unfortunately the formation is accompanied by an expansion in volume and a change in texture which tends to make the nepheline layer part company with the body of the brick. Further, this layer has a different coefficient of thermal expansion from that of the unaltered brick, so that with each change in direction of gas flow, there is a tendency for the face of the brick to become detached. Thus, when nepheline formation becomes a predominant factor, the brick tends to become coated with a layer of less compact material, often as thick as $\frac{1}{2}$ in., which is not firmly in contact with the relatively unaltered core of the brick. At best this means that as the body of the brick is partly insulated it cannot play its full part in the heat exchange and the temperature in the lower parts of the setting is therefore increased and the destruction of refractory material extended. At worst, these nepheline shells can detach themselves from the brick and fall down into the setting thus helping to choke up the passages.

Whether a slagged face, or a face 'shelled' by the formation of nepheline, will form depends on two main factors: the alumina content and the temperature. It would be very laborious to work out the whole process in detail
from the phase-rule diagrams and also differences are introduced by impurities and by the physical texture of the brick. From observation of many different furnaces, however, a fairly coherent and simple pattern of behaviour does become apparent. Silica brick, having no significant alumina content, is of course not liable to nepheline formation, and in practice it appears that no serious formation does occur until the alumina content of an alumina–silica brick reaches about 25%. At that alumina content, nepheline formation increases with increasing working temperature until a temperature is reached at which nepheline is completely absorbed and obliterated by the formation of a normal glazed surface. In general, that critical temperature increases with increasing alumina content. No precise figures can be given, but examination of any regenerator setting after a campaign will give ample indication of what changes, if any, should be made in choice of refractory material in order to obtain better durability on a second campaign.

Silica, ‘semi-silica’, and highly siliceous material will in general be judged entirely by loss in volume sustained by the bricks. If slagging has been excessive with fireclay containing more than 25% alumina the obvious remedy is to use material of higher alumina content, but it is advisable to proceed with caution. The ideal to aim for, as complete absence of attack is not attainable, is to have a brick which will glaze just sufficiently to form a good mullite layer thus slowing down further absorption of alkali considerably, rather than a brick which forms a nepheline shell. Thus it has been noted in practice that when test ‘blocks’ were made up of various bricks in one furnace under comparable conditions

- bricks of 25% to 35% $\text{Al}_2\text{O}_3$ showed excessive loss due to slag corrosion,
- bricks of 40% to 43% $\text{Al}_2\text{O}_3$ were glazed under a ‘fur’ of adherent material, indicating slag attack which had reached equilibrium, with the beginning of a tendency to choking up,
- bricks of 50–80% $\text{Al}_2\text{O}_3$ were covered with a shell, rich in nepheline, ready to part completely from the core.

In this example the 40–43% alumina bodies are the best for the conditions, and the special high alumina bodies can be said to ‘shell’ and ‘fail’. But if the temperature of the checker were increased by 50 or 100°C the 40–43% alumina material would lose weight by increasing slag attack and the 50% alumina would almost certainly show a glazed surface instead of a nepheline shell, while bricks of higher alumina content might still display the shell. At higher temperatures the highest alumina bodies would be most suitable.

The differences between special high alumina bodies of similar alumina content but based on different raw materials have, in the few works’ trials known, shown up very clearly in their use as checker fillings, not only in glass-melting furnaces but in steel-melting furnaces.

As special high alumina materials can be used at working temperatures of 1600°C, much above what is likely to be called for in glass furnace
regenerators for a long time to come, the furnace designer and operator can choose materials from the alumina-silica group which will give optimum performance and endurance. But the use of special high alumina materials is more likely to be justified where regenerator temperatures are unusually high.

Nevertheless, as glass-melting furnaces have a life extending over two or three years, and it is not as simple to determine the conditions in the regenerators as those in the furnace, it may take a considerable time to discover by experience what is the best brick to use for checkering. Considerable interest is being shown in the possibility of using basic regenerator checkers. Basic refractories are almost completely unattacked by alkali and by batch materials at normal regenerator temperatures, and any material deposited on them can be easily removed by mechanical means. They have the further theoretical advantage of a higher bulk density and thus heat capacity:

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (lb/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>43% alumina</td>
<td>125</td>
</tr>
<tr>
<td>50-80% alumina</td>
<td>135 to 165</td>
</tr>
<tr>
<td>Magnesite</td>
<td>175</td>
</tr>
<tr>
<td>Chrome-magnesite</td>
<td>185</td>
</tr>
</tbody>
</table>

Considerable success has been reported from trials in the U.S.A., but up to the present time no really large-scale results of trials in this country have been made public; even in the steel-melting furnace, where lives are much shorter, trials of basic checker materials are still in their infancy.

Any glassmaker may make trials but it should be emphasized that small trials cannot be expected to yield useful information, because the reactions between small patches of basic material with neighbouring silica and alumina silica can be, and often are, more serious than those between the brick and the corrosive vapour and dust. Thus a patch of magnesite, chrome–magnesite, or similar material should not only be wide enough to ‘isolate’ the influence of neighbouring silica or alumina–silica material, but it should be carried to such a depth in the checkers that the risk of reaction with the lower part of the setting is completely eliminated. In the American experiments it was found to be essential to surround the basic checkers by chamber walls and roof of similar material, as siliceous ‘wash’ from normal refractories was found to be very destructive.

In planning a large-scale experiment account should be taken of the following points:

1. Magnesite is liable to crack even under the comparatively small and slow temperature changes occurring in regenerators.

2. Any basic brick containing chromite, or chromium oxide, may be subject to differential attack by sodium oxide in particular, and may be deleteriously affected by changes in the oxidizing or reducing character of the atmosphere. It has to be remembered that water vapour may have a strongly reducing action. Thus basic bricks which have been safeguarded from spalling by the incorporation of chromite may be found to swell
sufficiently to cause serious choking, to split, and even crumble to such a friable condition that while appearing to be fairly sound they can only be removed as powder.

Zircon refractories have been tried in regenerators on a very small scale several times within the last twenty years. Results were good, and no complicating drawbacks were apparent. Further progress in this direction is dependent on the commercial production of zircon bricks but at present the market is restricted.