Refractory Materials

A course on refractory materials compiled by Frans Nyikos

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Chapter 1

REFRACTORIES FROM THE BEGINNING

HISTORICAL BACKGROUND

The first industrial refractories were naturally-occurring siliceous rocks such as schists, used in iron furnaces from the middle Ages up to the Nineteenth century. The size, complexity and production rates of furnaces gradually made shaped natural stone far too expensive and bricks made from heat-resistant clays became more common, i.e., fireclays as opposed to building brick and tile clays. Naturally, many of the fireclay deposits had previously been used for building brick purposes until their true value was made apparent by the Industrial Revolution, which took place at different times in different countries.

Many of the requirements of the Nineteenth Century Iron and Copper Industries' were satisfied by the refractory properties of silica and silica brick production then started. This has, of course, continued to the present day, although it has now lost its major position to basic linings, this is due to the use of oxygen in open hearths, the advent of the basic oxygen steelmaking processes and electric arc furnaces with increased power and steel output.

Magnesite

Before the beginning of the present century, refractory bricks were being produced from magnesite and chrome ore. These bricks are far more resistant to attack from highly basic slags. The crystalline magnesia, or periclase, MgO, used in these products was and, in many cases, still is obtained by calcining naturally-occurring magnesite, $MgCO_3$, originally mined at Veitsch, in Austria. This "dead-burned magnesite" was thereby rendered unreactive and was not liable to hydration or shrinkage in service.

MgO development was boosted by the production in the 1930's of synthetic magnesia from the hydroxide remaining after the solar evaporation of seawater. Soon after that, simultaneous extraction of magnesia from seawater and dolomite ($MgCO_3.CaCo_3$) opened up tonnage supplies of MgO for basic brick making.

Although the natural mineral is still a major source of raw material, seawater magnesia is now used for the production of most basic bricks. Dead-burning is required for either natural or seawater magnesia, prior to brick manufacture, but the calcined product from seawater cannot qualify

for the term "dead-burned magnesite", since the magnesia never existed as magnesite (MgO_3) at any stage in its production.

Dolomite

Dolomite was recognised as a refractory material about the same time as magnesite when Bessemer conversion went basic, to assist phosphorous removal from pit iron. Fired dolomite bricks, however, only made their appearance shortly before the Second World War. Development has been less rapid due to hydration and the dicalcium silicate inversion which takes place over a period. Semi-stable bricks are now manufactured, having their grains coated with glassy phase or pitch to prevent hydration; stabilised bricks contain additives to convert lime to inactive silicate or to prevent dicalcium silicate inversions.

The high alumino-silicates, usually referred to as high alumina products, range upwards from 45% alumina and were first produced from sillimanite-kyanite-andalusite type minerals and bauxite around the 1920's. The short-lived naturally-occurring mullite, synthetic mullite, corundum (usually fairly impure in nature); tabular and fused alumina came much later and bring us up to date on alumina-containing refractory materials.

In recent years, silicon carbide, silicon nitride, zircon, zirconia and ceramic fibres have increased the list of materials and products available to the Refractories Engineer.

MELTING POINT OF OXIDES AND MINERALS

Table 1 shows the approximate melting point of some pure oxides and materials used in the production of refractories.

TABLE 1

Name	Symbol	Melting Point (°C)
Alumina	Al_2O_3	2 050
Silica	SiO_2	1 720
Magnesia	MgO	2 800
Chromia	Cr_2O_3	2 200
Zircon	$ZrSiO_4$	2 550
Zirconia	ZrO_2	2 700
Silicon Carbide	SiC	3 400
Carbon	C	3 700

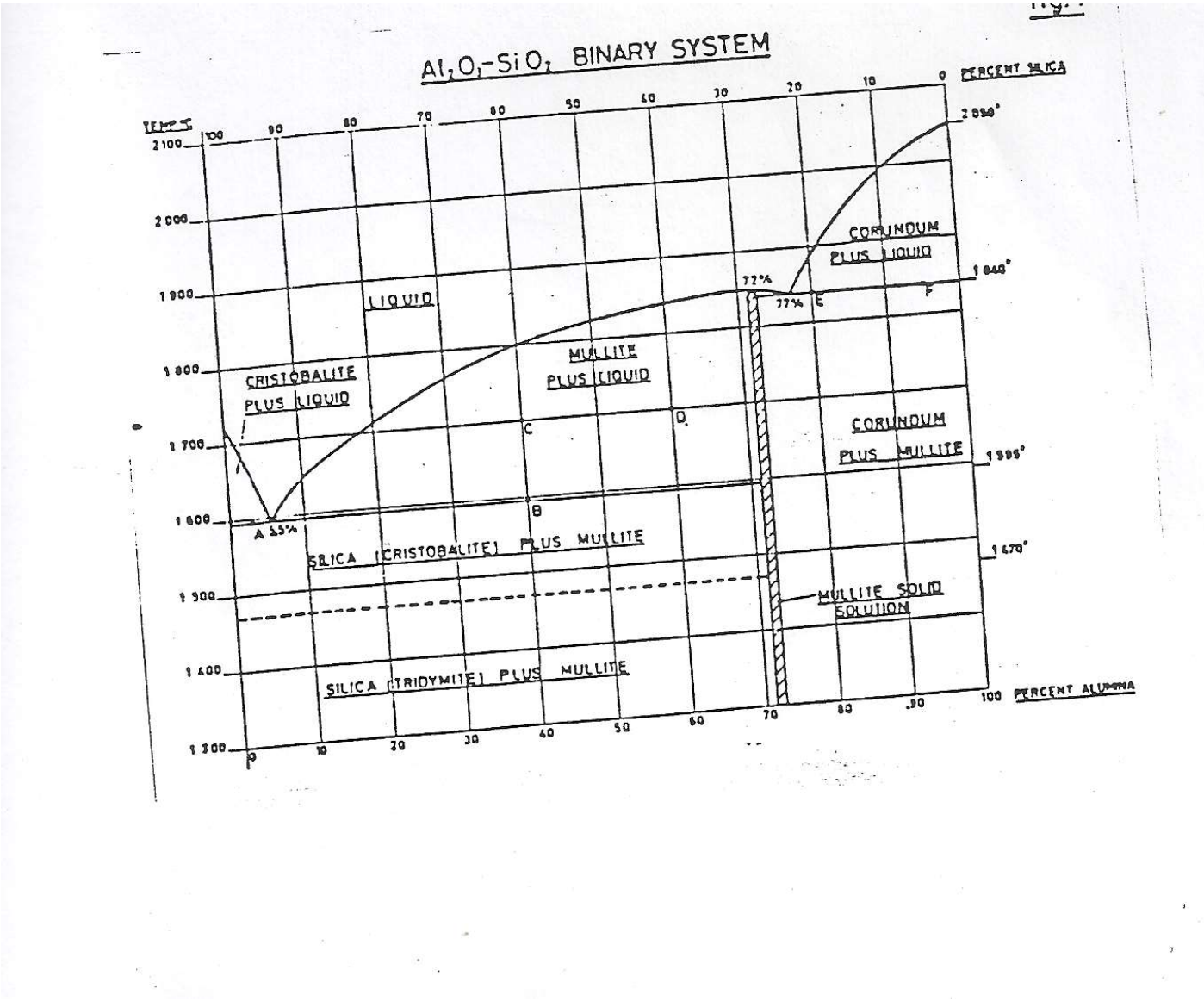
TABLE 2		
Name	Symbol	Melting Point (°C)
Andalusite	$Al_2O_3.SiO_2$	1 850 *
Bauxite	$Al_2O_3.2H_2O$	–
Corundum	Al_2O_3	2 050
Cristobalite	SiO_2	1 720
Diaspore	$Al_2O_3.H_2O$	–
Gibbsite	$Al_2O_3.3H_2O$	–
Kaolinite	$Al_2O_3.SiO_2.2H_2O$	–
Kyanite	$Al_2O_3.SiO_2$	1 850*
Mullite	$3Al_2O_3.2SiO_2$	1 850*
Sillimanite	$Al_2O_3.SiO_2$	1 850*
• Andalusite begins to dissociate into 88% mullite and 12% free silica at 1350°C. kyanite at 1325° and sillimanite at 1530°C		

Table 2 shows the composition and approximate melting points of some of the minerals involved in the alumino-silicate system when alumina and silica react either naturally or after heating.

It may appear from table 2 that all refractory compositions of silica and alumina will have melting points occurring between 1720°C and 2050°C. However, this is not the case for two reasons:

a) The presence of impurities, inevitable in all commercially-viable refractories employing natural raw materials, lowers the melting point from that of the pure combination of alumina and silica.
b) More fundamental still, the phase diagram describing most binary metal or mineral systems exhibits a minimum melting point temperature, for a certain ("eutectic") composition, below that of either its primary constituents.

Fig. 1 depicts the binary system describing the alumina-silica system and it can readily be seen that the 1720°C melting point of pure silica is lowered by additions of alumina to 1595°C when the "eutectic composition" (5,5% Al_2O_3; 94,5% SiO_2) is reached. Further alumina additions raise the melting point back to that of silica when 25% of alumina is present and thereafter almost steadily up to 2050°C, the melting point of pure alumina or corundum.



MULLITE

Perhaps the most significant feature of the alumina- silica phase diagram, in relation to today's refractories, is that mullite, with the composition 3 $Al_2O_3.2SiO_2$ is in equilibrium with silica up to the eutectic temperature of 1595°C. Mullite, therefore, containing about 72% alumina, is not only present in a 72% alumina brick- it is also present in fireclay refractories and has a specific melting point around 1850°C. Mullite is the only stable compound formed between silica and alumina.

Phase diagrams of this nature are extremely useful in predicting the behavior of refractories at elevated temperature. However it must be emphasized that phase diagrams apply strictly to completely pure materials and to conditions of complete equilibrium. In practice, the first is

never met by commercial refractory materials and the second is seldom met by normal furnace operating conditions. Also, phase diagrams cannot predict rates of reaction or viscosity of liquid phases present. Nor, for example, can the diagram shown in fig.1 be precisely applied when conditions are favourable for the volatilization of silica, such as the presence of reducing atmospheres or temperature above 1800°C.

However, let us consider the strict application of the alumina-silica phase diagram to the amount of liquid present in a few refractory compositions at elevated temperature.

3% Al_2O_3 (siliceous) (point A)

Liquid or bond melt will start to appear at 1595°C, at which temperature there will be 3÷5,5 = liquid. The brick will thus fail early due to glass formation, although it must be stressed that silica brick resists deformation better than a fireclay brick with the same liquid content, due to the higher viscosity of its liquid. The liquid, incidentally, contains all of the alumina, together with excess silica remaining in the solid form as cristobalite.

40%Al_2O_3 (fireclay) (points B and C)

From a mixture of cristobalite and mullite, liquid formation also starts at 1595°C, the amount formed being (72 – 40) ÷ (72 – 5, 5) = 48% by mass. At the higher temperature of 1700°C (point C) the liquid content is (72 – 40) ÷ (72 – 18) = 59%, since the point at which the liquidus curve is at 1700°C represents 18% alumina. All unmelted solid will have the mullite composition, more mullite being taken into solution as the temperature rises. The temperature of complete melting is about 1800°C.

60% Al_2O_3 (point D)

At a temperature of 1700°C the amount of liquid will be (72 – 60) ÷ (72 – 18) = 22%. The temperature of melting is almost constant from 60% to almost 80% alumina.

72% Al_2O_3 (mullite)

No liquid forms until about 1850°C at which temperature mullite melts completely. Due to the eutectic between mullite and corundum, at 77% alumina, all compositions above 72% show liquid formulation starting at 1840°C, at which temperature an 80% alumina brick will be (100- 80) – (100 – 77) = 87% melted (point E) whereas 95% alumina brick would be only 22% liquid (point F).

If the glassy liquid formed is highly viscous, high temperature deformation is resisted to a greater degree. Unfortunately, viscosity falls with increasing alumina content. Silica brick glass is thus highly

viscous, does not run so easily and prevents further attack to a marked degree. It has been mentioned that few alumino-silicate refractories behave as equilibrium products – the presence of free quartz even after firing and of impurities such as the oxides of iron, titania and the alkalies prevents this. Thus table 3 shows the liquid present in various alumino-silicate refractories at various temperatures taken theoretically from the diagram. In practice, it has been found that impurities have the effect of lowering these temperatures by as much as 200°C.

Table 3
Liquid content of acid Refractories

Brick % Al_2O_3	Theoretical temperature (°C) 1595	1700	1850	1900
Silica	55			100
3	100			100
Fireclay	48			59
40	100			100
Andalusite	18			22
60	100			100
Mullite	Nil			Nil
72	99			100
Bauxite	Nil			Nil
85	65			79
Corundum	Nil			Nil
90	22			53

CLASSIFICATION OF REFRACTORIES

Since the above discussion on melting points and liquids formation has already broached the subject of siliceous, fireclay and high alumina bricks, it is appropriate to consider the conventional classification for refractory products. Although various systems have been proposed and are, indeed, in use throughout the world, it is conventional here to group the products into acid, basic and the so-called exotic grades. A disadvantage is that chemically, high alumina and chrome bricks are essentially neutral, although they fall into acid and basic categories respectively. Although the categories now to be considered mainly describe the brick product, each also includes monolithic or speciality products made from the same raw materials – in many cases from the appropriate recycled brick. Thus there are siliceous, fireclay, high alumina and basic castables, mouldables, gunning mixes and mortars.

ACID Refractories

I. Siliceous

Quartzites, ganisters and sand are used to make silica bricks, sandclay ladle bricks and semi-silica bricks. The latter incorporate fireclay with a high amount of free silica, having high resistance to thermal shock, deformation under high temperature loading and chemical fumes. Sandclay bricks are unfired and exhibit surface melting in the steel ladle form a continuous and highly viscous liquid skin which inhibits further attack of the brick by molten metal and slag. Silica bricks withstand considerable load right up to the melting temperature, have good resistance to acidic attack and thermal shock so long as they cycled slowly through the large volume-change quartz inversion at above 613°C.

II. Fireclay

The raw material fireclay consists of hydrated alumino-silicates and often free silica. They are plastic when finely crushed and wet and become rigid when subsequently dried.

The amount and nature of impurities present, including free quartz, determines their refractoriness at high temperature (refer to the earlier discussion on liquid formation).

Thus normal duty, high duty and superduty bricks contain progressively lower amounts of free quartz and fluxing impurities. Pure kaolinite or china clay is now rare and South Africa is fortunate in having quarry deposits suited to superduty fireclay brick production. This material is called "flint clay". It is usually calcined at about 1400°C, where it reaches its highest density, and then it is called "chamotte". Chamotte contains 46% alumina and hence a 43% alumina fireclay brick must contain 94% of the pure kaolinite mineral. Degradation of fireclays is due principally the presence of free quartz, although there may be as much as 3% Fe_2O_3 in low quality fireclay bricks, the main cause of the yellow coloration on firing. CaO, MgO, Na_2O and K_2O are also present, causing melt formation at temperatures below the 1595°C eutectic.

Fireclay bricks exhibit relatively small thermal expansion and a fair insulation. They are not readily attacked in highly acidic environments, but fail rapidly when exposed to high temperatures basic slags.

III. High alumina bricks

Based normally on the andalusite-kyanite-sillimanite A-K-S group of minerals and/or on bauxite, the bricks ranging from 45% to 85% alumina are now augmented by those incorporating synthetic mullite, sintered and fused alumina, the latter being capable of producing a brick with over 99%

alumina. The A-K-S groups each contain 63% alumina in the pure state. Bauxite is a clay-type mineral consisting of hydrated alumina together with silica and iron oxide, calcined to an alumina content of some 90%. Bauxite may be used to enrich kaolinite, the A-K-S group of minerals, or in its own right to produce bricks with up to 85% alumina.

Whilst clay is frequently added to bond the lower range of high alumina bricks, alumina sulphate or phosphoric acid may be used in the higher grades. Firing temperatures are gauged so as to develop sufficient flux bonding and to produce volume stable bricks.

This latter factor is important, since the decomposition of the A-K-S minerals into mullite and cristobalite is expansile, much more so for kyanite than for the other two minerals. Hence although andalusite and sillimanite can be used for brick making directly, Kyanite is first calcined to effect the conversion before brickmaking. Raw kyanite may be added to aluminosilicate products to combat shrinkage. It is obviously important that as much mullite formation as possible has taken place before placing the bricks into high temperature service.

The refractoriness of these high alumina bricks increases with alumina content, but they are all suitable for use above 1650°C, highly resistant to chemical attack and deformation under load. Thermal expansion is lower than fireclays, but heating-up schedules should be monitored due to their generally lower shock resistance.

The extra high alumina bricks above 85% alumina, use fused or sintered aluminas usually with non-clay binders. They are characterized by even greater refractoriness up to 1850°C and higher, chemical stability, and ability to withstand attack by basic materials such as lime.

BASIC REFRACTORIES

Basic Refractories are compositions of dead burned doloma, dead-burned magnesia, chrome ore or compatible mixtures of magnesia-doloma or magnesia chrome. Impurities of silica, iron oxide, alumina and others lead to the formation of eutectic alloys with greatly reduced refractoriness and hence the properties of basic bricks are governed largely by the phases formed by these adulterating constituents. As with all refractories, exceptionally high purities can be obtained but only at corresponding high cost.

Magnesite

During the calcination of magnesite to form magnesia (MgO), or periclase, dissociation begins around 800°C but the material is still reactive and will swell by hydration on pickup of moisture, the amount depending upon the calcinations temperature. Non-reactivity is reduced by dead-burning or, even better, by fusion.

Addition of borax also assists in deadening reactivity. The temperature of dead-burning, normally done in rotary kilns, varies from 1550 to 1850°C, depending on the purity. The thermal reaction $MgCO_3$ -> MgO + CO_2, incidentally, is accompanied by a 52% loss in mass. One ton of sea-water magnesia requires the treatment of three hundred tons of seawater. CaO, SiO_2, Fe_2O_3, Al_2O_3 and B_2O_3 impurities in dead-burned magnesia can vary widely obviously then, so can the MgO content. The effect of some of the phases thus formed on the 2800°C melting point of pure magnesia can be seen from Table IV. The lime: silica ratio is an important factor in determining which phases will form.

TABLE IV.

Constituents	Composition	CaO:SiO_2 ratio	Approximate melting point (°C)
Forsterite	$2MgO.SiO_2$	0-0,5	1900
Monticellite	$CaO.MgO.SiO_2$	0,5 -1,0	1500
Merwinite	$3CaO.MgO.SiO_2$	1,0-1,5	1600
Dicalcium silicate	$2CaO.SiO_2$	1.5-2,0	2130
Tricalcium silicate	$3CaO.SiO_2$	>2,0	2000

Hence the properties of a magnesite brick, particularly its hot strength, are determined largely by the properties of the less refractory constituents formed by impurities. In extreme cases, for instance if the lime is not fully taken up with silica, it is possible for a lime-alumina-iron oxide reaction to form the disastrous brownmillerite, which starts melting at under 1400°C.

Obviously, then, all these considerations cannot be depicted on a binary diagram, as was done with the essentially less impure Al_2O_3 - SiO_2 system. Even a ternary diagram, complicated as it is, cannot fully describe the effects of four, five or more major constituents upon the onset of melting of the phases thus formed. Figure 2 attempts to show the effect of the third constituent on the melting curves of the binary diagrams describing the MgO –SiO_2, CaO – SiO_2, MgO- CaO systems. Although the overall brick composition may show only 2, 5% CaO and 1, 0% SiO2, the relevance is in the formation of admittedly small quantities of secondary phases, usually bonds, into which all the impurities are concentrated. The composition and distribution of these ultimately determines the refractoriness of the brick. A periclase brick with 3% CaO or one with 3% SiO2 will both be better than one with 1% each of CaO and SiO2.

Consideration of this type of diagram tells us much about the ultimate serviceability of basic refractories: forsterite bricks, for instance, can be seen to have high refractoriness, with a melting point close to 1900°C.

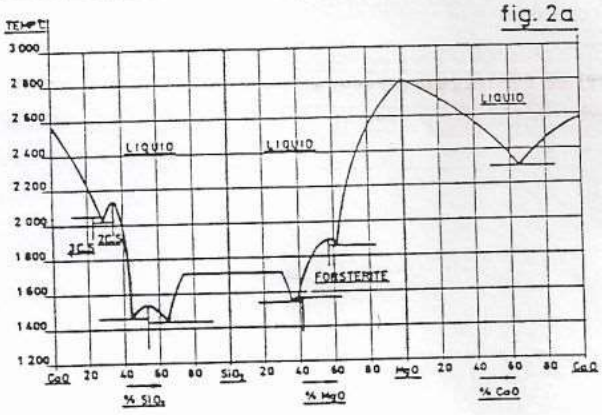
Unfortunately forsterite has a much lower slag resistance than periclase bricks, particularly above 1650°C, and tend to crumble after repeated thermal cycling; Refractories with dicalcium silicates can be seen to be much more refractory than those containing monticellite; low melting point cordierite phases in the $MgO-Al_2O_3$ system explain the inadvisability of having fireclay bricks in contact with magnesite at steelmaking temperatures, although materials made to such compositions are of interest as pottery-firing saggars, due to their very low thermal expansion and high shock resistance.

The slag resistance of magnesite bricks can be further increased after firing by tar/pitch – impregnation, which facilitates the retention of carbon inside the bricks after initial commissioning in the furnace.

Whilst thermal shock resistance of magnesite bricks is poor, it can be improved by the practice of metal encasing the brick.

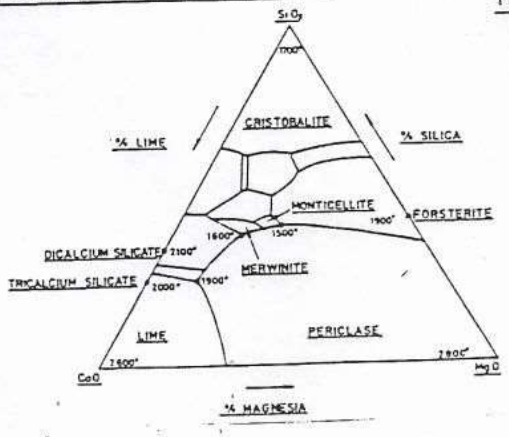
THE LIQUIDUS CURVES OF THE CaO/SiO_2, SiO_2/MgO AND MgO/CaO BINARY PHASE DIAGRAMS

fig. 2a



THE LIQUIDUS SURFACES OF THE MgO-CaO-SiO_2 TERNARY PHASE DIAGRAM

fig. 2b



Magnesia –chrome and chrome-magnesia

Chromite added to magnesia provides a range of mag-chrome and chrome-mag bricks with improved thermal shock resistance and resistance to slags. The 70MgO: 30Cr_2O_3 composition probably has the best combination of the properties of basic refractories, although pure magnesite has better alkali resistance. Normally, large magnesia grains and smaller chromite grains are used, once again with a glassy bonding phase. Impurities are now almost inevitable, due to the composition of the chrome ore used.

Transvaal chrome ore, for instance, contains only 48% Cr_2O_3, the balance being Fe_2O_3, Al_2O_3 and MgO, with SiO2 being a particularly deleterious impurity for many applications.

Since the refractoriness of basic bricks is determined by the impurities forming networks throughout the brick's structure, highest quality bricks nowadays adopt one of several approaches: the bonding network can be produced to a chemistry compatible with the charge being borne by the vessel (e.g. dicalcium silicate – bonded bricks for cement kiln hot zones; the impurities can be kept to absolute minimum to inhibit penetration into grain boundaries (necessarily increasing the cost of the raw materials); in conjunction with control of raw material purity, firing techniques can be used which promote "pocketisation" of the impurities rather than continuous networks – the so –called direct –bonded brick, in which periclase and chromite grains are directly bonded together without the presence of intervening networks. At high temperature the chromia goes into solid solution with the magnesia. On cooling, the chromia migrates out again and forms picrochromite which creates bridges between the magnesia grains. These bridges keep the structure solid, preventing the silicate molten phase between the grains from allowing the brick to deform. At the other ends of the scale, a 70Cr_2O_3: 30MgO chrome-magnesia brick also has excellent thermal shock resistance, finer magnesia particles now surrounding larger chromite grains. In general, such bricks tend to rely on the low melting silicates for bond between the chrome and magnesia.

The lower amounts of glassy phase and its encapsulating into discrete pockets makes the direct-bonded brick more able to withstand loads at high temperature and chemical attack of aggressive slags and mattes, as for instance in the converters used in the copper and nickel industries. The melting of the glassy phase does not deplete the brick of its bonding mechanism.

Mechanically or tar-bonded basic bricks are also available, the volatiles having been driven off in service and degree of ceramic bonding necessary for the application being formed by the temperature of the vessel. These allow more "give" in the brick and lower tendency to spall in service. Steel plates are often fixed to both burned and chemically bonded basic

bricks, oxidising in service and reacting with the bricks on either side to give almost monolithic surfaces. This inhibits "peeling off" of the brick surface should cracks form behind the hot face for thermo-mechanical, or chemical diffusion reasons. Thermal expansion of the brick can also be accommodated by providing for this within the steel-casing.

Summarizing basic brick attributes, magnesia is most resistant to iron oxide attack, has the highest refractoriness, thermal expansion and thermal conductivity but is subject to thermal spalling; magnesia- chrome bricks have lower cost, thermal expansion and thermal conductivity, good resistance to load, volume-stability and higher spalling resistance; chrome – magnesia bricks have even better volume –stability and resistance to spalling.

EXOTICS

I. SILICON CARBIDE

Silicon carbide is produced by passing an enormous electrical current through a pile of sand and carbon mixture. Silicon carbide is extremely hard, 9 0n the Moh scale. Bricks can be clay-bonded, direct-bonded, reaction bonded, nitride bonded, sialon bonded or other types. They are characterized by very high thermal conductivity, abrasion resistance, volume-stability, excellent hot strength and chemical resistance. Various other carbides, nitrides and borides have been developed for specific purposes. They are not used extensively due to their high cost, but posses some interesting properties. Silicon nitride, for instance, has excellent shock resistance and maintains its strength well up to 1400°C. Nitrogen passed over silicon powder at 1100°C produces a nitride compact which is easily machinable. Further nitrogen reaction at 1200°C then gives a dense, hard, non-shrinking product of up to 400Mpa strength, which resists the action of molten aluminium, lead, tin and magnesium better than any other conventional refractory.

II. ZIRCON

Zircon is a mineral found in granite and is mined together with titanium minerals in heavy sand deposits. It is separated from the other heavy sands by virtue of its extreme electrical insulation. Zirconium silicate containing about 65% ZrO_2 and 35% SiO_2 is manufactured into bricks and nozzles having a high softening point, volume –stability and good resistance to thermal shock and high temperature loads. It has very high resistance to attack by alkalis and other fluxes. This makes it suitable in gold smelting vessels. Although the melting point of zircon is over 2500°C, it dissociates into zirconia (ZrO_2) and cristobalite above 1700°C. In addition to zircon's use in bricks, the mineral may be added to fireclay bricks to improve their resistance to slag attack, for instance

in steel-casting ladle bricks. Zirconia, on the other hand, can be solid up to 2300°C but has a drastic volume change at 1000°C unless stabilized with lime, when it has excellent thermal shock resistance, is extremely strong and resists abrasion, chemical and molten metal attack.

III. CARBON

Carbon may be used when inert or reducing atmospheres are present, up to 3000°C. Many carbonaceous refractories are made from natural or synthetic graphite, coke and bonds of either clay or pitch. Thermal expansions are low and thermal conductivity high to very high, as required. They have a high resistance to thermal shock, good hot strength, are impervious to molten metal and slag and inert to most chemicals. They are largely non wetting to molten metals. Their main disadvantage is that they are oxidized at high temperature by air, water and carbon dioxide.

IV. FUSED GRAIN AND FUSION CASTINGS

Silica, alumina, mullite, magnesia, magnesia-chrome and zircon can all be electrically fused to produce grain which is subsequently used for brick-making. The product is extremely dense, strong and volume-stable and is less resistant to thermal shock. Similar remarks apply to fusion-casting blocks obtained by solidifying the electrically-fused product directly into brick and block shapes, when densities approach those of the mineral from which they were shaped. The magnesia-chrome fusion casting used in electric arc furnaces sidewalls are one example –they have higher abrasion and slag resistance than sintered products, but thermal shock resistance is poor and they are frequently cracked on delivery. Although porosities are virtually nil, the blocks do contain large casting blowholes, as do the zircon-alumina blocks used in glass furnaces, essentially composed of interlocking crystals of zirconia and corundum, with a glassy silicate binding phase.

V. CERAMIC FIBRES

Kaolin is melted in an arc furnace and poured onto a rapidly spinning roller or through a high velocity gas stream, giving "spun" or "blown" fibre. The fibres are collected on a bed and needle felted into a blanket. In most furnaces, the blanket is folded into modules, to overcome shrinkage problems. Other products made from ceramic fibres are fibre paper, yarn, rope, textiles, mastics and plasters. Rigid fibre boards are manufactured by vacuum forming. Kaolin, alumina, silica and zirconia fibres have been produced, capable of withstanding temperatures as high as 2500°C ZrO_2) although the usual aluminosilicate products are limited to 1260°C. Similar techniques can be used to form alumina and zircon into small, hard hollow spheres or bubbles for the production of high temperature insulating bricks and castables.

REFRACTORY CONSUMPTION BY INDUSTRY

The refractories industry worldwide has a somewhat different structure to our own, in that many producers specialize in refractories for a particular industry; glass, aluminium, copper, power generation, cement kilns, certain sectors of the steel industry etc. Similarly, the industrial split varies from country to country. In America, for instance, the iron and steel industry accounts for 47% of refractory production, with the remainder being split as follows:

	USA (%)	SA (Steel = 71%) (%)
Non-ferrous metals	5	3
Glass	6	1
Ceramic	8	
Minerals processing	4	2
Chemical/petrochemicals	3	1
Public utilizes	1	2
Contractors	7	4
Export	6	15
Other	2	
Not specified by industry	11	

In South Africa, the major difference to this supply pattern are that 70% of refractories produced are used by the iron and steel industry (including ferro-alloys, some 15% are exported and apart from non-ferrous users(3%) and contractors (4%), the other categories account for only 1 or 2% each. It should be remembered that many of these users also import refractories, either because the sophisticated grades needed are not produced locally or because they will not alter their traditional supply pattern. Today imports from China and India make up at lot of our consumption.

DEVELOPMENT TRENDS

Raw materials

Over time there has been a shift from natural minerals to higher purity synthetic minerals. Most of the refractory changes in blast furnaces, basic oxygen steelmaking, electric arc furnaces, ladles, continuous casting, ingot casting, secondary steelmaking etc. have revolved around the development and processing of basic and high alumina raw materials.

The boron (B_2O_3) content of seawater magnesia (SWM), can markedly affect the hot strength of magnesia bricks, if present above 0, 2% in the grains. The best (and most expensive) magnesia grades contain only one tenth of this amount. Record BOF lining lives have been achieved using linings of

low boron seawater magnesia. Co-burned clinkers of magnesia, chrome and dolomite compositions are now prepared for the hard wear areas of almost all basic linings.

The expansion and development of high alumina products has been even more prolific. Far Eastern Bauxite is now able to compete with the traditional Guyanese source, to provide a low iron calcine suitable for use in bricks and monolithics containing 60-85% alumina. Our own andalusite is being used more and more worldwide, both as a raw material and as exported finished products, for stove checkers, torpedo and steel casting ladles, carbon-baking furnaces and other applications where 50-60% alumina products are required together with high creep resistance or slag, wear and alkali resistance.

Blast furnaces

With blast furnaces sizes, temperatures and production rates rising, there has been an upward trend in the requirements for hot blast stove checkers. Superduty fireclay has had to give way in the higher sections, to high alumina and silica, the former often being upon high purity andalusite, to restrict deformation by creep to a minimum. This is obviously an important property in the huge higher temperature stoves now being used. The design of these has also had to change to reduce complex structural movements caused by temperatures gradients, especially in the wall diving the checker and combustion chambers. Ceramic fibre expansion joints and the careful use of insulation are also used to minimize thermal movement effects. Similarly, the furnace itself has had to undergo radical changes in lining materials: at one time, superduty fireclay linings were inevitably specified for the hearth, bosh, belly and the stack areas.

An advantage of South African fireclays was that blast furnace bricks could be produced containing 43-44% alumina, less than 1% Fe2O3 and, with best practice 8 or 10% apparent porosity. This is not the case throughout the world and the latest furnaces have thus been designed around 60- 90% alumina, silicon carbide and carbon for the more severely operated areas. Water and air cooling of carbon hearths and walls is now common practice. Concentration of alkalies, from both the charges now used and the oxidation-reduction cycles within the furnace, have dictated changes in the lower stack and bosh. Extra high to withstand such alkali attack sufficiently, even then often requiring external water cooling systems to keep lining wear within acceptable limits.

Silicon carbide is also incorporated in the newer high alumina iron runner ramming materials improving materials, improving the iron tonnage formerly achieved with conventional mixes.

Torpedo Ladles.

Lining these units for long campaigns has become a problematical area, with higher production blast furnaces, large new BOF shops and the practice of ladle desulphurisation. Long distance transport of up 300tons of swaying molten iron, soda ash corrosion of the bricks during desulphurization and very long holding times without skull protection all dictate a change from the conventional fireclay brick lining. Volume-stability and resistance to erosion, slag attack and carbon monoxide are all important. Whilst dolomite or basic linings have been tried, blast furnace technology and torpedo ladle slag compositions are now countered economically by lining the ladle with high alumina bricks. Even here however, it would, be wrong to think "the higher the alumina, the better". Slag attack can seriously penetrate the matrix and grain boundaries of an 80% Al_2O_3 bauxite brick, giving a deep softened zone and high erosion during transport. A 55%Al2O3 andalusite brick, however, softens on the working face, rapidly sealing the internal structure and showing less slag penetration.

Hot Metal Mixers.

Before hot metal is introduced into the BOF, mixes are frequently used to contain the iron. Once again size, temperature, throughput and the rotating action bring their own peculiar problems to the basic linings normally used and special qualities of magnesite bricks have been developed to counter these effects. High alumina special shapes are also used to reduce the effects of reversible thermal expansion on the integrity of the lining.

Hot metal availability to the steelshop has been increased even further by the development of induction furnaces similar in appearance to the larger hot metal mixers. These units are capable of rapidly super-heating the molten by means of multiple channel type induction heaters: over 300tons per hour can be super heated by 200°C, bringing obvious scrap consumption benefits. High heating demand highly efficient thin wall channels and magnesia castables have the best erosion resistance. Barrels use high alumina bricks and a reducing atmosphere internally contributes towards longer refractory life.

BOF Units

Whilst the introduction of the Basic Oxygen Furnace drastically reduced the consumption of refractories previously used by open hearth furnaces, the quality of the dolomite or the magnesia brick used has had to be improved tremendously –the cost of refractories per ton of steel produced has changed far less than the volume of refractories used. Whilst magnesia bricks are used exclusively in South Africa, many other parts of the world use dolomite bricks, also tar-impregnated or tar-bonded. This is partly because the dolomite availability and the technology are long-

established. Higher operating demands are changing this picture, as overseas operators are turning at least to magnesia- enriched dolomite produced in the form of co-burnt clinkers, or to magnesia itself. Zoning of linings, both as to quality and thickness is also receiving much attention. The development of basic gunning mixes is following a similar pattern and is partly responsible for some of the lining lives now achieved in Japanese vessels.

Arc Furnaces

Several water-cooled lining systems have been devised for both sidewalls and roofs, in an effort to reduce operating costs, increase furnace availability and make the operation more energy-efficient. Tubes or panels in the upper sidewalls and outer roof portions are replacing the great majority of refractories normally used. To complement thermal efficiency and thereby keep pace with the higher throughputs, new generation refractories are essential for the furnace portions still requiring linings. Direct bonded co-clinkered chrome–magnesia bricks and resin-bonded high magnesia–carbon bricks are now used to increase wear resistance, reduce slag penetration and transfer heat more efficiently.

Roof performance is suffering from limitations imposed by alumina refractories, even highly sophisticated 85% Al2O3 types and basic bricks are being more and more considered. Due to their mass and the tendency for all basic domes to buckle out of shape with temperature changes, suspended hold-up/hold-down systems have been tried, using direct-bonded chrome-magnesia bricks and basic ramming for the centre portions. Interest is also being shown in checker-patterned or balanced linings to study the probable benefits of alternating high strength brick sections with high yield brick sections, thus combining adequate hot strength with an ability to yield prior to fracture, as these properties cannot be optimized in a single brick.

Pouring

Ladle linings, tundishes, nozzles, sliding gate valves metal stream protection and runner systems have all received much attention both as the design and quality of refractories. Pre-formed and monolithic refractories have undergone drastic changes in all fields; higher alumina qualities are now generally used, frequently enriched with zircon. Furthermore, wholly-zircon linings have been used for ladles in some countries. Low cement or even cement-free castables have been developed to increase the refractories and ease of placement of aggregate mixes used in tundishes. Sliding gate systems abound in both continuous casting and ingot- pouring shops; zirconia nozzle inserts are used in some shops to replace the former zircon nozzles. All these advanced technology refractory developments have been aimed at allowing faster and cleaner steel-pouring in grades ranging from low carbon to highly alloyed steels.

SECONDARY STEELMAKING

The development of secondary steelmaking processes in the 70's also required improvements in the range of acid and basic refractories available and zoning of refractories is normally used to even out wear and make the operation as economical as possible. AOD vessels, for instance, use dolomite, magnesia bricks variously in normal, high wear and tuyere area combinations. This paper has not included refractories for coke ovens, open hearth and induction furnaces, or the various kinds of reheating units used in steel fabrication. With the exception of open hearth furnaces, refractory developments are continuing in all of these fields. Although by-products coke oven installations are likely to dwindle with the suppliers of good coking coals, few initial changes are foreseen in the use of conventional silica and fireclay brick construction. Oven doors are now being lined with fused silica and calcium aluminate-bonded monolithic for resistance to thermal shock and lower thermal expansion and conductivity. Induction furnace linings are becoming more sophisticated, with chrome-alumina mixes, expanding spinel mixes, phosphate binders and many new patching materials. Reheat furnaces, from soaking pits to walking beams, utilize ceramic fibres, fusion-cast blocks and high→intermediate strength monolithics.

INSULATION

No thumb-nail sketch of recent refractory developments would be complete without reference to the effect of insulation on energy-saving measures. Whilst bricks and castable insulation have been improved somewhat, the greatest strides have been made with ceramic fibres. Although expensive, ceramic fibre insulation is becoming more economic as oil prices increase.

Fixing methods, maximum operating temperatures and resistance to gas have all received attention. Longer fibres in both medium and high alumina qualities have been developed. Vacuum-formed fibre boxes containing bulk fibre can now be built in almost like bricks. Easily shaped fibre veneer systems and improved fixing cements are now available for initial installation or refurbishment of a furnace.

Whilst the standard fibre grades available will now withstand up 1600°C (95% Al2O3), with a thermal conductivity of 20% that of a superduty fireclay brick, the industry has yet to be introduced, as it surely will be, to the even more sophisticated zircon and zirconia fibres.

Author John Carroll

Chapter 2

Properties of refractory materials and test methods

A number of laboratory tests have been developed to evaluate the quality of refractory bricks and as most of these tests have been standardized, the test results obtained quite often refractory made by different manufactures. These tests furthermore provide a powerful tool for controlling the quality, both in process and that of the final product.

It must be remembered, however that these tests are of comparative value only as they are not designed to simulate the destructive value conditions which usually prevail in many industrial processes. The final proof of the quality is given by the performance of the refractory under working conditions.

The usual standard tests used to evaluate the quality of refractories are:

1. Chemical analysis
2. Porosity, bulk density and relative density
3. Permeability to air
4. Cold crushing strength (CCS)
5. Modulus of rupture (MOR)
6. Thermal shock resistance (TSR)
7. Permanent linear change on reheat (PLC)
8. Pyrometric cone equivalent (PCE)
9. Refractoriness under load (RUL)
10. Resistance to creep under load at high temperature
11. Linear thermal expansion (LTR) Reversible)
12. Thermal conductivity (TC)
13. Slag attack – pot –slag/rotary slag testing
14. Abrasion resistance
15. CO disintegration

Other tests which are performed on green bricks and speciality products are:

16. Screen analysis and moisture content
17. Grab time
18. Pressing factor(PF)

1. CHEMICAL PROPERTIES

Chemical composition serves as a basis for classification of Refractories, and as a guide to their chemical properties and melting behavior.

An important application of chemical analysis is in the control of both the raw materials and the finished products.

Minor components, once thought unimportant now recognized as controlling factors in the performance of many refractories.

Some of the important considerations are the Al_2O_3 and Fe_2O_3 content of clays, the alkali content in clay and the SiO_2 and CaO levels in magnesia.

The chemical composition of a refractory may not be the most important of its commercial utility, as bricks of almost identical compositions may differ widely in their behavior under the same furnace conditions.

Chemical analysis alone of a refractory does not permit evaluation of such properties as its volume-stability at high temperatures, or its ability to withstand pressure, slagging or spalling.

POROSITY, BULK DENSITY AND RELATIVE DENSITY

Definitions

Open pores: pores from which air is readily removed by evacuation

Closed pores: pores completely surrounded by impervious solid matter. The air in these pores cannot be extracted by evacuation.

Bulk volume: the volume of solid material (solid volume), plus the volume of open and sealed pores volume calculated from linear measurements represents bulk volume.

Apparent porosity: the ratio of open pores to the bulk volume expressed as a percentage

Closed porosity: the ratio of closed pores to the bulk volume expressed as a percentage

True porosity: (total porosity) is the ratio of open plus closed pores (total volume of all pores) to the bulk volume expresses as a percentage.

From the definition of bulk volume it can be seen that:

Bulk volume = solid + open pores + closed pores

= apparent solid volume + open pores

Since in the field of refractories we deal with three different volumes, namely bulk volume, apparent solid volume and solid volume we may obtain:

Bulk density: the ratio of the mass of the material to its bulk volume

$$BD = \frac{mass}{\text{bulk volume}}$$

Apparent relative density: the ratio of the mass of the material to its apparent solid volume

$$Apparent\ relative\ density\ = \frac{\text{mass}}{\text{apparent solid volume}}$$

True relative density: the ratio of the mass of the material and its solid volume

$True\ relative\ density = \frac{\text{mass}}{\text{solid volume}}$As bulk volume > apparent solid volume > solid volume it follows that

Bulk density<Apparent relative density < True relative density

By now it will have been noted that everything would have been relatively simple had it not for the presence of closed pores in Refractories.

It will be that clear that if the amounts of closed pores are nil, the apparent relative density and true relative density are equal.

If the amount of open pores are also nil, then the apparent relative density equals both the true relative density and the bulk density.

DETERMINATIONS

The test method can be briefly summarized as follows:

A test piece taken from the brick and weighed after drying (dry mass = D). The test piece is then placed in vacuum desiccators and evacuated for a specified time. Water is then allowed to flow into the desiccators to completely cover the test piece.

By means of a special scale the test piece is weighed while suspended in water (immersed mass = I). The test piece is now dabbed with a moist cloth to remove excess water adhering to the surface and weighed immediately (soaked mass = S).

From these three weighing the following can be calculated:

Apparent porosity $AP = \frac{\text{S} - \text{D}}{\text{S} - \text{I}}$ x 100%

Bulk Density $BD = \frac{D}{S-I}\ (g/cm^3)$

Apparent relative density $BD = \frac{D}{S-I}\ (g/cm^3)$

It is left to the reader to prove these simple formulae, since it will be realized that:

S – D represents the water in the pores

S – I represent the bulk volume of the test piece

D – I represent the apparent solid volume of the test piece

It will be realized that the three properties for a given test specimen must be related:

$$\% AP = \left(1 - \frac{BD}{ARD}\right) X\ 100\%$$

The true relative density (TRD can be determined only by destroying the closed pores through fine grinding of the specimen (usually finer than 0,2mm). The TRD can then be determined using Rees- Hugill flask (volume displacement method). The flat bottom flask has a thin long graduated neck. A pre-weighed powdered sample is fed into the flask, which contains a known quality of liquid. The liquid level rises and the TRD can be read on the graduated neck.

It does not take much imagination conclude that same previously –mentioned relationship will also exist between:

% TP, BD and TRD

Therefore the % TP can be calculated from the formula:

$$\% TP = \left(1 - \frac{BD}{TRD}\right) X\ 100\%$$

Example:

The reader can now experiment with the following values obtained on a superduty brick:

Dry mass = 42,4g

Immersed mass = 26,3g

Soaked mass = 46,2g

True relative density = 2,72g

The following answers should be found:

AP = 17, 1%

BD = 2,13g/cm³

ARD = 2,63g/cm³

TP = 21, 7%

PERMEABILITY

The permeability of the material to gas can be defined as the rate by which the gas moves through a material under a specified pressure gradient. Permeability is a directional property and is greatest in a direction perpendicular to the direction of pressing.

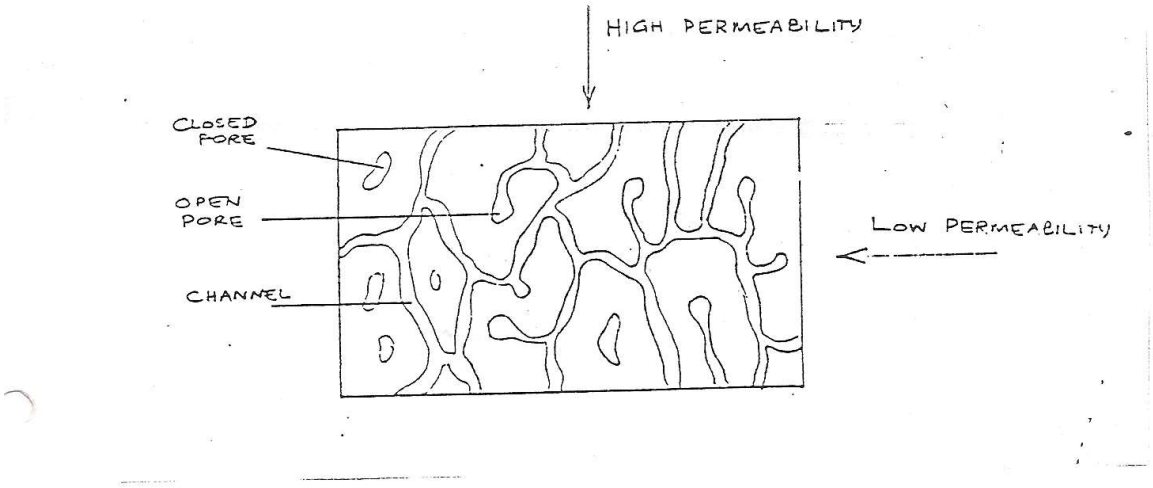
Porosity and permeability are two important factors in the resistance which a refractory will have to slag attack. Slag will easily penetrate a high porosity, high permeability material.

During the manufacturing process the forming pressure of the presses influences the porosity. As the forming pressure increases, the density increases and the porosity decreases. If bricks are pressed too dense, springiness can develop which forms laminations on release of the pressure. These laminations will form cracks and will increase the permeability.

The inherent grain porosity of the grains of materials used in making brick can also influence the porosity of the brick.

It can be said that a high permeability material will have a high porosity however the reverse is not necessarily true.

The following sketch will illustrate the relationship of porosity to permeability.



Cold crushing strength (CCS)

Various methods are used determining this property depending upon the type of material.

The CCS is calculated by determining the force required to fracture a standard sample under specified test conditions. The pressure is always applied in the same direction as that of pressing of the brick.

Sample sizes are as follows:

Insulating bricks: 114 x 114 x 76mm high

Chrome- magnesia mixtures and sand

Bricks: 50 x 50x 75mm high

All other bricks: 50mm diameter x 50mm height

The force required to break the brick sample is then divided by the cross sectional area of the sample to give CCS in Kg/cm^2. The new ISO unit for expressing CCS is MPa (Mega Pascal)

1 MPa = ±10Kg/cm^2 (approximate)

The CCS supplies information on how high a brick has been fired and whether the brick can be transported and handled. Low CCS values normally are associated with high porosities, bad firing and could also lead to low abrasion resistance. A very high CCS on the other hand may indicate a high glass content, which will adversely affect the temperature strength of the material.

MODULUS OF RUPTURE (MOR)

Bricks seldom fail due to crushing and normally bending movements are more common and can break the brick into two portions. This test can break the brick into two portions. This test can be done at both room temperatures, as well as elevated temperatures.

The sample size and test conditions are specified by the standard test methods.

A brick or sample is placed on two knife edges a specified distance apart and a load is supplied centrally between the knife edges. The load required to break the sample is recorded and the MOR is calculated using the formula:

$$MOR = 3/2 \ \frac{F1}{bd^2}$$

Where F = force required
1 = distance between knife edges
B = with of sample
D = thickness of sample

THERMAL SHOCK RESISTANCE (TSR)

Basically thermal shock resistance or spalling resistance is based upon unequal distribution of stress in a body resulting from an unequal temperature distribution. In practice a brick is mostly heated from one side only resulting in unequal temperature distribution within the brick.

Various factors influence the thermal shock resistance of a material.

Generally it can be said that an increase in porosity will increase the thermal shock resistance. A coarser-grained material will also have the same effect.

Certain materials have characters that will affect this property. A low reversible expansion or the absence of minerals with marked changes at their inversion temperatures will make a material more resistance to thermal shock e.g. unconverted quartz in a fireclay body can affect the performance of the material due to quartz and cristobalite inversions at temperatures below 600°C.

The high thermal expansion of magnesia also results in poor thermal shock resistance. The addition chrome to magnesia brick will result in an improved thermal shock resistance.

The test is performed by alternately heating to 1000°C and cooling a specimen (50 x 50 x 75mm) cut from a brick. The number of heating and cooling cycles which a sample can withstand is a measure of its resistance to thermal shock.

Thermal spalling is the term used when an unused brick is subjected to alternating temperatures. Slag attack or reactions with materials such as alkalies will change the chemical composition and physical properties of the refractory, resulting in structural or chemical spalling.

PERMANENT LINEAR CHANGE ON REHEAT

The PLC of a refractory material is determined by measuring a sample accurately, before and after firing to a specified temperature. The difference in measurements relative to its original length will give the PLC of that material.

The linear change on reheat gives an indication of how well the refractory has been fired during manufacture and the value is normally very small. The linear change will give an indication as to what extent the joints between bricks will open up during use, or on the other hand what forces can be in the structures with certain expansion allowances.

If the shrinkage is more than 1% then there is the danger that the shrinkage is more than the thermal expansion of the brick at the higher temperature. This will cause joints to open up and will result in metal penetration and in extreme cases 'floating out' of bricks.

PYROMETRIC CONE EQUVALENT (PCE)

This test is normally only carried out on silica and alumino-silicate materials. It is not a melting point determination, but is an indication of the temperature where a liquid with a low viscosity formed, resulting in the sample deforming under its own mass.

The structure of the sample can also affect its softening temperature.

A small pyramid is cut from or formed of refractory material and then in a kiln alongside cones of known softening point. The number of the standard cone that softens at the same time as the sample is noted and the sample is then quoted to have a PCE of the number of the standard cone.

REFRACTORINESS UNDER LOAD (RUL)

In this test a cylindrical test specimen, which is under a specified load, is heated at a prescribed rate and the changes in height are recorded of the test piece as the temperature increases. From the graph, the temperatures were 0, 5%, 2% and 5% deformation have occurred can be read.

This test gives an indication of the temperature where low melting point phases are formed to allow the specimen to be deformed under a given load. The values determined are variables amongst of bricks. However, the values do not furnish any direct indication of the limits of application for the material tested.

RESISTANCE OF CREEP UNDER LOAD AT HIGH TEMPERATURE

Creep tests (long time deformation at high temperature) of Refractories give useful engineering data for furnace design; especially structures operating over long periods of time e.g. blast stoves. Because energy conservation will promote the insulation of furnaces, interior walls will operate at higher average (mean) temperatures and will therefore be more prone to deformation.

The test is performed in an apparatus similar to that of the URL with the same sample size. The load specimen is heated at a prescribed rate to predetermined temperature, which is then maintained either for a specified time or until a specified deformation occurs.

Some factors can influence the creep in compression of a refractory can be the following, namely:

a) Loaded applied

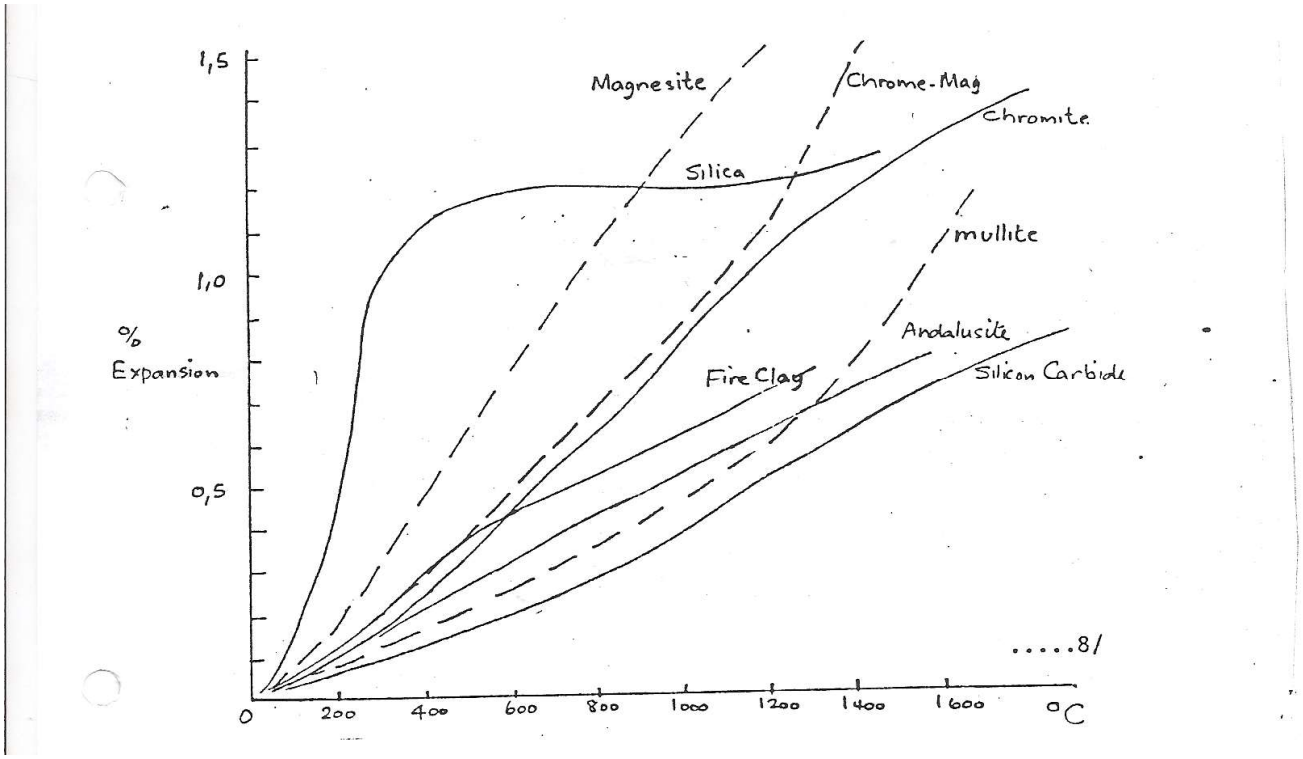
b) Temperature
c) Chemical & mineralogical composition
d) Porosity
e) Atmosphere during testing or use
f) Original firing temperature.

LINEAR THERMAL EXPANSION (LTE) REVERSIBLE)

The reversible linear thermal expansion of a solid material is characteristic of that type of materials. As the name implies this property is reversible and the heated specimen will return to its original length after cooling.

Every brick is composed of different phases with differing thermal expansion co-efficient. During the construction of a furnace, allowances must be made for this expansion with increased temperature since enormous stresses can be formed. These stresses can destroy the bricks or the metal shell if no expansion gaps are built into the brick lining.

The graph shows how the percentage expansion increases with increased temperature.



THERMAL CONDUCTIVITY

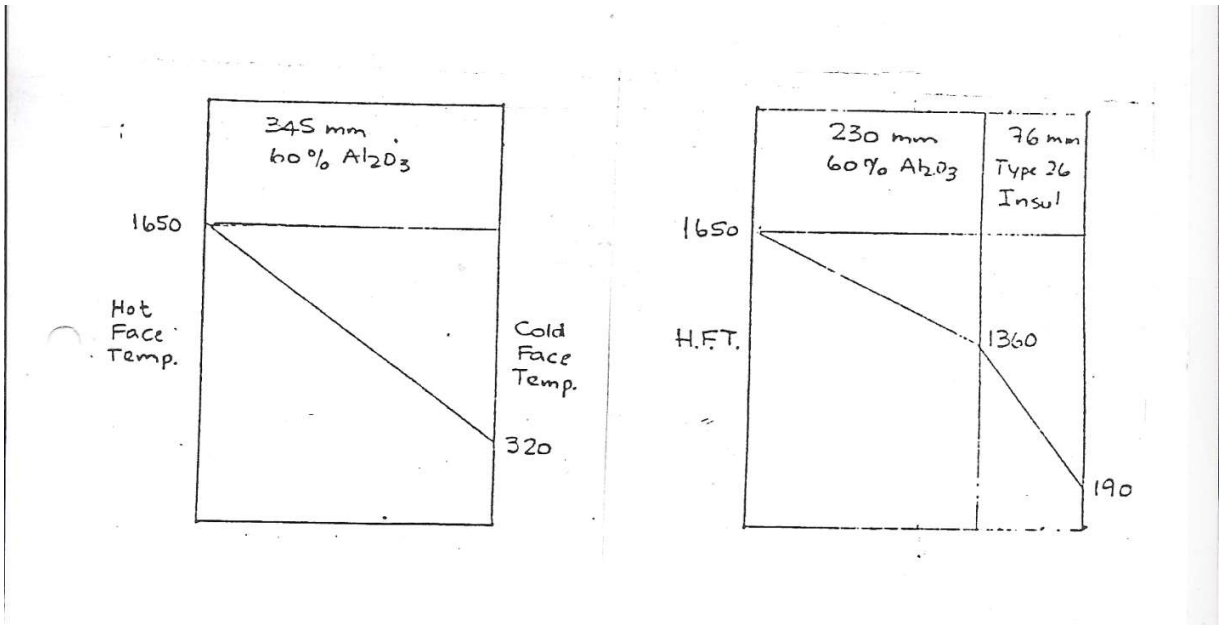
Thermal conductivity is the process whereby energy is transferred from a higher level to a lower level in solid material and is defined as the amount of heat flowing through a body of unit area thickness in a specific time.

Various factors influence the thermal conductivity of a material besides its chemical and mineralogical composition.

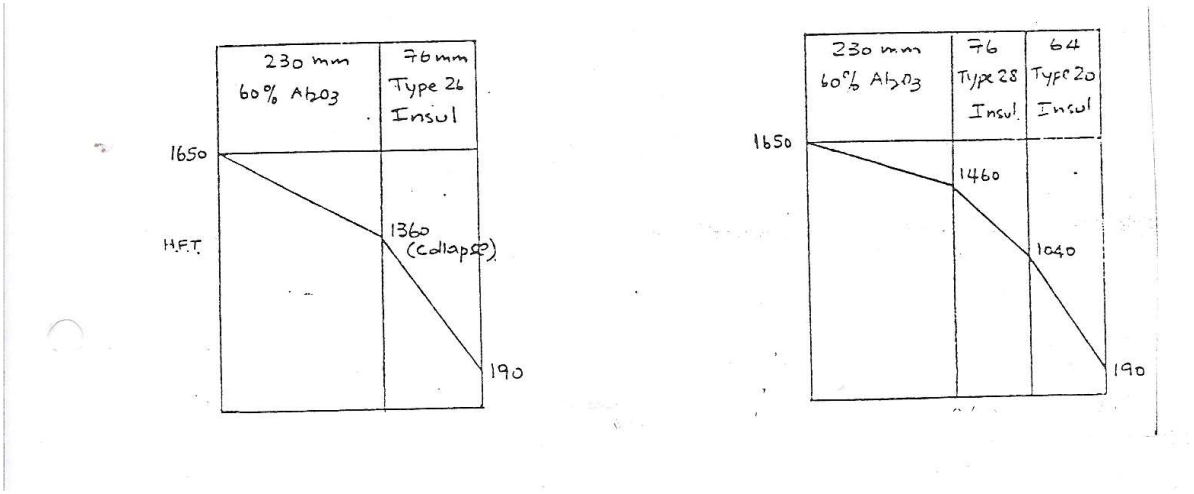
The amounts of pore spaces are usually the most dominant factor affecting the K value. If the pore spaces are small and the temperature relatively low, increasing the proportion of pore space will reduce the amount of heat transfer. However, at higher temperatures, the radiation of heat across open pores becomes important and together with increased permeability can actually increase the thermal conductivity. Large pressure differences between the cold and hot face can further increase the thermal conductivity.

The pressure of hydrogen can have a significant effect on heat losses since the conductivity of hydrogen is ± seven times that of air. The thermal conductivity of glass increases and that of crystalline phases generally decreases with an increase in temperature and that of fireclay increases with a rise in temperature.

Thermal conductivity figures are required in order to calculate heat losses as well as interface temperature if a wall is being built of more than one type of refractory material. This can seriously affect energy savings.

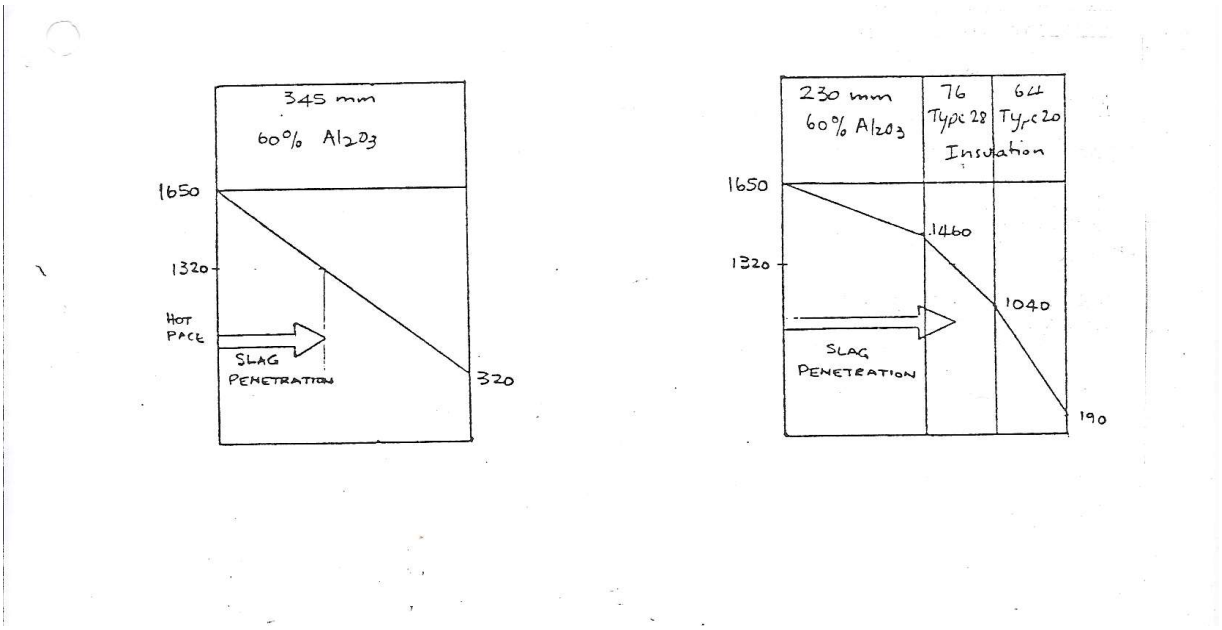


Insulation can also be dangerous and can result in a more severe environment for the material. Over-insulation can increase the interface temperature and cause subsidence e.g.



The gradient shift caused by the insulation effect can also result in a hotter lining adversely affecting a refractory exposed to slag attack. Slag attack increase in direct proportion to temperature.

The following example shows the effect of slag attack of a slag that solidifies or becomes viscous at 1300°C.



The thermal gradient after insulation shifted enough to allow the slag to penetrate completely through the high alumina brick into the insulation lining before freezing.

SLAG ATTACK

The slag resistance of a refractory material is a very important property. There are many factors influencing slag resistance and as many problems exist in simulating operating conditions by any test method.

Some factors influencing slag attack:

a) Chemical and mineralogical composition of the refractory
b) Chemical composition and melting point of the slag
c) Porosity and permeability of the refractory
d) Temperature gradient through the brick which governs the depth to which the slag will penetrate
e) The tendency of the slag 'wet and penetrate the refractory
f) Rate of reaction between the slag and the refractory

The temperature at which the brick and the slag react is often the principal factor governing the maximum allowable operating temperature. In some cases rates of reaction increase rapidly with only small increases in temperature. Therefore a change in furnace practice which raises the temperature only slightly may necessitate a change in the type of refractory used.

In the simplest static test, a cup or 'pot' is filled with slag and exposed to high temperatures. This is a quick test to compare slag reactions on different refractories under the same test conditions.

More sophisticated slag test use a thermal gradient in the sample, atmospheric control, dynamic slag conditions, introduction of fresh slag and thermal cycling.

ABBRASION RESISTANCE

In many types of application, Refractories are subjected to the impact of heavy pieces of material charged into a furnace, abrasion by moving metallic or non-metallic solids, or direct impingement by abrasive dusts in rapidly-moving gases.

For greatest resistance to these actions, the brick should be mechanically strong and well-bonded. The hardness of the aggregate and matrix is also very important.

A common test method is to blast the surface of the refractory material with material such as silicon carbide in a modified type sand-blaster and compare the wear with that obtained on a standard sample.

CARBON MONOXIDE DISINTEGRATION

In applications where refractories are subjected to CO, such as in blast furnaces, any free compounds of iron will be reduced to free Fe. The metallic Fe will catalyse the following reaction:

$$2CO -> C + CO_2$$

Resulting in the deposition of carbon in the pores of the brick. The build-up of carbon around the Fe grains can build-up forces great enough to disintegrate the brick's structure.

For bricks to be resistant to CO_2 the Fe_2O_3 content must be as low as possible and the bricks must be fired to high temperatures in order to convert the Fe_2O_3 to more stable compounds with the SiO2 and Al2O3 constituents in the brick.

Samples are tested in the laboratory by subjecting a brick sample to a constant flow of CO gas at a temperature of ± 500°C for periods up to 200 hours and observing the reactions.

Chapter 3

ALUMINO-SILICATE SHAPED PRODUCTS

SILICA

Silica is the major component forming the earth's crust, making up to about 60% of its composition. It occurs both independently and in combination with other oxides.

Chemically, silica consists of SiO_2, which melts at about 1713°C in its pure form. It shows distinct acid properties, which become important when used as a high temperature refractory.

Silica is cheap and plentiful so we would expect it to be very frequently used as a refractory material. In fact it used to be very common refractory material, however today it is very rarely utilized, expect for bricks lining coke ovens and in monolithic for induction furnaces.

The main problem with silica as a refractory is that it occurs in a number of different crystal forms called polymorphs. When silica is heated the crystal structure changes a number of times, notably at 240°C to 275°C and at 573°C. When this change occurs the volume of the crystals change and this severely cracks bricks unless the alteration is very carefully controlled.

ALUMINA

Another common element in the earth's crust is alumina. It is most commonly found together with silica in various compounds. More or less pure forms of alumina found in nature are corundum emery, sapphire and ruby.

Chemically, alumina consists of Al_2O_3 and melts at 2050°C. Chemically, alumina is generally regarded as neutral. In fact it is amphoteric which means that it is able to show both acid and basic properties. It can react with silica (an acidic raw material to form mullite and with magnesia (basic raw material) to form spinel.

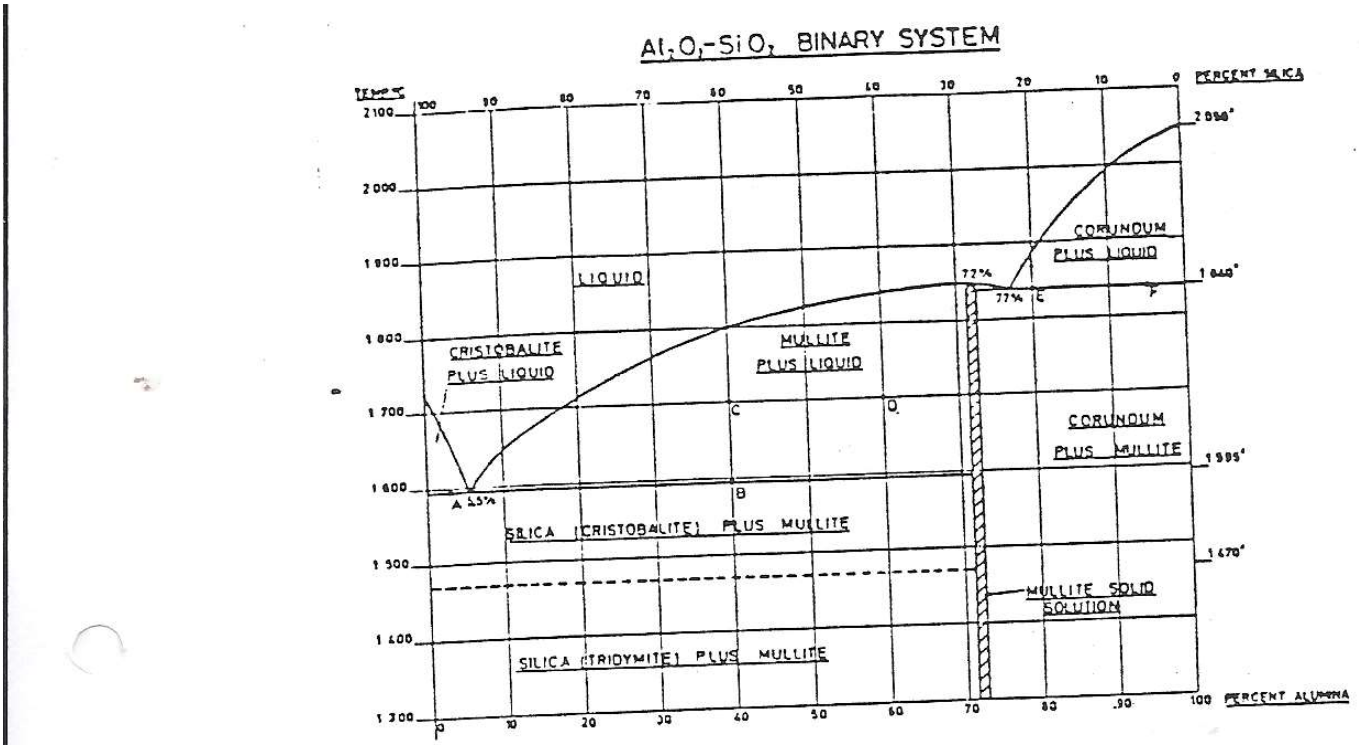
ALUMINO_SILICATE

Melting of mixtures of two minerals occurs over a range of temperatures.

The temperature at which at which melting is complete depends upon the relative amounts of the minerals present.

The easiest way to study the melting of mixtures is by means of phase diagrams.

The phase diagram for Al_2O_3 – SiO_2 is given below.



For this course we only want to look at some of the main points.

On the left of the diagram we have pure silica which, as we have seen, melts at 1723°C.

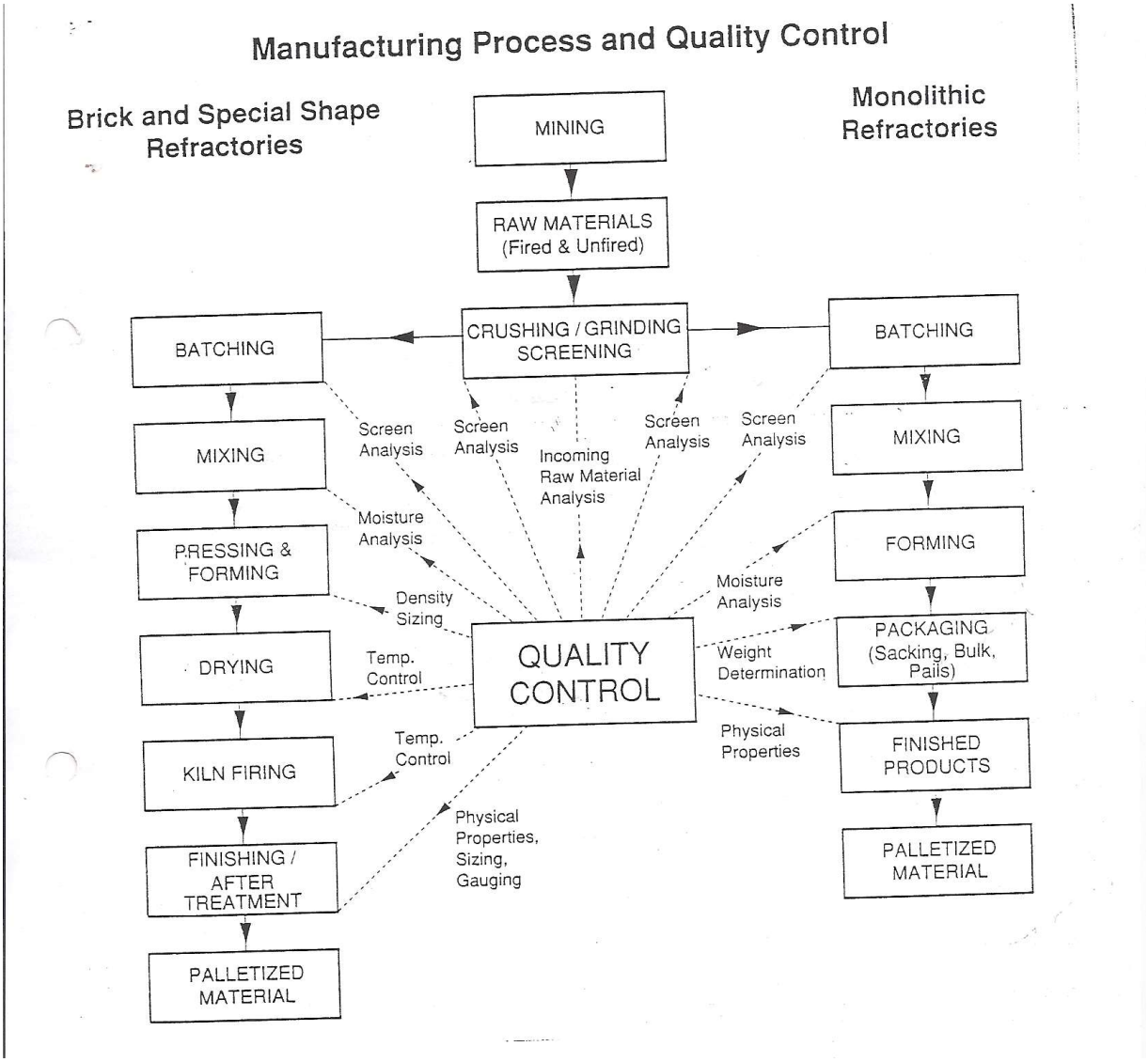
As we move across the diagram to the right we have more alumina and less silica, until at the far right we have pure alumina which melts at 2050°C.

The main point I want you to understand on the phase diagram is that when you begin adding alumina to silica, melting begins to occur at only 1595°C and when we reach 5,5% Al_2O_3 and 94,5% silica the whole mixture will be melted at this temperature.

As we continue to add more alumina the amount of melt decreases until at 72% alumina and 28% silica, we have the compound mullite $3Al_2O_3.2SiO_2$ which only melts at 1850°C.

If we continue to increase the alumina content beyond that of mullite we will get mixtures of mullite and alumina. In this system melting begins at 1840°C. The quantity of liquid present decreases until at 100% alumina we would get pure alumina which melts at 2050°C

Before we look at the various types of brick, let us quickly look at the brick manufacturing process. The next diagram was produced by Harbison-Walker.



REFRACTORY CLAYS

Clays were amongst the first raw materials used to make refractories. Chemically, clays are largely compounds of silica and alumina.

Most fireclay bricks consist mainly of pre-fired high alumina clay (chamotte) bonded with plastic clay. This mixture is then fired to form a stable brick.

Examples of clays

	Chamotte	B13 Ball Clay
SiO_2	52,0	58,0
Al_2O_3	43,0	24,8
TiO_2	1,5	0,7
Fe_2O_3	1,0	2,0
CaO	0,3	0,5
MgO	0,3	0,3
Na_2O	0,24	0,27
K_2O	0,09	2,8

These bricks normally cover the range from about 35% to 44% alumina. From the phase diagram seen earlier, we can see that they are relatively low cost bricks suitable for less arduous applications.

These bricks are generally known as normal duty, high duty and super duty refractories.

Super duty fireclay bricks have good strength and stability of volume at high temperatures and an alumina content of 40% to 44%. Some super duty bricks have superior resistance to cracking or spalling when subjected to rapid changes of temperature. There are several possible modifications in the super duty fireclay class; including bricks fired at temperatures several hundred degrees higher than the usual product. High firing enhances the high temperature strength of the bricks, stabilizes their volume and mineral composition, increases their resistance to fluxing, and renders them practically inert to disintegration by carbon deposition in atmospheres containing carbon monoxide gas.

High duty fireclay bricks are used in large quantities and for a wide range applications. Due to their greater resistance to thermal shock, high duty fireclay bricks can often used with better economy than medium duty bricks for the linings of furnaces operated at moderate temperature over period of time while being subjected to frequent shutdowns.

Medium duty bricks are appropriate in applications where they are exposed to conditions of moderate severity. Medium duty bricks within their serviceable temperature ranges can withstand abrasion better than many bricks of the high duty class.

Normal duty fireclay bricks find applications as backings for bricks higher refractoriness, and for other services where relatively moderate temperature prevail.

Uses

Cupola

Blast furnace

Blast furnace stove

Pouring pit hollow ware

Soaking pits – roof, side walls

Reheating furnaces – hearth, roof side wall

Boilers- walls, arches flues

Rotary kilns – cooler sections

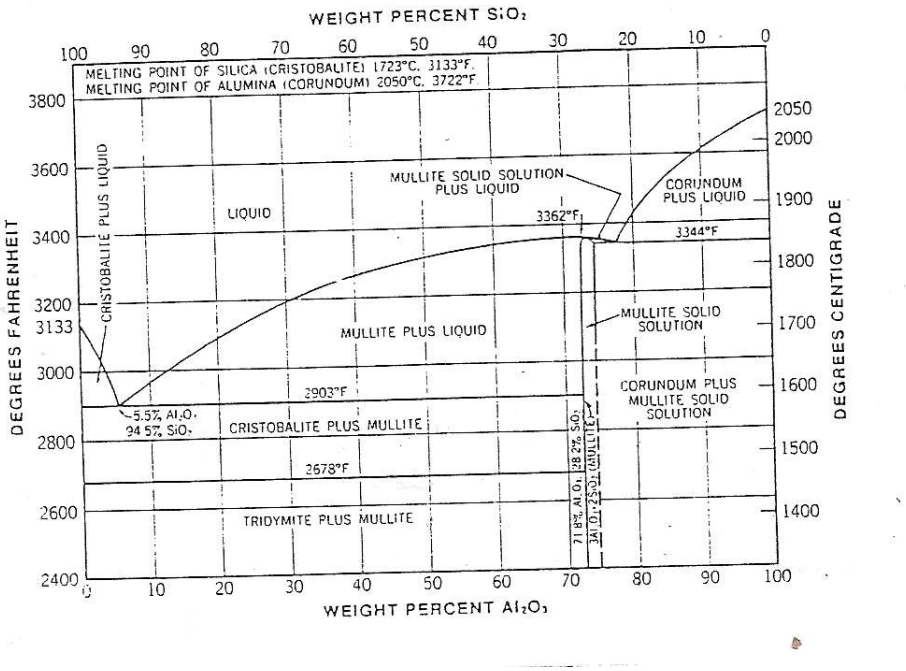
ANDALUSITE SILLIMINATE KYANITE

These are natural alumina silicates. They normally contain about 60% Al_2O_3, with the remainder composed primarily of silica with small impurities of iron.

Examples of Andalusite Sillimanite Kyanite

	Andalusite	Sillimanite	Kyanite
	A	B	
SiO_2	38,0	36,1	39,9
Al_2O_3	60,3	61,9	56,0
TiO_2	0,17	0,16	1,80
Fe_2O_3	0,72	0,59	1,60
CaO	0,11	0,06	0,04
MgO	0,09	0,011	0,04
Na_2O	0,06	0,06	0,16
K_2O	0,22	0,13	

When andalusite, sillimanite or kyanite are heated to between 1300°C and 1400°C, the minerals change to mixture of mullite and cristobalite



Andalusite forms the basis of many high alumina materials. The high purity and coarse crystal structure of andalusite and sillimanite gives good high temperature creep resistance.

Kyanite has high expansion when it converts to mullite. This is used to counteract shrinkage in monolithic products.

60% alumina bricks

Bricks based on andalusite are popular class of products. These bricks generally have low porosity, excellent hot strength and creep resistance and good volume stability at high temperatures.

Uses

A major application for bricks in this class is the checker setting of blast furnace stoves where load bearing ability and creep resistance is critical to prevent slumping.

The bricks are also widely used in other application including steel ladles, ladle safety linings, rotary kilns and incinerators.

Tar – impregnated bricks are used in hot metal transfer cars (torpedo ladles)

MULLITE

Mullite is not found in commercial quantities as a naturally – occurring mineral. However, mullite is an excellent refractory and is produced synthetically for refractory use largely by burning bauxite, kaolin or from bauxite and kaolin.

Uses

This is a very commonly used brick because of its excellent and cost-effective performance in many environments. It is commonly used in ladles, hot metal transfer cars, cement and lime rotary kilns and petroleum coke calciners.

In South Africa there are no worthwhile deposits of bauxite and kaolin so most applications use either 60% alumina or 80% alumina bricks.

BAUXITE

In the raw state bauxite consists of either gibbsite ($Al_2O_3.3H_2O$) or diaspore AlO (OH) together with accessory clay minerals.
Bauxite deposits vary from location to location and are scattered worldwide in a board band close to the equator.
Refractory grade bauxites are calcined in a kiln from selected low iron, low alkali bauxite.

Typical Refractory Grade Bauxites

	Guyana	China	Brazil
SiO_2	6,5	5,6	9-10
AL_2O_3	88	87,5	85-87
TiO_2	3,25	3,64	1,9-2,3
Fe_2O_3	2,0	1,56	1,6 -2,1
CaO	0,02	0,06	<0,2
MgO	0,02	0,62	<0,2
Alkalis	0,01	0,62	<0,01
Bulk Density (g/cm^3)	>3,10	3,20	3,15 -3,20

80% alumina bricks

These products are based primarily on calcined bauxite, with additions of clay and fine alumina. Due to the expansion that occurs when clay and bauxite are fired together, they are generally fired at relatively low temperatures in order to maintain consistent brick sizing.

As the bricks are relatively inexpensive, perform well and are resistant to most slag conditions, they are often used in steel ladle applications.

Alumina products

There are a number of different types of aluminas used in the refractory industry. The main types are fused alumina, tabular alumina and calcined alumina.

The original material for alumina production is normally bauxite, which is generally processed by the Bayer Process to produce a chemically-pure alumina.

Clacined aluminas are generally calcined at moderate temperatures and milled for use as additives in refractory products.

Tabular and fused alumina consist of pure alumina grains either melted above 2050°C or sintered at about 1900oC to form a hard chemically resistant aggregates.

Examples of alumina

	Calcined Alumina	Tabular Alumina
SiO_2	0,03	0,04
Al_2O_3	99,4	99,7
TiO_2	0,03	0,01
Fe_2O_3	0,04	0,06
CaO	0,06	0,04
MgO	0,02	<0,001
Na2O	0,19	0,16
Crystal size (µm)	3,5	
Bulk density (g/cm^3)	-	3,55

90% to 99% alumina bricks

As we can see from the phase diagram these bricks are generally very pure and contain mullite and corundum.

Brick properties such as hot strength, creep resistance and slag resistance benefit from the low levels of impurities. Due to their high cost, these bricks are used only in the most demanding of applications.

Before we leave the topic of alumina bricks there are a few specialized classes of products worth discussing.

Chemically bonded bricks

These are unfired with a chemical binder, generally a phosphate. After pressing they are heated to 300°C to 500°C. Phosphate-bonded bricks have a very low porosity and permeability and high strength at intermediate temperatures (800°C to 1200°C). Phosphate –bonded bricks are

widely used in the Aluminium Industry and in the Mineral Processing Industries.

Alumina – chrome bricks

Alumina –chrome bricks consists of combinations of the two oxides fired to develop a solid –solution bond. A wide range of products are available depending upon Cr_2O_3 content. These include a 90% Al_2O_3-10% product based upon high-purity sintered alumina and pure chromic oxide. The solid – solution developed in firing results in bricks with exceptional cold strength, hot strength and load-bearing ability. In addition the solid solution bonded between the alumina and chromic oxide is inert to wide variety of slags. This premium product is used in slaglines of induction furnaces, carbon –black reactors, and other specific areas where slag corrosion is a major consideration.

Bricks with higher Cr_2O_3 content are also available. Based upon a special fused grain high in chromic oxide, these products are selected for the most extreme cases of high temperature and corrosiveness.

Alumina –carbon bricks

In this class, bricks are bonded by special thermosetting resins that yield a carbonaceous bond upon pyrolysis. A wide variety of compositions are possible, based upon the various high-alumina aggregates now available. Graphite is the most common carbonaceous material, although silicon carbide is also used. These products are used in applications where reducing conditions prevail, such as during hot metal transfer or in torpedo cars.

Chapter 4

BASIC PRODUCTS AND APPLICATIONS

1. INTODUCTION

The classification of refractories into three main groups i.e. basic, neutral and acidic originated from the periodic table of elements. Those elements which can easily release one or two electrons to form a stable configuration are classified as being alkali to basic. The Group II Elements (see table 1) can release two electrons to form double positively-charged ions (e.g.) Mg^{++}; Ca^{++}).

Moving to the right-hand side of the periodic table, elements are becoming more and more reluctant to release electrons and Group IIIA and IVA elements can be regarded as being neutral. Even further to the right – hand side of the periodic table, the affinity for electrons becomes stronger and therefore also the degree of acidity. Materials which are therefore classified as basic are magnesia (MgO), doloma (MgO.CaO), magnesia-doloma combinations, magnesia-chrome ore combinations (MgO-C).
Basic Refractories are compositions of dead-burned doloma, dead-burned magnesia, chrome ore or compatible mixtures of magnesia-doloma or magnesia-chrome. Others may contain forsterite or magnesia-alumina spinel and many may have additions of carbon or graphite.

Impurities of silica, iron oxide, alumina and others lead to the formation of eutectic compounds with greatly reduced refractoriness and therefore the properties of basic refractories are also governed to a very large degree by phases formed by these adulerating constituents. As with all refractories, exceptionally high purity may be obtained but only at correspondingly high cost.

The properties of these refractories are such that at high temperatures they have high strength and are all highly resistant to the corrosive action of basic slags (a slag with CaO: SiO_2 ratio > 2), solid or liquid oxides, dusts and fumes.

2. There are many possible ways of classifying basic refractories. One classification would be to group them w.r.t. their predominant mineral phase or combination of phases or even the manner in which the mineral phases were treated prior to incorporation into the final product e.g.

- no pre-treatment (reaction in situ)
- pre-reacted - co-clinkered through a rotary kiln
- co-sintered - ball-milled
  - pelletised/briquetted - shaft or rotary kiln
- fused grain
- fusion-cast

These refractories could be further subdivided according to the nature of their bonding, together with differentiation into pressed and monolithic products.

MONOLITHICS

DEFINITION: Monolithic refractory materials are mixtures which contain aggregates and binders prepared ready for use either directly in the condition in which they are supplied or after the addition of suitable liquids. They are usually grouped together by the method of installation i.e. casting, gunning, moulding or ramming.

FEATURES: The more important features of monolithic refractories are:

a) Design flexibility and easy construction of complex linings either in situ or by prefabrication.

b) Ready availability, eliminating stocking of special shapes.

c) Rapid installation in difficult circumstances.

d) Freedom from joints.

e) Excellent resistance to thermal shock.

f) A limited shelf life normally.

Monolithic refractories themselves can be further subdivided or classified according to:

- installation method
  vibrating/ramming
  sprayed on/trowelling
  poured-in concrete

- setting characteristics
  air-set/hydraulic
  heat-set/chemical
  physical state
  powder/plastic/paste

- bulk density
  lightweight/dense

- temperature application
  1400°C / 1600°C/ > 1600°C

The variety, features and application of principal monolithic Refractories are shown in table 2

2.1 Let us start with magnesia refractories i.e. those consisting predominantly of the mineral phase periclase MgO.

2.1.1 Natural magnesia

Magnesia was originally obtained from naturally-occurring magnesium carbonates - magnesite $MgCO_3$. The raw material is calcined at high temperatures to drive off CO_2 to give densified MgO. (]BD ± 3,20 g/cm³)

2.1.2 **Synthetic magnesia**

These magnesias are extracted from other sources e.g. seawater magnesia and have definite advantages as listed below.

- higher purity (original B_2O_3 problem)
- silicates in pockets - direct bonding
- higher BD
- larger crystal size
- consistent quality and chemistry.

In order to obtain 1 ton of magnesia it is necessary to treat about 300 tons of seawater. For a schematic reclamation of MgO from seawater (See Table 3).

2.1.3 Fused magnesia

Produced by melting in an electric furnace. Mainly used in magnesia-carbon refractories.

Advantages

- chemical purity
- large crystal size

Cost is a disadvantage.

2.1.4 Typical analysis of some magnesias (See Table 4).

2.1.5 **Factors determining use**

The amount, composition and distribution of the secondary phases which greatly influence magnesia refractories. (See Table 5 - Effect of Impurities).

The $CaO:SiO_2$ ratio is particularly important in determining the refractoriness, since different mineral phases will form on firing with different characteristics.

Properties

Magnesia refractories have good resistance to iron oxide attack, but tend to shrink and spall at high temperatures. They may have a good hot

strength, but generally have a very high thermal expansion. (Also see table 6).

Applications

Including:

- EAFs, basic oxygen vessels (figure 1 AEF)
- non –ferrous furnaces – hearths
- Safety linings of casting ladles.
-

3. MAGNESIA - CHROME AND MAGNESIA PRODUCTS

3.1 The chrome spinel-chromite, when added to magnesia provides a range of:

- magnesia-chrome. 50% magnesia and
- chrome-magnesia > 50% chromite
- products with improved thermal shock resistance and in some cases slag resistance

Briefly the spinels have a general formula:
ROR_2O_3

Where R = Mg^{++} Fe^{++}

R_2 = Fe^{++} Al^{++} Cr^{+++}

The mineral phase chromite would be
$(Mg, Fe)\ O\ (Fe, Al\ Cr)_2O_3$.

3.2 These products may be further classified w.r.t the manner in which these phases are combined (as previously mentioned in situ, co-sintered, fused, etc.).Pre – processing has many benefits e.g.

- stabilization of the chrome ore
- controlled chemistry
- use of fines

3.3 further classification of bricks according to the type of bonding

3.3.1 Silicate bonding

The original mag-chrome/chromag bricks introduced in the 1950's were silicate bonded. The magnesia crystallites themselves being bonded by silicate and the chromite grains also being bonded onto the periclase grains by silicates. Silicate-bonded bricks may be limited in their refractoriness, but can have good thermal shock resistance and high pressure flexibility.

3.3.2 Direct Bonded bricks

In an effort to improve the service life of linings, it was found that by lowering the impurity content and by high firing the bricks- a direct-bonded brick could be produced in which the chromite reacts with the periclase to form a highly refractory spinel $MgOR_2O_3$ "direct" bond.
The MgO crystals themselves may be directly-bonded or connected via a complex spinel phase. Silicates already present are displaced into the interstices of the periclase – chrome structure and thus no longer constitute the actual bonding mechanism of the brick.

Advanatages

- Improved hot strength
- Lower porosity and permeability
- Improved spalling resistance
- Better slag resistance
- Lower amounts of densification and
- Migration of impurities.

3.3.3 Chemically-bonded bricks

Chemically-bonded bricks (unfired bricks) are formed with the aid of selected additives, which provide structural intergrity without the necessity of high temperature sintering (ceramic bonding) – they offer significant energy savings. Chemically-bonded Refractories using $MgSO_4$, $MgCI_2$, H_2SO_4 and various phosphates as bonding agents have been available for many years. These are more often than not stell-encased, with the expansion due to the oxidation of the steel casing helps to offset any shrinkage at high temperature. In service the plate oxidize and react with the refractory, bonding adjacent bricks and forming a monolithic lining.
Application
Reverb furnace roofs and cooper smelting furnaces (see fig 2)

4 Magnesia –spinel

$MgO.Al_2O_3$ melting point 2135°C. (See table 7 for melting points of Refractory Minerals)

Several magnesia-spinel products are available with varying Al_2O_3 contents are formed by combining magnesia with magnesia –alumina spinel.

Application

- Cement rotary kilns
- EAF roofs
- Working linings of steel casting ladles

5 FURTHER DEVELOPMENT OF MAGNESIA REFRACTORIES

5.1 Pitch –impregnation

Advantages:

- Carbon residue – inhibits slag penetration
- Reduced porosity

5.2 Pitch –bonding

Advantages

- Energy –saving
- Spall –resistant properties
- Additional carbon added

5.3 Resin –bonding

Advantages

- Energy saving
- Health /environment
- Good strength
- No danger of slumping

5.4 Magnesia –carbon

5.4.1 Raw materials

5.4.1.1 Magnesia

The magnesia used can be natural, seawater or magnesia –rich brines.

By the manufacturing process and source of raw material, magnesia can be divided into 2 groups sintering and electrofusion.
In general electrofusing is carried out in an electric arc furnace at more than 2800°C, which includes a lengthy fusing process enabling large crystal growth of MgO.
By contrast with fusion, the sintering process has a limitation in obtaining larger crystallized MgO because of its different manufacturing process by rotary kiln.

Crystallites of high quality fused MgO are usually at least 10 times larger than crystallites of sintered magnesia.

Typical sintered magnesia - crystallite size 60 to 80µm
Typical fused magnesia - crystallite size 500 to 1800µm

Improvement in sintering has been established and Mgo grains with higher density and larger crystal sizes (up to 150µm) with low B_2O_3 content are possible.

For the manufacture of MgO-C bricks, sintered Mgo or a combination of sintered MgO with fused MgO or just fused MgO can be used, with a respective increase in cost. In general fused MgO has better corrosion resistance than sintered magnesia.

5.4.1.2 Graphite (carbon)

a) The following materials are sources of carbon: pitch, carbon black, amorphous carbon, natural graphite and synthetic graphite.

Typical Characteristics

Carbonaceous Material	Relative rate of oxidation	Effective temperature range °C
Pitch	Fast	300-500
Amorphous carbon	Slow	400-800
Natural flake graphite	Very slow	700-1100

b) For the manufacture of MgO-C Bricks, natural graphite is mainly used. Artificial graphite is not normally used primarily because of the high porosity of 10% to 15%, compared with 2% to 3% for natural graphite.

c) The purity of the graphite has the greatest effect on the life of MgO-C bricks. Hot properties decrease with increase in impurities (ash) and consequently there will also be a decrease in the corrosion resistance of the MgO-C brick.

d) The use of fine flake graphite results in a dense brick texture with low permeability and porosity, which retards chemical reactions and thus improves oxidation, abrasion and corrosion resistance. However, the coarser flake graphite is more oxidation-resistant than that of the finer flake. Thermal shock resistance also increases with increase in flake size.

5.4.1.3 Binders

Binders used are pitch, resin or a combination of pitch and resin.

Resins have become the most important binders for MgO-C bricks. Several types of resins are being used in the industry, however phenol formaldehyde resins, which are available in resol and novalac qualities are more popular.

Advantages of resin against pitch

a) the hot process associated with pitch can be eliminated, thereby brick production can be simplified and the working environment is improved.

b) Improved oxidation resistance
c) Improved physical properties i.e. hot strength up to 1000°C.

Advantages of pitch-bonding
a) can better absorb the stresses which develop in the lining during burn-in and in-service

b) pitches yield higher carbon content than resins.

5.4.2 Properties (also see Table 8)

5.4.2.1 Refractoriness

MgO-C bricks possess high refractoriness, because there are no liquids (eutectic) forming between magnesia and carbon.

5.4.2.2 Slag resistance

a) The presence of graphite in the structure prevents the ingress of slag liquids, because of its non-wetting character and by reduction of ferrites (FeO) to iron metal, thereby lowering the reactivity of the slag.

b) During the oxidation of the carbon by oxygen or FeO in the slag, CO is generated which creates a positive pressure against the penetrating slag.

c) At high temperatures which exist in steelmaking, the MgO is reduced by the carbon to Mg vapour, which migrates to the surface, Oxidises and forms a dense MgO-zone behind the hot face.

5.4.2.3 Thermal shock resistance

The absence of a brittle ceramic bond, together with a thermal expansion mismatch between the magnesia and graphite produces a structure which is resistant to crack propagation and renders the brick practically immune to thermal shock damage.

5.4.2.4 Thermal conductivity (see Figure5)

High thermal conductivity produces a reduction in the temperature of the interface between slag coating and brick and thereby slows the rate of dissolution of magnesia into the slag, particularly with higher graphite contents.

5.4.2.5 Oxidation (resistance)

The disadvantage of MgO-C bricks is that oxidation of the carbon (graphite) can occur which exposes the magnesia to chemical attack (corrosion) by the slag whereby the MgO-grain can be washed into the slag.

Oxidation can take place by oxygen and/or FeO in the slag.

In order to combat oxidation, mostly metals are added as anti-oxidants because of the affinity of some metals to oxygen, at the critical temperature range, is stronger than that of carbon. Each metal or metal combination has a different oxidation- resistance characteristic. By protecting the graphite and the bond network from oxidation, and through the formation of carbides and nitrides, the metals improve the elevated temperature strength, in air and reducing atmospheres.

The most popular anti-oxidants are Al, Al-Mg alloy and Si.

5.4.1 Application

5.4.1.1 Electric arc furnace (see figure 1)
Slagline, hot spots and wall

5.4.1.2 casting ladles and ladle furnaces (see figure 3)
slagline, barrel and sometimes even floors.

5.4.1.3 BOF linings (see figure 4)
Cone, trunnion, charge pad, tap pads slagline and bottom

6 Doloma Products

Doloma is obtained by dead-burning the double carbonate of Mg and Ca $(Mg,Ca)CO_3$ i.e. the naturally-occurring dolomite. First CO_2 is released from $MgCO_3$ between 300 - 600°C and then CO_2 from the $CaCO_3$ between 600-1000°C.

As with magnesia the brick products may be:

a) Fired –used in cement rotary kilns (burning zone and AOD converters.
b) Pitch-bonded and tempered
Ladle working linings
c) Resin –bonded
Ladle floors

Additions of magnesia-increases resistance to ferruginous slags

Carbon – various forms – to inhibit slag penetration
Problems: free CaO – hydration
Inversion of dicalcium silicates
Sensitive to FeO in steelmaking slags

Advantages of doloma:

- Relatively low cost in comparison with magnesia and magnesia – carbons
- Low oxygen potential-clean steel (see figure 6) – more stable than MgO.

For properties of doloma bricks (see table 9).

The variable features and application of principal monolithic Refractories

MATERIAL	FEATURES	APPLICATION
1. Castables	Refractory materials consisting of coarse and fie refractory grains, with a suitable bonding cement. Installed by pouring after mixing with water	Ladle linings Non-ferrous Industry
2. Rambles	Tempered with water and /or added with a binder, which have suitable plasticity to be rammed into place	Used around bricks to take up expansion. Dry ramming used for EAF hearts and ladle backfill
3. Gunnites	Coarse and fine refractory grains, mixed with a suitable bonding agent and installed with a gunning machine.	Used for ladle, EAf and BOF maintenance. Copper converters/ladles. Tundish coatings
4. Mortars	Fine –ground materials which are trowellable when tempered with water.	Used for laying and bonding refractory shapes
5. Slinging refractories	Installed with a slinging machine	EAF fettling

TABLE 3

CHEMISTRY OF THE SEAWATER NAGNESIA PROCESS

The seawater magnesia process is based mainly on the following reaction:

$$Mg^{++} + 2OH \longrightarrow Mg(OH)_2$$

And required the following raw materials:

SEAWATER as a source of magnesium ion Mg^{++}
LIMESTONE (DOLOMITE) as a source of hydroxide ion OH

The whole process consists of the following reactions and processes:

a. Limestone (Dolomite) CALCINATION
$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$
b. Lime (Dolomite) SLAKING and HYDRATION
$$CaO+H_20 \longrightarrow Ca(OH)_2$$

c. REACTION between seawater (Mg^{++}) and calcium hydroxide
$$Mg^{++} + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + Ca^{++}$$
d. SETTING, W.ASHING and DEWATERING of Magnesium hydroxide slurry
e. CALCINATION of Magnesium hydroxide paste
$$Mg(OH)_2 \longrightarrow MgO+H_2O\uparrow$$
f. BRIQUETTING of Magnesium oxide powder
g. SINTERING of Magnesium oxide pellets

In principle the process is very simple chemically, but unfortunately the easy chemistry of the process is complicated by several factors, mainly because:

- seawater is a very complex solution: more than 60 elements are dissolved, some of them interfering strongly in the precipitation reaction;
- limestone and dolomite, although they are abundant, are never to be found free of impurities.

TYPICAL ANALYSES OF SOME MAGNESIA

	NATURAL					**SYNTHETIC**			**FUSED**
Type	A	B	C	D	E	F	G	H	I
SiO_2	5.5	4.38	3.9	0.73	1.92	0.75	0.40	0.01	0.40
$Al2O_3$	0.70	1.26	1.9	0.28	0.50	0.18	0.20	0.02	0.20
FeO_3	0.65	1.19	0.9	0.94	0.36	0.12	0.15	0.06	0.60
CaO	1.4	1.78	1.4	1.50	6.42	0.72	1.90	0.74	1.80
MgO	88.78	90.90	91.5	96.5	98.20	97.5	97.0	99.2	97.00
B_2O_3	-	-	-	-	-	0.30	0.06	10ppm	-
$CaO:SiO_2$	0.25	0.41	0.36	2.05	3.3	1.0	>3	-	4.5
BD g/cm^3	3.25	3.18	3.21	3.27	3.34	3.24	3.44	3.45	3.53

EFFECT OF IMPURITIES
BASIC MATERIALS

MINERAL	COMP.	°C
Forsterite	2MS	1900
Monticellite	CMS	1500
Merwinite	3CM2S	1600
Dicalicium silicate	3CS	2000
Magnesia	M	2800
Lime	C	2625
Silica	S	1725

TYPICAL PHYSICAL AND CHEMICAL PROPERTIES OF A HIGH QUALITY FIRED MAGNESIA BRICK

PHYSICAL PROPERTIES	
Apparent Porosity (%)	16.5
Bulk Density (g/cm³)	2.93
Cold Crushing Strength (MPa)	35
Thermal Conductivity W/mk @ 1000°C	4.76
Hot MOR @ 1500°C (MPa)	>4
Permanent linear change 2 hrs 1500°C(%)	+0.10
CHEMISTRY (%)	
MgO	96
SiO_2	0.5
Al_2O_3	0.40
Fe_2O_3	0.30
CaO	2.3

REFRACTORY MINERALS
MELTING POINTS (°C)

Alumina	2 050
Lime	2 625
Silica	1 725
Carbon	(3 700)
Magnesia	2 800
Zircon	2 715
Silicon Carbide	(2 500)
Zircon	(1 775)
Mullite	1 840)
Doloma	2 450

CHEMICAL AND PHYSICAL PROPERTIES OF
MAGNESIA – CARBON BRICKS

CHEMISTRY(%)			
Mgo	82	76	71
Fixed Carbon	10	16	23
PHYSICAL PROPERTIES			
Bulk DENSITY(g/cm^3)	2.98	2.90	2.83
Cold crushing strength(MPa)	60	50	38
Modulus of Rupture @1500°C (MPa)	15	-	-
Modulus of Rupture @ 1400°C (MPa)		12	4

CHEMICAL AND PHYSICAL PROPERTIES OF A TYPICAL DOLOMA BRICK PITCH-BONDED

SiO2	1.3
CaO	59
MgO	38
Al_2O_3	0.4
Fe_2O_3	1.1
PHYSICAL PROPERTIES	
Bulk Density (g/cm3) As Received After coking @950°C	 2.95 2.88
Cold crushing strength (Mpa) As Received After coking @950°C	 40 25

FIGURE 1

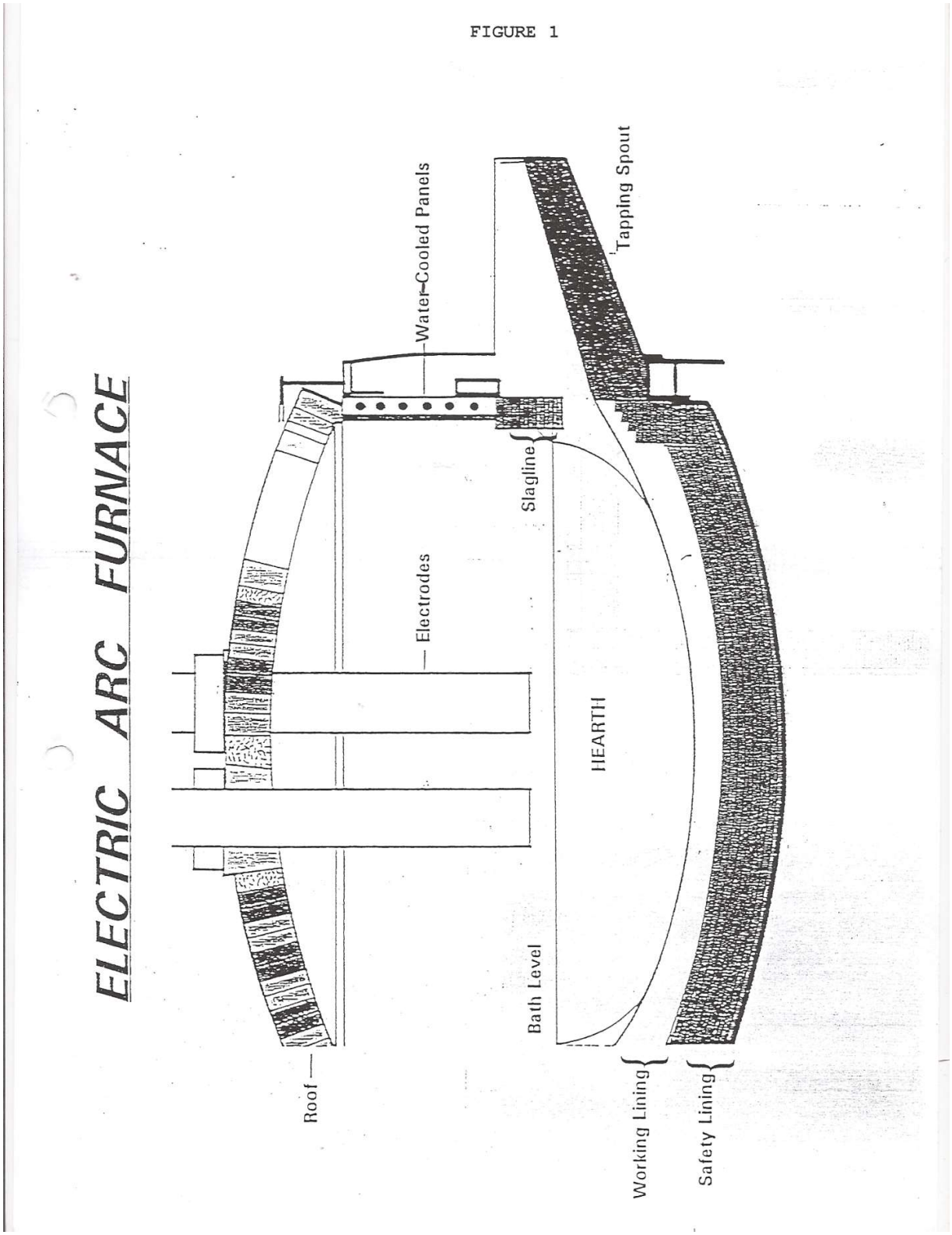
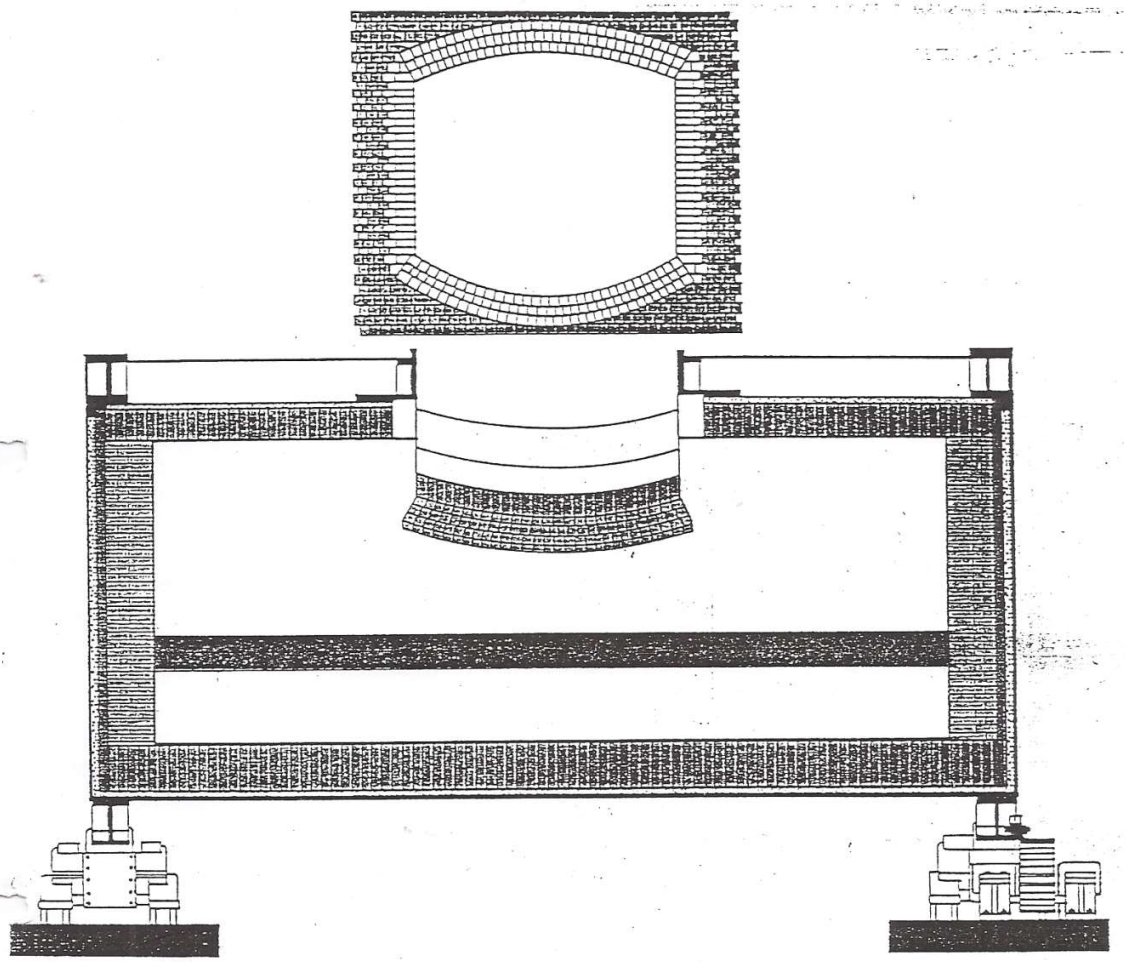
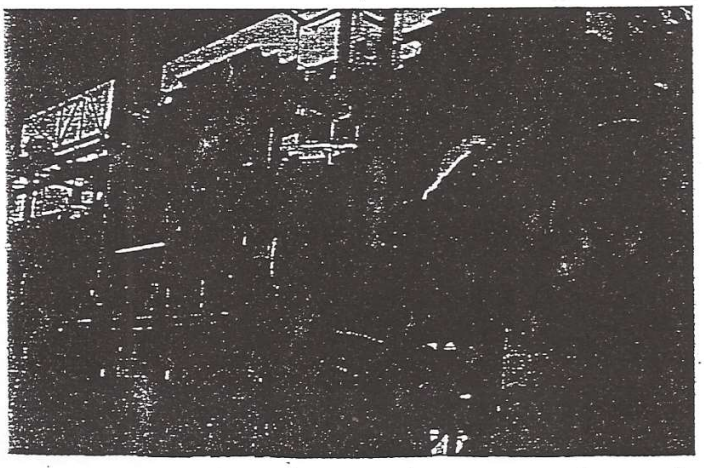

ELECTRIC ARC FURNACE
Water-Cooled Panels
Tapping Spout
Slagline
Electrodes
HEARTH
Bath Level
Roof
Working Lining
Safety Lining

FIGURE 2





Cucon

Cucon or Steel Plate

Oxrad or Cucon

S.D.

Basicon X

Throat Repairs:
Basigun 210 or Basicon X

21

FIGURE 3

STEEL CASTING LADLE

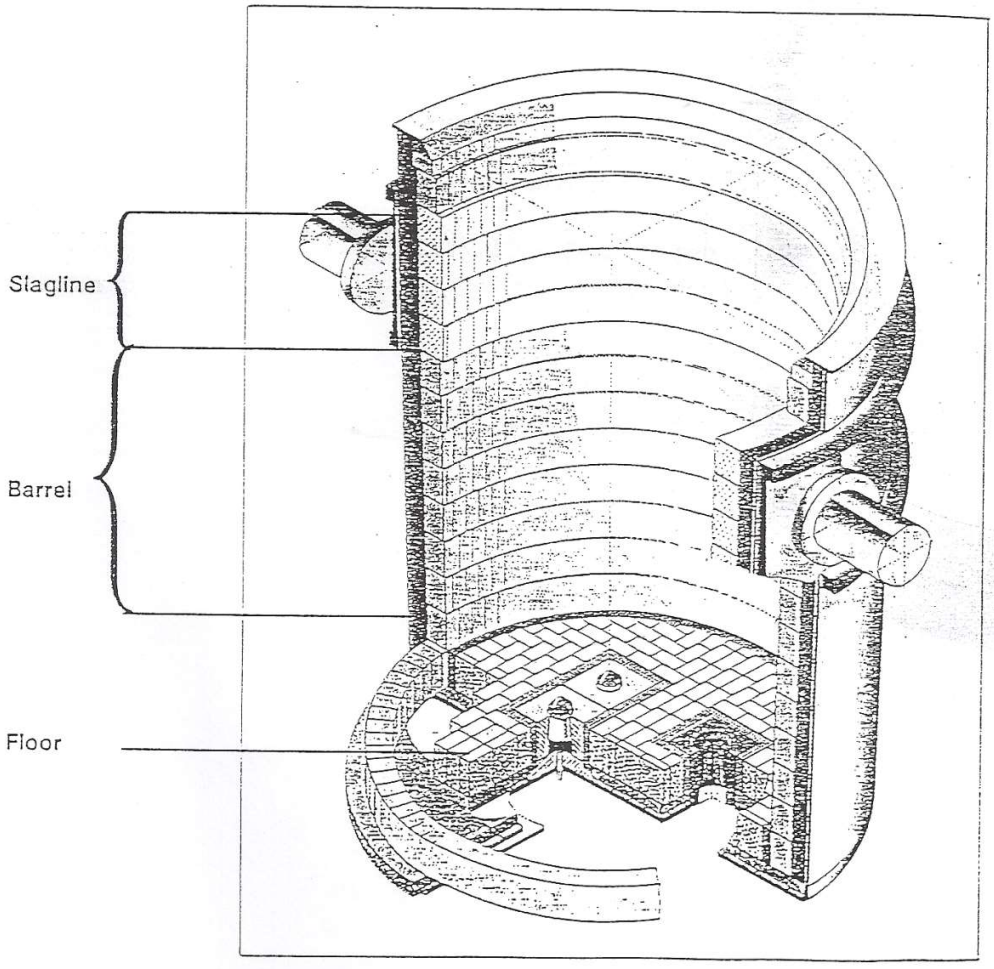
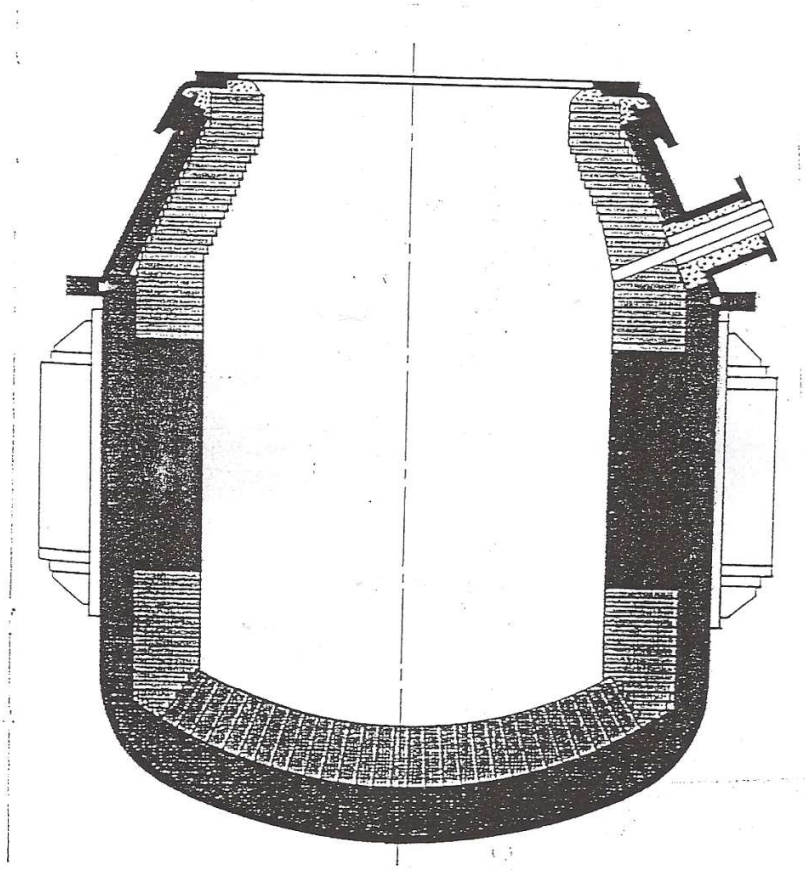


FIGURE 4

BASIC OXYGEN FURNACE
(LD CONVERTER)



EFFECT OF GRAPHITE ON THERMAL CONDUCTIVITY OF MgO-C BRICKS

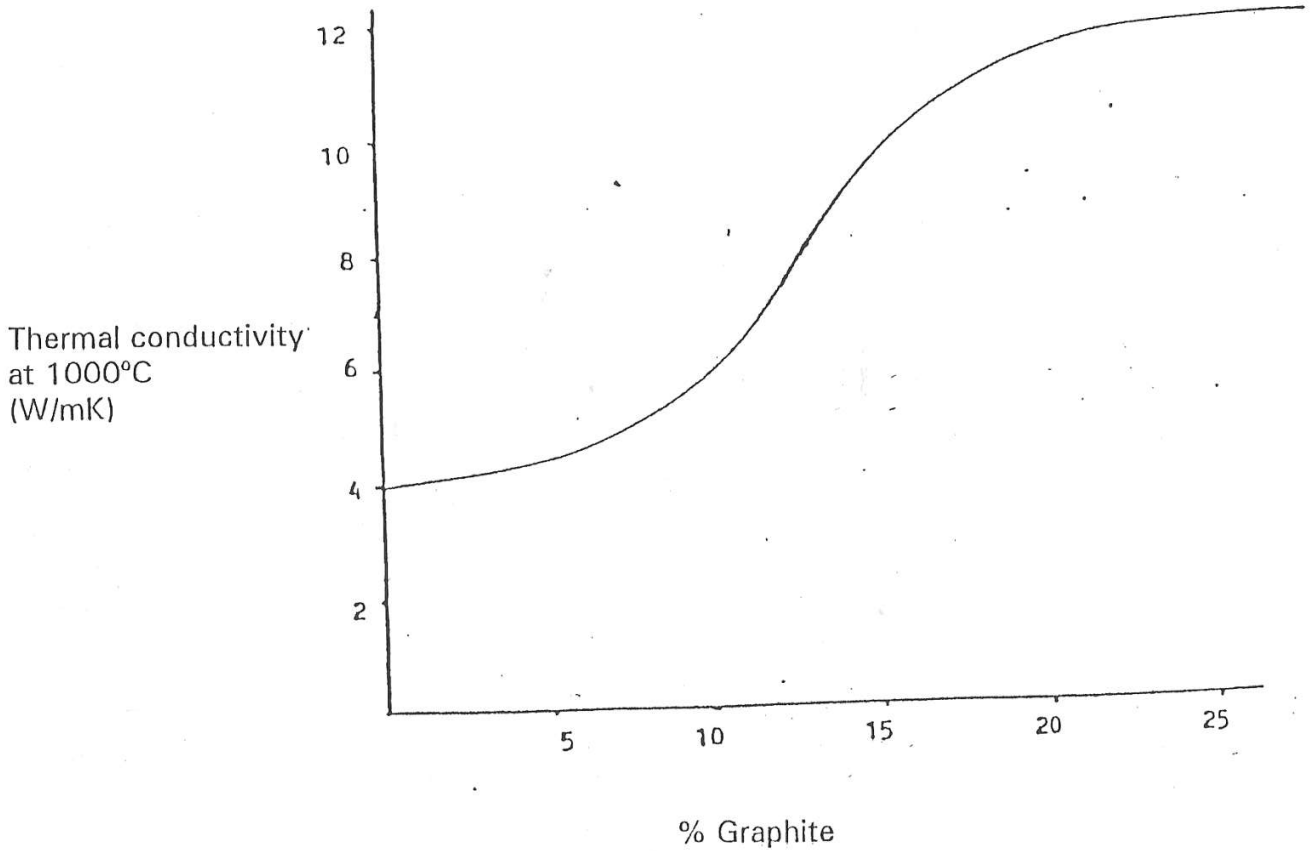


FIGURE 5

FIGURE 6

2C + O2 = 2CO
2Si + O2 = 2SiO2
Si + O2 = SiO2
4/3Al + O2 = 2/3Al2O3
2 Mg + O2 = 2MgO
2Ca + O2 = 2CaO
-100
-200
-300
F°
500
1,000
1,500
2,000
Temperature °C
Free energy of formation of the common refractory oxides

Chapter 5

Unformed Refractory Materials

What are monolithic refractory materials?

DEFINITION: monolithic refractory materials are mixtures which contain aggregates and binders prepared ready-for-use, either directly in the condition in which they are supplied, or after the addition of suitable liquids. They are usually grouped together by their methods of installation i.e. casting, gunning, moulding or ramming.

These materials may be either dense or insulating. Those mixtures having a true porosity of over 45% and a bulk density less than 1.46 g/cm^3 are commonly classed as "insulating". Mortars for brick setting and coatings are excluded.

FEATURES: more important features of monolithic Refractories are:

a. Design flexibility and easy construction of complex linings either 'in situ or by prefabrication.
b. Ready availablity, eliminating stocking of special shapes.
c. Rapid installation in difficult circumstances.
d. Freedom from joints
e. Excellent resistance to thermal shock
f. Easy provision of stable, fully-anchored structures.

BONDING SYSTEMS
As a function of the hardening process, both initially and during services, these various bonding mechanisms include:

I. CERAMIC BONDING: particularly characteristic of materials based on clays usually featuring a relatively low-dried strength which increases progressively by sintering with higher burning temperatures.

Usually applies to mouldable and ramming materials.

Also referred to as "heat-set, which is a material that sets solely with the application of heat. These products develop their bond temperature in the 980°C to 1425°C range. This "heat –set" is normally a ceramic, bond, which is a diffusion process where microscopic particles recombine **without** melting. The rate of bonding depends largely on the chemical make-up of the material and the amount of heat involved. **Heat setting materials** must be fired 'in situ' immediately after installation. In products which depend solely on heat-setting characteristics for usually due to the interaction of clay and water, which is designed to provide enough support until the ceramic bond develops. The "initial bond of clay and water will deteriorate if material is allowed to dry out prior to firing.

In a gunning mix, the addition of clay by itself is generally insufficient to hold the material until a ceramic bond develops. A "heat-set" cannot be relied upon solely for bonding a castable, as the casting would disintegrate during drying before a ceramic bond could be achieved. Therefore, while a "heat-set" bonding system is **very** important to the success of a material in the upper temperature ranges, it is generally employed by **itself**.

II. **Hydraulic bonding:** i.e. hydraulic setting and hardening at ambient temperature to produce high initial strengths. On heating, strengths may drop to varying degrees during the thermal destruction of the hydraulic bond and increase again as subsequent sintering or fluxing occurs. Minimum strengths are usually in the range 500°C to 800°C, however some materials show very little decrease in strength. Three main groups cements are commonly used:

a. Portland cement: refractory cement where careful formulation is necessary to produce satisfactory products. These materials generally suffer in service, because initial heating release free lime which rehydrates in the presence of moisture.
b. Brown High Alumina Cements: exhibit rapid hardening properties and are thermally stable. They are relatively impure and contain significant amounts of iron. The most common cement in Europe in this class is Ciment Fondu.
c. White High Alumina Cements: have much greater purity than the brown cements and can be used to higher temperatures. Iron contents are usually low and some cements are suitable for reducing and CO atmospheres. Several products of this type are available, having particular characteristics which must be examined before selection for a particular application is made.

In some cases, ceramic bond temperatures are never reached (low temperature in service and the hydraulic-set ends up as the sole bonding mechanism. A successful installation of a material with this type of bonding system is greatly dependent upon the application procedures followed. Failure to follow the simple rules and precautions necessary can result in a weak and/or faulty installation. One of the most important steps in the installation of any hydraulically-set material is the water addition and subsequent mixing. Small quantities can be mixed by hand, but mechanical mixers or even concrete trucks may be necessary for large applications. No matter what the method is, it is important the refractory and the proper amount of water mixed uniformly, since dry lumps in the casting will weaken the structure. Too little water can result in excessive densities and produce a mix that is too hard to work. In an extreme case, too little water may not provide enough to fully hydrate the cement, resulting in a weak bond. The recommended amount of water should always be adhered to closely. The elapsed time between water, mixing and placing should never exceed 30minutes-a longer period will reduce the strength of the bond. The other, standard rules and precautions regarding the application, curing and firing of hydraulically-set products are also **extremely** important for a successful installation.

III. Chemical, mineral or organic bonding:
Involves hardening by chemical other than hydraulic reaction at ambient temperatures (= air-setting), or at some temperature below that of sintering. The most common of these are based on phosphoric acid and its derivatives. This bonding produces high strengths when heated to temperature above about 150°C. Other bonds of this type are aluminum sulphate and sodium silicate. These air-setting products also develop a heat-set or ceramic bond at higher temperatures, which produces their maximum strengths.

IV. **Organic bonding:** Hardening at ambient or higher temperatures. This type of bonding is not widely used on its own, but may be included to modify the rheological properties of other bond types.

V. **Special bonds:** in addition to the previously-mentioned bond types I-IV, there is an increasing number of special bonds which may be based on one or more of the first four types, but with modifications to produce special properties. For example, there are a number of low-cement castables on the market, which exhibit a more uniform strength to temperature relationship than with normal hydraulic bonding. These products are usually more critical in application and the manufacturers' procedures must be strictly followed.

Metal fibres may be added to form a modified bonding of the castable.

GROUPING
Ramming Materials: are relatively free-flowing before use. They comprise refractory aggregates, binders, and if necessary, liquids.
The bond form may be (I) (III) or (IV).

The installation is by mechanical ramming behind shuttering. Hardening is usually by heat.

MOULDABLE Materials (Plastics): supplied to a plastic consistency ready-to-use. They contain refractory aggregates, binders and liquids are developed as soft cakes, slab or unformed masses.

The bond form is (I), (III) or (IV).
Installation is normally by chemical ramming, together with hardening by heat.

CASTABLE MATERIALS: mixtures of refractory aggregates and binders. They are delivered dry and are used after mixing with water or other liquids.

The bonds form is (II) or (III).

They are placed by vibrating, tamping or possibly ramming.
Bonding and hardening occurs without heat.

Castables:
There are several different types of castables:

Castables

Conventional	low cement LC	ultra-low cement ULC	cement-free
15-25%	3-8% cement	<3%	0%

Easy to install ⟶ good installation needed

Not very refractory ⟶ very refractory

Comparison of typical properties of these castables:

		1600	1600LC	1600ULC	1600 Cement Free
Porosity Fired 1000°C		22	18	17	17
CCS (MPa)	110°C	60	80	50	25
	1000°C	45	80	50	80
	1500°C	130	120	70	80
Chemistry: CaO		5,4	2,2	0,8	trace

GUNNING MATERIALS: mixtures which are free-flowing before use, specifically prepared for placing by pneumatic or mechanical projection. They may be supplied ready-to-use complete with binders, or require the addition of water or liquids before use.
Bond type may be (I), (II), (III) or (IV).

FETTING: dry graded refractory aggregates, which are normally placed manually onto a hot furnace hearth as a protective coating.

MORTARS: refractory binders used for jointing refractory bricks. Mortars can be of the "heat-set" or "air-set" type.
The bond is formed (I), (II) or (III).

AGGREGATE SELECTION
The purpose of this section is to briefly describe the main materials available as aggregates to the manufacturer of monolithics.
The materials have been classified under three general headings namely:

- Naturally-occurring materials;
- Naturally –occurring materials requiring heat treatment and synthetics
- Lightweight materials.

A refractory aggregate can be defined as follows:

A granular material which can be united by a bonding medium to form a solid mass.

NATURALLY-OCCURING AGGREGATES
This group includes all refractory aggregate which do not require any form of heat treatment such as calcination, to render them suitable for use. In most cases, however, they require some type of beneficiation and processing to make them suitable for use in Refractories.

SILICA SiO_2: silica aggregates are used to produce a wide range of acid monolithic including ganisters and san sling compositions.
ZIRCON SAND $ZrSiO_2$: Zircon sand is recovered from heavy mineral-bearing beach sands which contain around 2% zircon. A beneficiation process is used which upgrades the initial feed to a heavy mineral content of more than 95%.

Chrome ORE: this is a naturally-occurring material containing chromium, iron, aluminium, magnesium and oxygen, combined together in complex solid solution called spinels. Associated with these spinel phases are gangue ores, chiefly of a siliceous nature.

Chrome Ore is found in the USSR. Turkey, Cyprus, the Philippines, South Africa/Zimbabwe and North America, but the major UK suppliers come from the Transvaal and the Philippines.
The various deposits vary widely in both physical and chemical properties, for example the spinel phase of the Philippine Ore consists of Cr_2O_3 with Fe2O3 as the main secondary oxide.

ANDALUSITE: the only member of the andalusite –kyanite sillimanite A-K-S group of minerals which can be used without prior heat treatment.

It is an alumino-silicate with an Al_2O_3 content of 50%-60% and on heating forms stable mullite and cristobalite

HEAT TREATED MATERIALS
The group of materials referred to as 'heat-treated' includes naturally-occurring materials which are calcined before they are used synthetic materials which are produced from other raw materials, the action of heat being an important aspect of the production process.

DOLOMITE $CaMg(CaO_3)_2$: consists of a mixture of $MgCO_3$ and $CaCo_3$ molecules. In the pure form, equal molar proportions of both carbonates are present, but in nature they are vary widely and associated impurities such as SiO_2, Al_2O_3 and FeO_3 are generally present.

In order to produce a refractory aggregate, the mined dolomite is first dead-burned in rotary kilns at temperatures around 1800°C and then crushed and graded.

Magnesia is also produced from seawater by a precipitation process.

SILICON CARBIDE: produced form a mixture of high purity silica sand carbon, generally being in the form of finely- ground petroleum coke.

ALUMINO-SILICATE AGGREGATES 20% - 45% Al_2O_3: Usually includes flint clays, chamottes and calcined kaolins, which are produced from raw alumino-silicate clays extracted from the ground by various mining methods and then processed into a form suitable for calcinations.

For calcining in tunnel kilns, the raw clays are normally processed into briquettes or dobies which are stacked onto the kiln cars and passed through driers to reduce the moisture content to less than 1% before entering the kiln. The calcining cycle can take up to four days, each kiln car remaining in the hottest zone of the kiln for around 25% of this time. For rotary calcining, the raw clays are calcined in rotary kilns which can be 150 feet or more in length. For both tunnel and rotary kiln calcining, the temperatures are governed by the type of material being processed and are usually in the range 1400°C-1600°C.

BAUXITE 80% - 88% Al_2O_3: formed by a weathering process known as laterisation of alumina-bearing rocks on elevated land in monsoon climates. Over a long period, the more soluble constituents including a high proportion of the silica have been leached out to leave bauxite which consists of various hydrated forms of alumina, monohydrates, and ferric oxides. Open-cast mining methods are employed to recover the refractory grade bauxite. The cleaned lumps are then dried and calcined rotary kilns at a minimum temperature of 1600°C. During the calcinations process the alumina hydrates are converted to alumina and alumina-silicate hydrates to mullite.

TABULAR ALUMINA 99, 5% Al_2O_3: first developed during the Second World War as a sparking plug insulator and become available as a steel making refractory form the late 1950's.

It is manufactured by forming dense 2cm spheres of calcined alumina and then firing these spheres to around 2000°C. The effect of the high temperature treatment on the spheres is to collapse the pore structure of the calcined alumina by recrystallisation, followed by grain growth of the crystallites to between 20and 40 times their original size. The resulting material is a high density, insert dead-burned $\propto -Al_2O_3$, which is then processed further into suitable aggregate sizes for refractory applications by crushing, grading and milling.

Fused Alumina 99, 5%Al_2O_3: Originally developed for use as an abrasive by an American, Charles Jacobs, in the late 1890's. He produced fused grain alumina by reducing bauxite in an electric arc furnace.

There are two main varieties of fused alumina, namely brown and white. Brown fused alumina is produced by the reduction of bauxite in a Higgins furnace, the bauxite usually having alumina content in excess of 86%. Due to intricacies of the process, other constituents must be kept within close limits. White fused alumina is produced from calcined alumina already prepared from bauxite via the Bayer Process, with fusion occurring in a Higgins-type furnace.

Fused Mullite $\underline{3Al_2O_3.2SiO_2}$: Two types are usually available, one being produced from bauxite plus kaolin and the other from alumina and silica.

The type of fused mullite to be used depends upon the application, since the bauxite-based product contains rather more impurities than that of the calcined alumina-based product.

Sintered Mullite $3Al_2O_3.2SiO_2$: A synthetic aggregate having a well-developed mullite structure, with a density approaching the theoretical value and very low glass content. In the production of sintered mullite,the aim is to produce a material of consistent quality under controlled conditions. Temperatures of about 1750°C are employed during the firing cycle.

LIGHTWEIGHT AGGREGATES
These are used in the preparation of insulating monolithic, chiefly castables. A few aggregates used in this application are described in the following section.

VERMICULITE: has a mica-like structure with the property of expanding rapidly when subjected to shock heating. This property is called 'exfoliation' and occurs when the interlayer water converts rapidly to steam, causing disruption of the structure with a resulting expansion up to 15 to 20 times the original thickness.

Perlite: described as any acid volcanic rock containing 2% to 6% of combined water. Commercial grades contain silica levels between 71% and 75%, alumina between 12, 5% and 18% and alkali content between 8,0% and 9,0%. These rocks have the ability to expand when treated rapidly to the softening point of the glass. Expansion occurs because the combined water is evolved as steam and the rapid heating cycle is controlled, so that this evolution of steam causes the softened crude particles to bloat or 'pop'.

DIATOMITE: composed almost wholly of the skeletal remains of diatoms, which are minute aquatic planktons with external siliceous skeletons. This material is found deposited in beds, either in the form of a soft rock are as wet "boggy" material.
Raw mined diatomite can be used in certain applications without complex pre-treatments, although it is desirable for most applications to use a calcined product. Calcining is normally carried out in rotary kilns at temperatures around 1000°C.

Bubble Alumina Al_2O_3: produced from fused calcined alumina, by subjecting it to controlled air or steam pressure during a teeming process. Conditions of the manufacturing process such as alumina quality melt temperature, teeming rate, air or steam pressure and their configuration are all critical factors in controlling the quality of the resultant hollow spheres of fused alumina. These spheres or bubbles are then sized into suitable aggregate size distributions for refractory applications.

Reclaimed refractory materials as aggregates.

One should proceed with caution when considering reclaimed materials for crushing and grading as aggregates for producing monolithic refractories. Obviously all contaminated slag adhesions must be carefully removed and the physical operation of undertaking this work is not always done with

the care which should be applied, purely and simply from a cost point-of-view. When the work is carried out properly then reclaimed materials have a very useful function to perform.

The following materials are used:

- Hard electric insulators are used as abrasion-resistant materials in low temperature castables.
- Reclaimed firebricks in the ranges from 28% alumina to 42/44% alumina are used in mid-temperature castables.
- Reclaimed sillimanite blocks and bricks are used for similar purposes.
- Reclaimed bauxite bricks, next to firebricks, probably constitute the largest usage and there are claims made that bauxite bricks which have been additionally fired during usage produce aggregates which have less expansion problems than those associated with the use of bauxite in its virgin calcined form.

Basic materials are used for fettling and gunning mixes.

RAW MATERIALS CLASSIFICATION

TYPE	**NATURE**	**RAW MATERIAL**
Siliceous	Acid	Quartzite Silica and
Alumino-silicate	Acid	Clay Chamotte Andalusite Kyanite Synthetic Mullite Bauxite
High Alumina	Neutral	Brown Fused Alumina White Fused Alumina Sintered and Tabular Alumina
Chrome	Neutral	Chrome Ore
Magnesia	Basic	Natural Seawater Magneisa
Doloma	Basic	Dolomite Sinter
Silicon Carbide	-	Silicon carbide
Carbon	-	Graphite Carbon

SUMMARY

Aggregate for Castable

- Dependent upon temperature of application
- Type of application

Temperature: e.g.

- Lower temperatures (1100°C to 1500°C)
- Various grades of brick grog and chamotte
- Medium temperature (1600°C)
- High quality chamotte, andalusite
- High temperature (1700°C +)

- Bauxite, tabular alumina

Insulation: Refractory castables are often required for heat insulation properties, where lightweight porous aggregates are required e.g.

- 900°C vermiculite
- 1300°C Expanded clay
- 1700°C bubble alumina

Abrasion-resistance: The ability to resist mechanical abrasion is imparted by hard, dense high mechanical strength aggregates e.g.

- Low temperature-natural corundum or slag
- Medium temperature –andalusite or dense chamotte
- High temperature –tab alumina or zircon alumina

Chemical resistance: the chemical composition of the aggregate becomes important where the chemical environment is severe e.g.

- Basic aggregates (magnesia or chrome-magnesia) for resistance to basic slags.
- Very low Fe contents for CO atmospheres.

TEMPERATURE CLASSIFICATION

There is presently no widely recognized and accepted method for the temperature classification of monolithic refractories. However, classification based on PLC (permanent linear Change), determined by one of the approved test methods such as BS1902, and is frequently used.

Chemical analysis may be significant for some applications, but any classifications, based upon such analysis is often misleading and a full appreciation of all the characteristics is essential.

SELECTION

A. Consideration of all environmental conditions: in most areas of refractory of insulation application, a single physical property of the selected materials such as service temperature limit, insulating importance. It is extremely rare, however, to find a service area in which only one ambient condition, which could be detrimental to the selected material, is present. It is therefore advisable to consider all of the conditions which can affect the lining material in service. When this has been done, it should be possible to select a product with the combination of physical properties which will accomplish the primary function, in addition to resisting deterioration from various other severe conditions in the service area.

   Some conditions of concern which can have an effect on refractory or insulation materials in services are the following:

   1. Extreme temperature: exposure to temperatures beyond limitation of a refractory material can cause letting and failure under load.
   2. Thermal shock: extreme or rapid temperature fluctuations in services can cause disintegration and spalling of refractory linings. Some materials are better designed to handle cyclical services than other products.

3. Mechanical stresses: abnormal vibration can cause the rapid deterioration of some materials. Stress due to the expansion and contraction of the refractory structure can cause the loss of lining integrity, unless allowances for these conditions are included in the unit design.
4. Abrasion: Severe wearing of refractory lining can result from solid objects 'scouring or rubbing' on the lining surface.
5. Erosion: the movement of hot metallic phases in liquid form can 'wash' or erode refractory linings. Extremely fine particles (fly ash catalyst, etc.) being conveyed at high velocities in an air or gaseous stream and impinging upon lining surfaces. Can wear away refractory materials.
6. Chemical attack: some fuels contain impurities which can react with various refractory material components, causing 'slagging' and failure of the refractory lining. Alkalies and acids can, under certain conditions, involving temperature and dew point attack the components of a refractory lining causing and deterioration.
7. Reducing atmospheres: at certain temperatures, atmospheres containing hydrogen can cause a reduction of the silica contained in many refractories ($H_2 + SiO_2 \rightarrow SiO + H_2O$), resulting in lining decomposition. At certain temperatures, atmospheres containing carbon monoxide can result in a carbon build-up around the iron sites in a refractory material, causing spalling or deterioration of the lining.
8. Conductive gases: Some industrial process require the use of protective atmospheres, composed of various amounts of hydrogen and other highly conductive gases flowing through refractory-lined vessels and pipes. The use of these gases greatly increase the thermal conductivity of the lining materials and if not allowed for in the lining design can result in excessive shell temperatures.

B. Materials costs: it is only natural that economics must play an important part in any operation. However, one refractory or insulation materials is extremely low when compared with the costs of labour, equipment and most importantly, lost production time which can result from a premature lining failure.

   The main concern should always be the selection of the correct type of materials which will perform the services desired in the best manner possible. After this selection has been made, economics can be considered.

C. Acquire professional advice: Refractory and insulation product manufacturers and applicators are professionals in their field, and are usually well-informed regarding new materials and special application techniques. Most manufacturers are more than happy to offer comments and advice regarding product selection and application. Since the majority of this is offered on a no-charge basis, it is certainly advisable to take it into consideration.
D. General considerations: it is not possible to lay down "hard and fast" rules for the selection of the most suitable monolithic refractory. For example, it may be that in some particular application a mouldable refractory performs better than a castable.

However, because working time on site is limited a castable is preferred to a mouldable, as it can be placed more speedily, although curing time is still subsequently required.

Broadly speaking, a mouldable is the more resilient product and so better able to accommodate severe temperature gradient fluctuations and certain types of mechanical abuse. Castables have greater rigidity and are usually more suitable for thinner sections. Gunning grades behave similarly to castables.
Phosphate-bonded mouldables usually develop their strengths at lower temperatures than the more common clay-based materials and may also exhibit greater resistance to iron oxide slags.

E. Selection table: provides a guide to the choice of suitable product. After selection the correct installation and commissioning procedures are set out in the manufacturer's instructions, or the agreed installation specification must be followed.

Typical grade selection guide

Installation and Operating feature	Grade Performance		
	Mouldable	Dense Castable	Insulating Castable
Bulk density	High	High	Low
Strength impact Strength abrasion	Very good Fair	Good Good	Poor Poor
Thermal shock Resistance	Excellent	Very good	Good
Thermal insulation	½-¾ that of firebrick	½-¾ that of firebrick	$^{1}/_{5}$ - $^{1}/_{3}$ that of firebrick
Slag resistance	Increased with Al_2O_3 content	Increases with Al_2O_3 content	Poor
Minimum section thickness	90-100mm	50m	5mm
Storage life	6-12months	6moths	6months
Site mixing required	No	Yes	Yes
Installation method	Ramming or Trowelling	Casting, gunning or trowelling	Casting, gunning
Curing	None required	24hrs	24hrs
Air drying 100°C-130°C	Up to 12hrs	Up to 12hrs	Up to 12hrs
Initial heating rate	50°C/hr	25°C/hr	25°C/hr
Wall shuttering	None required	Casting -yes Gunning -no	Casting - yes Gunning - no
Roof shuttering	Yes	Casting - yes Gunning no	Casting - yes Gunning - no
Installation Rate Walls Installation rate roofs	Moderate Slow	Fast Fast	Fast fast

Anchoring systems

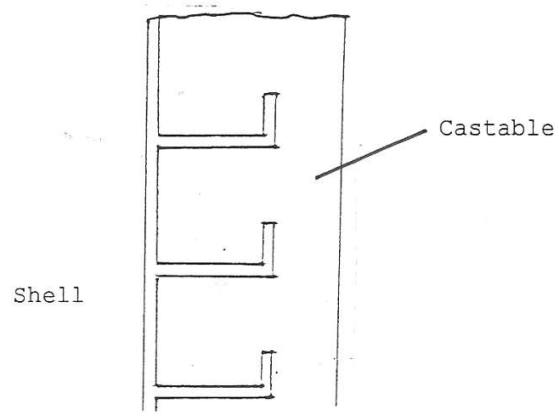
Almost all monolithic constructions require some form of anchoring device. An anchor system must be designed to provide robust anchorage sufficient

flexibility to eliminate structural failure, resulting from differential thermal expansions and movements between the metal and the refractory.

Where metal parts occur in the anchorage, they must be heavy enough to support the loads to which they are likely to be subjected, but not so heavy as to conduct excessive heat through the lining, so causing external temperatures and loss in thermal efficiency.
Detailed design of anchoring system is important when considering installation procedures and freedom for thermal movement service.
Types of anchor: anchors in heat resistance alloys steel are available for use to working temperatures of about 1100°C. For higher temperatures, a more satisfactory anchorage is based upon pre-fired anchor bricks. These projects through the lining to the working face where strengths are higher, whilst allowing their metallic components to be at much lower temperatures.

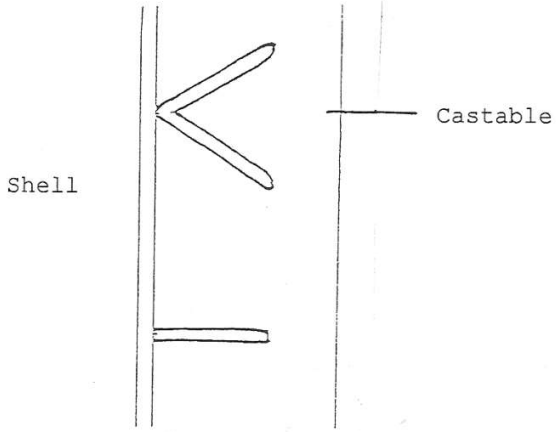
TYPICAL METAL ANCHORS

L ANCHORS



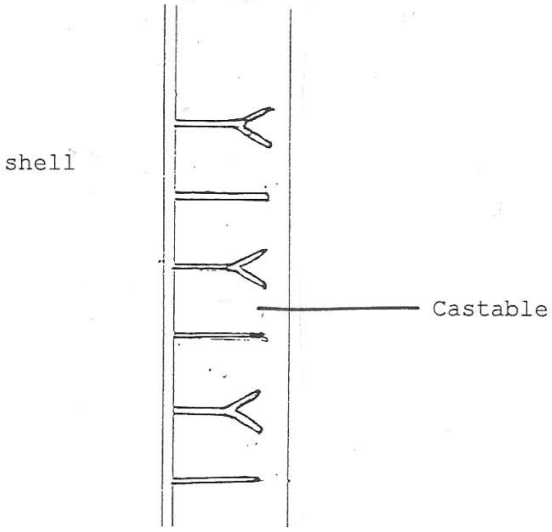
Used for single layer linings where strong support is needed.

V ANCHOR



Used for single layer castable linings requiring strong support, or when close fitting is needed.

Y ANCHORS



Y anchors are used for multi-layer linings, or for thick single layer linings.

Other anchoring systems

Weld mesh
Hexagonal Mesh
S Anchors
Ceramic anchors on steel hangers

A good system is essential for satisfactory lining performance. Detailed advice on anchor type, thickness and spacing is available anchor or refractory manufacturers'.
Anchor spacing: it is important design principle that anchors retain the factory lining to the furnace casing. The anchors do not support the lining except when used in a suspended roof construction.
Typical recommendations for centre spacing include:
Walls
Metallic anchors 300mm (12")
Refractory anchors 375-450mm (15"-18")
Roofs
Metallic anchors for lining
Thickness below 125mm (5") 200mm (8")
Metallic above 125mm (5")
Refractory anchors 300 – 350mm (12" – 14")

Application
The proper performance and maximum service life of any castable refractory or insulating lining is greatly dependent upon proper application methods. The following information may be used as a guideline regarding these methods:

A. Trowelling: Some monolithic refractory and insulation applications call exclusively for trowel work. Those that usually require trowelling of a highly plastic material, are concerned with insulating or coating the exterior area of a fired or heated vessel, duct, tank, etc. one exception to this rule is fireproofing, which normally requires a large amount trowel finishing over unheated structural areas. In this case a smooth, low porosity finish is desirable to achieve weather-resistance and an attractive appearance.
   A popular application method termed "slap-trowelling" is accomplished by throwing quantities of metarial with the trowel or by hand against the area to be insulated. Materials applied in this manner are sometimes completely mixed and then allowed to "sit" for 10 to 20 minutes before application. This allows the bonding action to get underway, so that the material becomes more "plastic" and will adhere more readily to the surface upon which it has been thrown. This method is often used in tight access areas where other methods are impractical.

   Surface coating of bonding mortars, castables, or special coating materials are sometimes applied with the trowel over existing furnace or vessel linings. This is usually undertaken to protect and/or repair deteriorating lining surfaces and is considered only as a temporary measure.

B. Hand-packing: commonly used to install materials in hex-steel reinforcing and wire mesh, when either the materials is not gunnable or the working area is limited. Many abrasion – and erosion-resistant linings are applied in this manner. With this method the material is spread over and packed into the hex areas by hand and then finished level with the top of the hex-steel. In some cases, the applicator will finish the job with "skim" coat, which covers both the hex-steel ends and the hand-packed material. This is not a recommended practice, as many times the expansion of the hex-steel ends during heating will cause the skim coat to 'spall off', sometimes taking with it material from the individual hex sections. During gunning operations, limited access areas such as flange necks, etc. are often hand-packed to insure void-free lining **integrity.**

C. **Casting**: a popular method of monolithic refractory application used basically when special shapes such as burner blocks are desired, or horizontal areas such as floors, etc. are to be protected. Certainly, much casting is still carried out involving walls, arches, ductwork, etc, but the majority of this type of construction is undertaken with a pneumatic gun. The formers necessary for any casting should be coated with oil, grease or polyethylene to prevent water migration and bonding of the material to the formers. The manufacturer's recommendations regarding water addition should be followed as closely as possible. Too much water mixed with the material can greatly affect not only the setting characteristics, but also the strength of the material in service. Too little water can make the material hard to properly work into the former and can result in weak areas where proper cement activation has not occurred. A good method of ensuring proper casting consistency is to form a ball of material with the hand and toss it a few inches or so into the air, allowing it to land on the palm of the hand. If the ball of material breaks or crumbles it is usually too dry, whereas if it flattens completely and flows between the fingers, it is too wet. The ball of material should flatten somewhat, but remain intact to indicate a good casting mixture. Only chemically clean water should be used, as impure water can contain compounds which will adversely affect the performance of the castable. A good rule to follow is to always use water that is approved for human consumption. The temperature of the mixing water should be between 15° and 25°C, unless abnormally cold or hot water is being used to aid proper setting under extreme ambient conditions. Correct mixing of the required water with the dry castable material is important to ensure proper cement activation throughout the casting. This mixing can be accomplished by hand with a mortar box, or mechanically with the use of a mortar or concrete mixer, the paddle-type mortar mixer being the most efficient.

It is recommended that work of any size be accomplished using a mechanical mixer. Normally, one to three minutes of mechanical mixing is considered adequate and the material should then be placed as soon as possible.

Over-mixing, or the addition of more water to re-mix the material, can result in greatly reduced-strengths, or failure of the castable in service. Any material left in the mixer for more than 20 minutes should be discarded.

Extreme care should be taken to avoid “honey-combed” or void areas in the casting. This may be carried out by hand-rodding, or mechanically vibrating the material as it is placed. The majority of the trapped air will occur near the formers, and these areas should be “worked” carefully. Exterior vibration of the formers themselves can be beneficial, and this can be done quite well with either a pneumatic tool such as a chipping gun, or by hand with hammer. It should be understood that mechanical vibration does tend to compact the material and “even working” can result in a denser lining than was originally desired.

D. Pumping: the use of positive displacement pumps is extremely advantageous in some areas of castable material application. The materials applied with this method are usually of the lightweight, fine aggregate type. With this procedure, the material is completely mixed and placed in the pump’s feed hopper, from where conveyed by the pump mechanism through a hose to the nozzle man for placement. At this point, in many cases, additional air is added to facilitate placement. The application pressure created by the larger pumps can approach those of conventional pneumatic gunning, allowing firm placement on a vertical structure. The primary advantage of this method is that the material is completely pre-mixed with an amount of water approaching the “casting” ratio, which results in lighter gunned weights and greatly-reduced rebound when compared with standard pneumatic gunning.
E. Pneumatic gunning: the dry or “nozzle mix” continuous feed gun is at this time the most popular type used by commercial applicators, because of its volume capability and low maintenance requirements. The “wet” and “batch” guns, while offering some advantages, have limited capacity and operating capabilities which make them uneconomic for general construction use. The continuous “nozzle mix gun produces a constant use. The continuous allowing a tremendous amount of castable to be placed in a relatively short period of time. The material to be gunned is usually pre-mixed with a certain amount of water in order to prevent excessive dusting, pre-active the binder and ensure lower rebound loss. The percentage of this pre-wet water is normally 3 to 10% by weight according to the type of material and the manufacturer’s recommendations should be carefully followed. “Rebound” or “cut-back” material should never be re-introduced into the gunflow as it will greatly upset the designed aggregate balance of the castable, resulting in poor installation. It should be noted that the final resultant gunned weights of any castable can vary considerably. These weight variations are dependent upon gun pressure, pre-wet water additions, distance of the nozzle man from the applications area and amount of water added by the nozzle man, can be controlled to some extent by the applicator. Pneumatic placement is a “craft” just as welding, pipe fitting, etc. The choice of a competent applicator can mean the difference between the success or failure of an installation.
F. Ramming: both ramming materials and mouldables are normally placed by techniques.
Workability is sensitive to moisture content and ready-to-use materials must be stored in a cool place to prevent the loss of moisture.

Pneumatic rammers of suitable size are preferable to hand-rammers. A long stroke of 65mm and a frequency of 1200 strikes per minute are adequate for most applications.
For mouldables (plastics), a rubber butt of 75mm diameter is preferred to steel or cast iron ramming head due to the lower risk damage to the anchoring system.
For ramming materials (which have a lower moisture content than mouldables), a proper high density can only be achieved if a V-shaped ramming head is used.
For ramming materials (which have a much lower moisture content than mouldables) a proper high density can only be achieved if a V-shaped ramming head is used.

CURING

Most castable refractories and insulation are formulated with "hydraulic" binders. This means that mixing with water and for some time thereafter, a chemical reaction occurs between the water and the cement. This reaction builds up heat within the body of the castable and results in the material taking a "set" or hardening. The time during this reaction takes place is generally referred to as the "curing period" which is very critical. If the material is to attain its designed physical properties, certain procedures must be followed namely:

1. The "curing period" begins immediately upon material application and should last for a minimum of 24 hours after the last segment of castable lining has been applied.
2. The ideal ambient temperature range for curing is 25°C+, but in any case, should be no lower than 10°C nor higher than 32°C without special precautions being taken.
3. If ambient conditions consist of high temperature and low humidity, it is recommended that either a water spray or membrane-curing compound be used in order to prevent the loss of water necessary for the hydration of the material. Such water loss can result in greatly strengths and possible failure of the installation.

DRYING

A cured, but unfired castable material still retains a large amount of water in its physical structure. If the presence of this water is ignored and the material is brought rapidly to service temperature, a build-up can occur within the material. This steam build-up can cause spalling, severe rupture, or an explosion, thereby destroying the integrity of the lining. It is for this reason that "drying schedules" are recommended for use in preparing a castable lining for service. A "drying schedule" is designed to heat-up the castable at a slow controlled rate in order that moisture present in the castable material can convert to steam and "bleed through" and out of the castable at a safe rate. These schedules must take into consideration not only the lining thickness, but also the density and/or porosity of the material being dried. It is important to note that "drying schedules should not commence until complete curing is attained. The "drying schedules" that follow concern only random lining thickness. It is recommended that the material manufacturer be contacted for "drying schedules" concerning lining thickness and designs.

Venting of the surface of installed castables and ramming materials can assist in the drying operation. Steam evolved during heat-up can force 'slabs of material off the hot face of the lining unless vent holes provide a means of escape. Using a 5mm diameter rod, holes are made at 10

to 20mm centres and the rod pushed fully into the plastic to a depth of up to 230mm.
For thicker walls, vent holes are made to minimum 230mm depth or alternatively to half the wall thickness.
Where plastic is rammed directly onto the steel casing, vent holes are made for the full depth of the plastic material.

Recommended heating-up schedule for castables

a) Ambient -130°C to 10°C per hour
b) Hold for a minimum of 12 hours
c) 130°C – 300°C at 15°C per hour maximum
d) 300°C – hold for 10 hours minimum
e) 300°C-700°C at 35C per hour
f) After 700°C at 50°C per hour

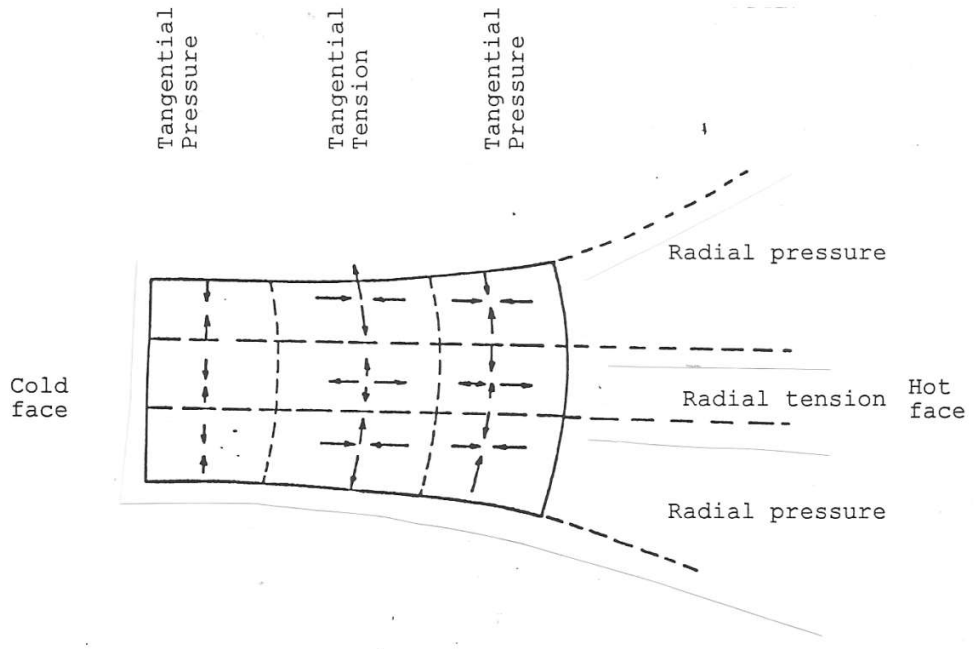
Joints – surface expansion cuts
Where joints are required by the designer, then should be formed and located as shown on drawings, although they should never coincide with the anchor positions. One should, however, be cogniscent of the fact that in practice the moisture content after air drying is higher than in laboratory tests, as, in most cases the humidity is higher than in a laboratory. On the other hand, in installations only one surface can give off water, whereas in a laboratory test the test body is exposed to air currents on all sides.

The following "rules of thumb" can be established:

- The lighter refractory concrete is, the more easily it will dehydrate.
- In dense refractory concretes the residual water contents are equally high, independent of the raw density.
- Ceramic materials are more easily dehydrated than chemico-ceramic materials.

In most cases however. The installations are heated-up according to the temperature gradient. In this case in addition to the problem of steam pressure, there is also the problem of a differentiated reversible thermal expansion, which shows itself in a build-up of stresses.

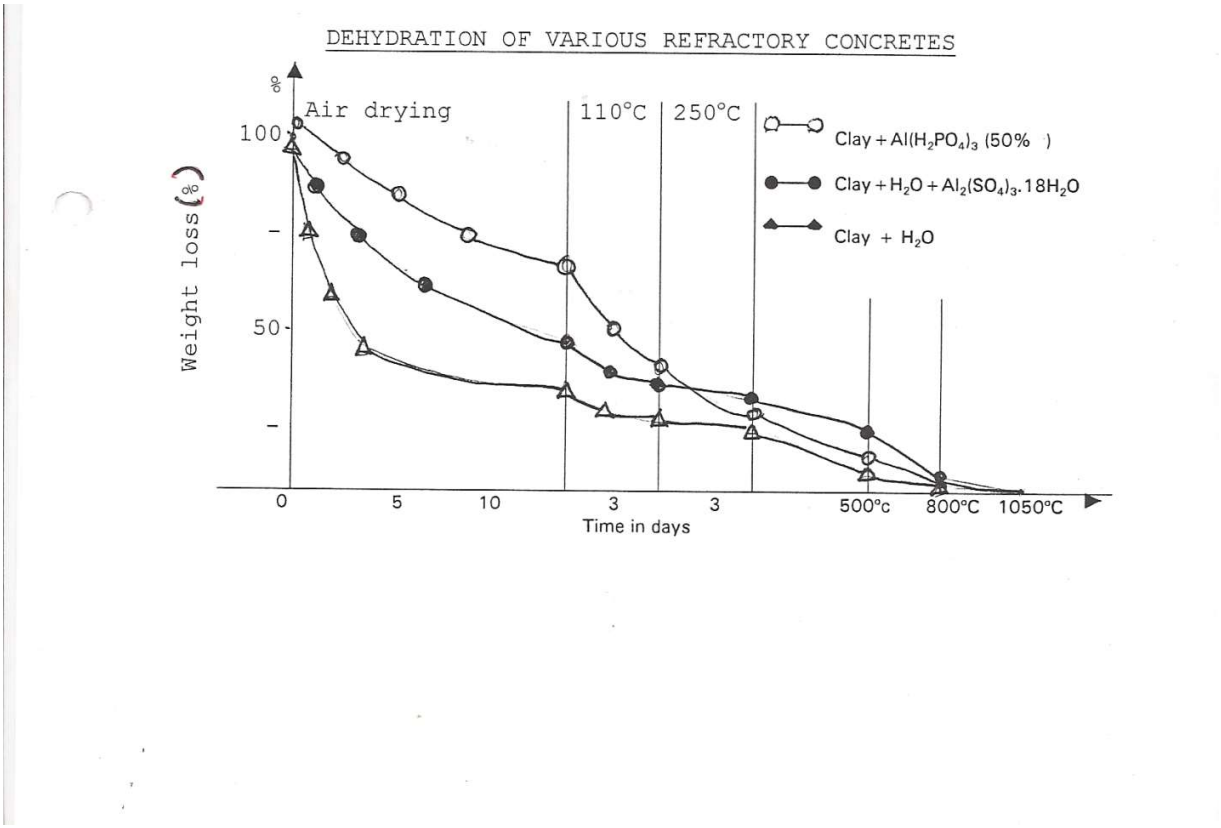
FIGURE 1 - STRESS DISTRIBUTION OF AN ONE SIDED HEATED BRICK



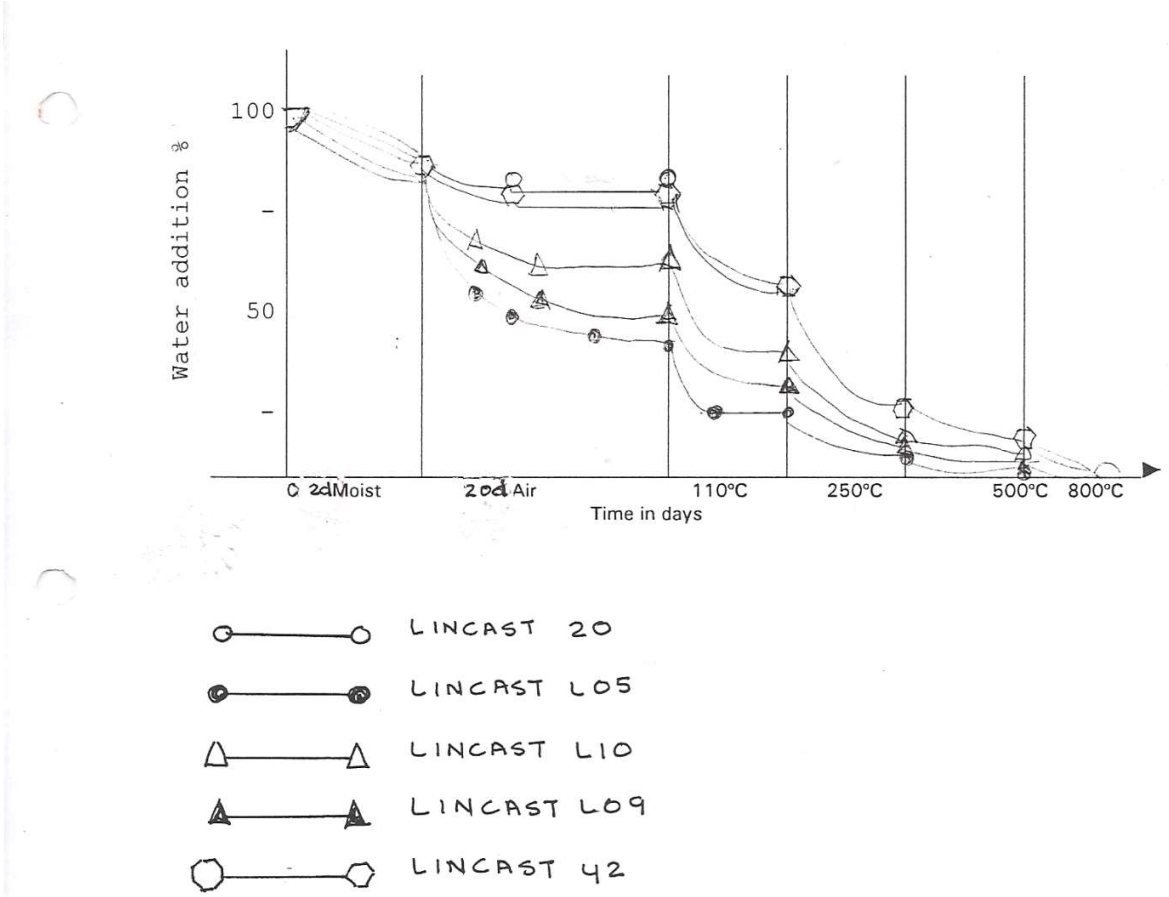
In this figure the strain and pressure tension due to unidirectional heating are shown. The initial heating, the pore pressure of evaporating water is added to these thermo-mechanical tensions. If the total tensions are greater than the inherent strengths of the building material, then a destruction of the bonding will follow. The faster the heating-up rate, the greater will be the steam pressure and so much greater will also be the mechanical stresses due to the temperature differences. Furthermore, this can lead to explosive "flaking –off" of material.

Ramming materials and plastic masses are able to withstand these strains much more easily, as the bond, or the bonding force is not as rigid as that of hydraulic one. In such materials one must however consider the fact that on heating too rapidly, water is no longer able to escape because of contraction but also the diffusion of salts on the surface closes up the capillaries. In such cases the formation of steam can cause the formation of a sludge layer in the cooler zones, which also could lead to "flaking-off". It is therefore generally correct to roughen the surface and to punch in steam vents.
Finally slow heating-up means greater penetration of heat into the lining. For reasons of dissipating stress, there is a period, thereby achieving a temperature compensation.

Drying curves have been established in the laboratory in order to determine the temperatures and times required to completely dry unformed materials.



The diagram implies that a refractory concrete which has been stored in air at room temperature can be dehydrated much more easily, the lower is its raw density. With the so-called dense refractory concretes, it really does not matter whether the raw density is 2,0g/cm³ (lincast 20) or 2, 9 g/cm³ (lincast42).
If one considers the curve for lincast L05, i.e. a pure vermiculite concrete with a raw density of 0,5g/cm³, then, after storage in air until constant weight is attained, it still contains about 40% of its added water. After heating to 110°C the remainder of the water is still about 20% to 25% of the original additional water added. Only after 250°C is the remaining water about the same for all refractory concretes (about 10%). An exception in this case is Lincast 42 having remainder of about 18%, which can be ascribed to the pore size distribution and to the use of Alcoa CA25.



Dehydration behavior with a ceramic bond

In this section the dehydration of the bonding systems in LICOTON and LICO-CLAY were studied. These experiments are a little more difficulty, as apart from the added water; there are also other volatile substances, e.g. the water of crystallization of the clay, salts organic materials in the bonding clay etc. which are recorded. Therefore for the mixtures examined, the loss-on-ignition is shown as a function of the various preparatory treatments made. In the experiments applied to mixtures having chamotte 32-35 and fused

alumina as a base, no differences could be found regarding the dehydration of the various raw materials.
In order to clarify the diagram, the parameters are applicable.

Clay + $Al(H_2PO_4)$ 50% Bond type used in LICOTON particularly construction units.

Clay + H_2O + $Al_2(SO_4)_3$.18H2O Bond type LICO-CLAY

Clay + H_2O Pure ceramic in LICOTON k

The diagram shows that a purely ceramic system dehydrates well, well with storage in air, whereas the MAP-bond behaves sluggishly. At 110°C and 250°C the types of bond move closer together.
Above these temperatures, only the sulphate bond behaves "abnormally" as between 500°C and 800°C SO_2 is given off preponderantly.
It can therefore be concluded that ramming materials, having an acid bond must be dried and heated-up slower than for example ceramic materials, furthermore, it should be noted the with plastic materials, appreciable amounts of SO_3 have to be driven off at higher temperatures.

Chapter 6

DESTUCTIVE SERVICE FACTORS

INTRODUCTION

Every Refractory Sales Representative is always looking for various subjects to discuss with refractory users in order to find one which will especially be of interest to them. Some are only interested in low prices, but most are interested in long furnace life which reduces their costs. In other words, they want to use the refractory in each part of the furnace which will give the lowest cost per tonne of product produced.

In order to recommend the refractory which will improve the life of the customer's furnace, it is necessary to know what is causing the destruction of the present lining. If the correct factor or factors are not determined, the wrong recommendation will be made and the customer's furnace will be of shorter rather than of longer duration.

Listed below are destructive services factors in order of importance, w.r.t. all types of furnaces.

1. Slagging
2. Spalling
3. Hot load deformation
4. Mechanical wear
5. Furnace atmosphere
6. Temperature

This order of importance is not the same for each sales application. For example, a salesman without metallurgical plants would generally find spalling to be more important than slagging.

It should be noted that there are only **SIX MAJOR DESRUCTIVE FACTORS.** This makes the problem of determining what is destroying the Refractories less difficult, but it is still not easy because there are **THREE TYPES OF SPALLING, TWO TYPES OF MECHANICAL WEAR, SEVEN TYPES OF FURNACE ATMOSPHERES** and **TWO CONSIDERABLY DIFERRENT THERMAL EFFECTS.** Occasionally, a laboratory test is required to ensure that the correct destructive services factor has been determined.

Many times there is not just one destructive factor, but two or three and one factor tends to cover up the damage that has been caused by another. It is not only important to determine what all the destructive factors are, but also their order of importance. It is not unusual to find both slagging and spalling occurring in the same furnace. The brick lining may spall with slag hiding the spalled area, thereby making it more difficult to analyse the severity of the spalling. However it is important that this analysis should be undertaken, as many times the refractory which is best for slagging is not as good for spalling and vice versa. If one factor is definitely more important than another, then a refractory is installed which will be best for that particular condition, however which has some resistance to the secondary condition. However, if both slagging and spalling are of about equal importance, a compromise has to be worked out

which will give reasonable resistance to both, although it may not be best lining for either condition when considered separately.

These destructive services factors will not be discussed in their order of importance as it is easier to explain their difference by first mentioning the effect of temperature as a destructive service factor and then dealing with slagging, spalling, hot load deformation mechanical wear and furnace atmosphere.

The discussion of each destructive services factor will be sub-divided into the following four headings:

1. Definition
2. Types, description and examples
3. Factors affecting severity
4. How to achieve improved refractory life

1. Temperature

Definition
Temperature is a measure of how hot the refractory lining may become in the furnace.
Description
To increase the temperature of the furnace energy is used in the form of heat. High temperature or heat can destroy a refractory or insulation lining without any other destructive service factor being present. This seldom occurs and for this reason it is considered last in importance as primary or direct destructive factor. As the other destructive service factors are discussed, it will become evident that increasing the temperature often increases the severity of the destructive action of the other factors. If this secondary effect is taken into consideration, then temperature would rate third in importance.

Temperature alone can destroy a refractory material in two different ways:
a) Permanent linear change
b) Melting

A. Permanent Linear change

Definition
Permanent linear change is a change in length of a refractory sample after having been subjected to high temperature without the application of any external stress. After the refractory has been cooled, any change in length is a permanent linear change caused by the high temperature.

How to achieve improved refractory life

1. Operate the furnace at lower temperatures.
2. Use a refractory or insulation material with less permanent linear change at the furnace's operating temperature.

B. Melting

Melting is the second means of destruction of a furnace lining which is caused solely by temperature.

Definition
Melting is a change of refractory from a solid to a liquid phase, caused by heating it to a high temperature when no other destructive service factor is present.
Description and examples
Slagging is often mistaken as melting. Melting was described first to make it easier to understand why it is seldom the cause of a refractory failure. It is important to remember that melting is caused by temperature alone. The correction of a melting problem can be quite different from the rectification of a slagging problem. An explanation of melting or softening of Refractories will probably be helpful. Ice has a true melting point because it melts to water at exactly 32°F or 0°C. When the temperature is below the melting temperature, ice-skating is fine, but don't try it when the water is one degree above melting for you will surely wet yourself.

Chemically pure crystals of silica, alumina or mullite also have a definite melting point, but Refractories for industrial furnaces are not such high purity materials. As a result, they do not have definite melting temperatures, but gradually soften as temperatures are increased. Refractories are more like molasses (or syrup). When very cold, molasses is hard like ice or a brick. As it is warmed up, it first softens but is still not pourable. At higher temperatures it pours very slowly. At still higher temperatures, it pours like water and has completely melted.

Silica bricks, which are quite pure, have a narrow softening range, whilst the range of fireclay bricks is much wider because of the different minerals which they contain melting at different temperatures. The softening is similar to molasses except it occurs at much higher temperatures.

Factors affecting severity
1. The higher the temperatures the more the refractory must withstand until it is completely molten.

How to achieve improved refractory life
1. Reduce the furnace temperature to below the softening or melting point.
2. Use a refractory product with a higher softening or melting point.

2. SLAGGING

Definition

Slagging of refractory is a destructive combination of the refractory product and some other material at a high temperature, resulting in the formation of a liquid.

Types, description and examples

There are two types of slagging. Most often there is a destructive chemical reaction between the refractory and the other material, which forms a completely new material with a lower melting point than the original refractory product.

The other slagging type is simply a mixture of the refractory and the destructive material as would occur when the latter penetrates the pores of the furnace lining. This mixture has a lower melting point than that of the refractory. A common example of this occurs when salt is put on ice. The melting point of the ice is greatly reduced when mixed with salt. This causes snow to melt from the surface of highways when the temperature is well below freezing.
It is not always possible to inspect the customer's furnace and establish which type of slagging is occurring and it is not always necessary to know in order to help him with his slagging problem. The important point to remember is that the formation of liquid occurs at a lower temperature than the softening of the refractory. It is not the refractory that is melting, but the product of the chemical reaction or the mixture of the two materials. The ASTM definition for slagging calls it a destructive chemical reaction and it will be referred to as such in the rest of this discussion as it is by far the most important cause.

Often a user thinks a refractory is poor in quality because they see slagging at a temperature hundreds of degrees below the actual softening point of the refractory and think the refractory is melting. Slagging is often seen in furnaces, but melting of the refractory by itself seldom occurs.
As is well known, iron oxide causes serious slagging in the foundry and steel industry. Silica and alumina have melting points of 1380°C, 1713°C and 2050°C respectively. However, when the three are mixed in the ratio of 12% alumina, 40% silica and 48% ferrous oxide and heated, the product of the chemical reaction has a melting point of only 1083°C which is far below that of any of the three original materials.
Thus far, the discussion has covered the destructive chemical reaction between the refractory and a solid material in the furnace, but the destructive material can be liquid at the furnace temperature. This liquid might be the material being processed or produced, such a borax or glass. It may be the ash from the coal or low grade oil. It can be a slag such as that produced when refining metals. The molten materials can react with the refractory just as a solid material does and the product of the reaction melts at a lower temperature than the refractory material.

In some furnaces, there are vapour phases such as alkalies, which similarly destroy the refractory.

The molten material generally runs off the refractory, or the movement of the charge carries it away exposing a fresh refractory surface to the destructive attack. The slagging continues until the refractory is destroyed.

Factors affecting severity

1. The higher the temperature, the greater the severity of slagging.

2. The viscosity of the molten material in the furnace is important, because the material which is more fluid and therefore has a lower viscosity-penetrates into the pores of the brick to a greater depth and increases the amount of refractory exposed to the chemical attack. If the product of the reaction is viscous and sticky, it can actually form a protective coating adhering to the refractory, such as the clinker which occurs in the burning zone of cement kilns.

3. The velocity of movement of the slag or charge in the furnace can make the condition more severe because a more rapid movement removes the slag from the surface more rapidly and quickly exposes a fresh surface of refractory lining to attack.

4. The chemical nature of the materials in the furnace is important because some materials react with the refractory much more rapidly than others.

How to improve refractory life

1. Reduce the furnace temperature.
2. Reduce the quantity of the destructive material.
3. Sometimes the nature of the destructive material can be altered to reduce its attack.
   a) In metal-refining, it may be possible to use a less destructive flux.
   b) Sometimes it is possible to increase the viscosity of the molten material.
   c) An oil or coal with a less destructive ash may be used.

4. Change the design or operation of the furnace to have less movement of the destructive material.
5. A refractory of lower porosity reduces the amount of penetration and, therefore, the attack is confined to a lesser depth in the refractory, thereby effecting a considerable improvement in lining life.
6. Use a refractory with a chemical composition which does not react chemically with the material contained in the furnace.

Many materials, including refractories, can be classified chemically as acidic, basic or neutral.
Vinegar is an acidic material because it comprises acetic acid. Other well-known acids are hydrochloric, sulphuric and phosphoric acids. Washing soda (sodium carbonate) is a household chemical of the basic type. Other common bases are caustic soda and hydrate lime. When an acid and a base are mixed, they vigorously react with each other. For example, hydrochloric acid and washing soda mixed together in the correct proportions completely react with each other and both are completely destroyed. The reaction produces water, carbon dioxide and sodium chloride or ordinary table salt. No-one would ever think of putting hydrochloric acid or washing soda on food, but salt is an entirely different material that makes a fried egg taste even better for breakfast. Salt is a neutral material with neither acidic or basic characteristics.

At high temperatures, silica, silicon carbide and zircon refractories become chemically acidic. Fireclay refractories with a high silica content are somewhat acidic and high alumina refractories with less silica are near neutral. Chrome-magnesia, magnesia-chrome, magnesia and doloma refractories belong in the basic classification. Carbon and chrome-containing refractories are chemically neutral.

A layer of chrome mortar is often used between the high alumina roof and the basic sidewall of an electric furnace in order to retard chemical reaction or slagging.
A similar chemical reaction will occur in a furnace if an acid charge or slag is used in contact with a basic refractory or vice versa. A good furnace lining which would usually last for months can be destroyed in a few hours if this aforementioned condition is allowed to develop.
Materials of a similar chemical nature do not react or, at least, react very slowly. Therefore, a basic refractory lining should be used with a basic charge or slag and an acid-type lining with an acid charge or slag. In electric furnaces in foundries, the slag is normally acidic, therefore silica bricks are used. On the other hand, steel foundries generally operate with a basic slag; therefore a basic lining must be used. Copper oxide and lead oxide are highly basic; so many basic refractories are used in these industries.

3. Spalling

Definition
Spalling is cracking of the refractory, which often results in portions of the refractory breaking or 'spalling away' from the lining.

Types, description and examples

There are three types of spalling:
a. Thermal
b. Structural
c. Mechanical

In the three types of spalling, a stress is developed in the refractory which is greater than it can withstand, resulting in cracking and portions of the refractory 'spalling away' from the remainder of the refractory lining.

A. **Thermal spalling**: is caused by heating and cooling the refractory too rapidly. As previously explained, nearly all refractories expand when heated and contract when cooled. When heated, the face exposed to the heat becomes hot and expands before the heat can penetrate to the cooler face of the lining and expand, causing stress in the lining. With rapid heating, the stress is greater than the refractory can withstand, resulting in cracking and pieces 'spalling away'. Thermal spalling on heating is characterized by cracking parallel to the hot face and by corners of the brick breaking off at a 45°C angle.

Just the opposite occurs when the refractory material is cooled. The face being cooled wants to contract, whilst the brick back in the wall is still hot and cannot. When the stress is too great, the refractory cracks. This type of spalling is characterized by cracks perpendicular to the hot face and also by corners breaking off at a 45°C angle.
Thermal spalling is often worse at temperatures below 800°C where the refractory is still quite rigid.

Factors affecting severity
1. Rapid heating and cooling increase severity.

How to achieve improved refractory life
1. Heat and cool the furnace more slowly.
2. Use a refractory material with better resistance to rapid temperature changes.

B. **Structural spalling:** is preceded by some type of change in the refractory's structure. One cause of such a change is heating the refractory to a high temperature which changes the normal structure to a vitrified or glassy phase. The other cause is the penetration of charge, slag or vapour phases into the brick matrix. When the temperature is high enough to result in a chemical reaction, a different structure is developed. (Note that this is the same as occurs in slagging, except the reaction has not proceeded far enough for the reaction products to completely melt and run. Whether the change in structure is caused by vitrification or chemical attack, the altered structure has a different coefficient of expansion than the remaining unaltered structure farther back in the wall. As a result, the temperature difference between the hot part and cold portions of the refractory wall can produce a much higher stress in the lining, thereby causing spalling. In addition, a less rapid temperature change may also be sufficient to cause spalling.

Factors affecting severity
1. Too high a temperature causes vitrification of the refractory at the hot face region and increases spalling.
2. The more reaction occurring between the impurities in the furnace and the lining, the greater the change in structure and the worse the effects of spalling.

How to improve refractory life
1. Reduce the furnace temperature to decrease vitrification and chemical reaction.
2. Use a more refractory furnace lining which will not vitrify at the furnace temperature
3. Use a refractory product which is more resistant to the chemical attack
4. Heat and cool the furnace more slowly.

C. **Mechanical spalling:** occurs when a mechanical force is applied to the refractory lining which is greater than it can withstand and the refractory cracks, chips or crushes. One of the most common

causes of mechanical spalling in not allowing adequate space for the normal thermal expansion of the refractory. Proper expansion joints should be built into the furnace lining so that it can expand and not crush or spall the bricks.

The reversible thermal expansion curve for silica shows that the expansion is much higher than fireclay bricks and it practically all occurs when a 650°C temperature is reached. A foundry built their electric furnace sidewall with silica bricks, but neglect to put in expansion joints at the necessary rate of 5/32" (4mm per 300mm). When the temperature had reached 260°C, the expansion of the hot face of the silica developed such high stresses in the bricks that the lining was badly damaged by mechanical spalling and the wall had to be rebuilt.

Another case of chemical spalling is rain spalling in rotary kilns. This occurs in the part of the kiln where the gas temperature is 870°C to 1100°C. Longitudinal troughs 6 to 12 metres long develop where the brick has been crushed to a depth of 50mm to 75mm. these troughs or crushed areas may be 180°, 120°, or 90° apart, and are caused by a sudden, very heavy rainfall which cools the kiln shell before the refractory lining can cool itself. Therefore, the contracting kiln shell subjects a very high pressure on the hot face of the lining. This pressure, or stress, is relieved by mechanical spalling of the hot face. Where sudden, heavy rains often occur, rotary kiln operators' have built roofs over their kilns to prevent spalling.
A lesser known, but important, cause of mechanical spalling is heating the furnace too rapidly initially. If heated slowly, the furnace has time to at least partly adapt itself to the stresses resulting from the thermal expansion of the refractory lining. Slow heating dries out water and allows the heat to penetrate through the lining to the steel shell before temperature on the hot face becomes high. Although the shell is much cooler than the hot face of the refractory, steel expands at 2½ to 3times the rate of fireclay bricks and helps to relieve the stress in the refractory lining.

Another reason for slow heating is that, even at intermediate temperatures, refractories compress slightly at a slow rate to help relieve the expansion stress. This mechanism will be discussed more under hot load.

When the stress is high, the steel shell may stretch to create expansion space.

Factors affecting severity

1. Inadequate expansion allowance puts excessive stress on the hot face of the refractory.
2. Cooling the furnace steel shell too rapidly may put excessive stress on the hot face of the refractory.
3. Heating the lining too fast initially may cause mechanical spalling

How to achieve improved refractory life

1. Install adequate expansion joints.
2. Avoid sudden cooling of the steel shell.
3. Heat the furnace slowly initially.

4. HOT LOAD DEFORMATION

Definition

This is plastic deformation of the refractory lining caused by subjecting it to more load than it can support at furnace operating temperatures.

Description and examples

The lightweight insulations are not considered here as they are strong at any temperature and the lining design should not impose a load on them. Neither does this include mechanical spalling where the Refractories fail by cracking of crushing.

As the temperature is increased, Refractories reach a point where their ability to carry a load decrease with further increase in the temperature. Depending upon the quality, the decrease in strength of fireclay bricks becomes significant at a temperature between 1040°C and 1250°C. With very high loads a little deformation will slowly occur at temperature as much as 280°C lower than previously mentioned.
When the customer heats his furnace slowly for the first time, he is allowing time for plastic deformation to take place in order to reduce the stress caused by thermal expansion.
Hot strength becomes especially important for walls having heat on both sides. Usually a wall is exposed to normal air temperature on one face and this part of the wall is cool enough that it will support the weight or load without difficulty. However, a wall with heat on both sides has no opportunity to cool and the entire wall thickness is at the same temperature as the furnace. Therefore it is necessary to use a refractory material which has good strength at the relevant temperature.

Another case is a well-insulated arch. With thick insulation, the top part of the service lining next to the insulation is almost as hot as the bottom part and the entire thickness may be in the temperature range where its hot strength is greatly reduced. The thrust of the arch causes a higher load on the refractory material than in a vertical wall. If the refractory cannot withstand the load, the arch will deform and settle down until it must be replaced.

Factors affecting the severity

1. High temperature makes the deformation worse.
2. A greater load increases the deformation
3. A reducing condition has the same effect as that of a higher temperature.

How to achieve improved refractory life

1. Reduce the temperature of the refractory lining by decreasing the furnace temperature or by using less insulation.
2. Change the furnace design to impose load on the refractory lining
3. Use a refractory lining with greater hot load strength.
4. Change the furnace atmosphere from reducing to oxidizing. A furnace has a reducing atmosphere when there is not enough air to completely burn the fuel. Oxidising conditions occur when there is more air (oxygen) than that needed to burn the fuel and combustion has been completed.

5. MECHANICAL WEAR

Definition

Mechanical wear is the abrasion or erosion of the refractory surface by the impingement or rubbing of moving solids, liquids or gases.

Types, description and examples

Often the terms abrasion and erosion are used interchangeably, but in accordance with the ASTM definition, mechanical wear is called abrasion when caused by solids and erosion when caused by liquids or gases.

The destruction is caused purely by local mechanical stress imposed on the refractory which breaks off or erodes away portions of the furnace lining. No chemical reaction is involved and it can occur from room temperature up to very high temperatures.

When feed is charged into a vertical lime kiln, the pieces roll down against the lining and portions of the refractory lining may be broken away. Then as the charge descends down the kiln, the sharp edges of the feed rub against the refractory abrading the lining. The same occurs in blast furnaces and cupolas. Fluid catalytic cracking units in the petroleum industry circulate a high quality of catalyst from the reactor through refractory lined ducts to the regenerator and back to the reactor. Even though the catalyst is very fine-grained, much study has gone into the development of refractory linings which will withstand the abrasion for several years before relining is required. In aluminum melting furnaces, the side walls are subjected to mechanical wear from cleaning tools used to remove the dross and also from the charging of aluminum billets or ingots.

A good example of the erosion of a refractory lining by a liquid is that which occurs on the bottom of a tundish used in the continuous casting process, where steel is tapped into it from a ladle above. The rapidly-falling molten steel has enough energy to break away portions of the refractory lining. Some American companies are using 381 x 343 x 114mm pre-fired blocks of chrome-alumina ramming material to withstand this wear mechanism and have found that considerable is saved, even though each block costs R98, 00. This type of mechanical wear may be combined with slagging.

Occasionally, a furnace has very rapidly –moving gases that will tear loose refractory particles, just as a strong wind tear pick up dust from a farmer’s field/ this is not nearly as severe as with solid particles or liquid phases.

Factors affecting severity

Abrasion

1. Characteristics of the particles or pieces
   a) Weight – the heavier the weight, the greater its destructive force.
   b) Shape-sharp corners cause more severe abrasion.
   c) Hardness-the harder the particles the more damage they will inflict.
2. Velocity – the destruction increases with greater velocity, as the faster moving particles impact or erode with greater energy. In fact the energy of a moving particle increases in accordance with the square of its velocity. This means that when the velocity is doubled, its energy is four times as great; when it is tripled. The energy is increase eight times, etc. Due to this rapidly- increasing energy, velocity should be considered a very important factor.
3. Angle impact – if the direction of movement is parallel to the surface of the refractory, it is not as severe as when it impinges at an angle. The greater the angle of impingement, the worse the wear will become.
4. Amount of material – the larger the amount of abrading material that comes in contact with the refractory per square metre per hour, the greater the abrasion effect.

Erosion

1. Density
2. Velocity
3. Angle of impact
4. Amount of material.

The same general comments apply here as for abrasion.

It should be noted that it is quite difficult to describe the severity of mechanical wear due to the number of factors which can be affected.

How to achieve improved refractory life

1. It would help the refractory life to change the characteristics of the particles so that they were less abrasive, although generally little can be done.
2. It may be possible to reduce the velocity by changing the design of the unit such as using larger diameter ducts or flues.

3. Anything that can be done to make the flow more nearly parallel to the refractory surface will help in improving refractory lining life. The reason for this is that the aggregate or larger particles in the refractory are often harder than the material which binds them together. When the flow of the wear is taken by the particles in the refractory material. When the angle of impingement is more nearly perpendicular to the surface of the refractory, the abrading particles will wear away the matrix or material which bonds then grains together, until there is insufficient bonding material

remaining and the hard particles are broken away by this method, the hard aggregate can be removed from the refractory lining without having been eroded away.
Another reason is that a particle moving perpendicular to the surface is stopped instantaneously and thus impinges with maximum energy, whilst one sliding along parallel to the surface is stopped gradually.

4. The amount of wear may be decreased by reducing the amount of abrading material, although this is generally an essential part of the industrial process and cannot usually be changed.
5. Use a refractory with greater resistance to abrasion and erosion at the furnace's operating temperature. A high-strength refractory will have better resistance to mechanical wear, although this is not necessarily direct proportional to its strength.
   For example, the loss from mechanical wear on a particular refractory lining rises gradually as the severity increases until a certain point is reached, when the loss increases at a much more rapid rate. As this condition is reached, it is very important that either the severity be reduced, or a better refractory be utilized.
   A refractory with greater hardness has better abrasion-resistance. For example, a product made with tabular has better abrasion resistance than one made of fireclay aggregate which is less hard in character.
6. Change the furnace design so that the abrading material impinges on itself instead of onto the refractory lining. When Portland Cement Clinker drops out of the rotary kiln into a grate-type cooler, it is customary to have flat refractory floor where the clinker builds up a deposit, thereby protecting the kiln floor from wear.

6. FURNACE ATMOSPHERES

These may contain impurities which will cause destruction of the refractory lining. In this section, only destructive service factors will be discussed, where a solid state chemical reaction occurs that destroys the refractory. In other words, there is no liquid formed as in the case of slagging.

The destructive factors of this type which are most frequently encountered are:

A. Reduced atmospheres
B. Oxidizing atmospheres
C. Hydration
D. Alkali vapour phases
E. Chlorine or hydrogen chlorides
F. Fluorine or hydrogen fluorides
G. Sulphur dioxide or sulphur trioxides

The abovementioned destructive factors will be discussed individually.
There is one other condition that is often more damaging to the steel shell of the furnace than to the Refractories, namely the effects of condensed hydrochloric, hydrofluoric, sulphurous and sulphuric acids, which will be commented upon at the end of this section.

A. REDUCING ATMOSPHERES

Definition

A reducing atmosphere is one in which there is not enough air (oxygen) to burn all the fuel.

Description and examples

A good example of a reducing atmosphere occurs in blast furnaces which convert iron ore to metallic iron. In addition to iron ore, the charge contains coke and lime. The lime reacts with the impurities in the iron ore to form a slag that floats on top of the molten iron.
Only enough air is introduced into the blast furnace to burn the coke to develop the necessary high temperature and convert it to carbon monoxide. It is very hot carbon monoxide that reacts with the iron ore (iron oxide) to produce the molten iron. If more air were introduced, the carbon monoxide would burn to carbon dioxide. Due to the high percentage of carbon monoxide in the blast furnace, the refractories are subjected to strong reducing conditions.

If there is black smoke emanating from the furnace's chimney, it means the burners are not properly adjusted. Either there is not enough air being introduced for the amount of fuel, or the air and fuel are not being properly mixed and incomplete combustion has resulted. In either case, the furnace lining is subjected to reducing conditions and this faulty operation wastes expensive fuel.

Some heat-treating furnaces in the metal-working industry use controlled highly-reducing atmospheres containing a high percentage of carbon monoxide and hydrogen to prevent the formation of a metal oxide scale.
There are many industrial processes where the charge is combustible and air or oxygen must be eliminated from the process. One of the most important examples is petroleum processing where the crude oil is being separated into different fractions and where various cracking or reforming processes are used to obtain the type of petroleum desired. When the Refractories are subjected to the

process atmosphere containing hydrocarbon and sometimes hydrogen, the conditions are highly reducing.

The refractory lining in contact with these atmospheres is usually grey-or black-coloured. This is caused by cracking of the hydrocarbons leaving a uniform deposit of carbon and by reduction of titana (TiO_2) and ferric oxide (Fe_2O_3) to oxides with oxygens which are dark in colour. When the refractory is heated in an oxidizing atmosphere, the carbon burns out and the oxides of titanium and iron ore re-oxidise to titania and ferric oxides. The colour returns to normal, indicating that no damage has occurred to the refractory lining.
This is not true at higher temperatures, because then a reducing atmosphere has the same effect as increased temperatures with an oxidizing atmosphere.
Perhaps it would augur well to give an example of how a reducing atmosphere can worsen some of the other destructive factors. Iron oxide is an impurity that occurs in most Refractories. In an oxidizing condition it occurs as hematite, a ferric oxide (Fe_2O_3). In a reducing atmosphere, it is changed to the oxide wustite (feO).

These oxides are more reactive chemically and are more harmful than ferric oxides. For example, ferrous oxide reacts with 85% Al_2O_3 at 1315°C, whereas ferric oxide does not react until 1480°C in a five hour laboratory test. This reaction at the lower temperature promotes the destructive of the refractory. For example, it has already been indicated that a reducing atmosphere will increase the hot load deformation. It can cause a vitrified structure to develop at a lower temperature, thereby increasing the severity of structural spalling. Insulation and insulating Refractories shrink at a lower temperature. In other words, a reducing atmosphere can worsen several other destructive factors, whilst not actually being the primary cause of the destruction.
The one type or reducing condition which can directly cause the destruction of a refractory is the presence of carbon monoxide under certain limited conditions.

B. CARBON MONOXIDE DISINTEGRATION

Definition

This is the cracking of the refractory caused by the growth of localized deposits of carbon which are derived from carbon monoxide.

Description and examples.

Two separate chemical reactions must occur to produce carbon monoxide disintegration:

1. Iron oxide + carbon monoxide forms iron carbide + carbon dioxide. The iron carbide acts as a catalyst for the second reaction which causes the actual disintegration. (A catalyst is a substance that alters the rate of a chemical reaction, but is not destroyed by the reaction).
2. Carbon monoxide forms carbon + carbon dioxide. It should be noted that the carbon monoxide is reacting with itself. Since this reaction takes place around the particles of the iron carbide catalyst, the carbon is deposited only in localized spots. The deposit continues to grow until it exerts such a great force that the refractory cracks. The deposits may be as large as 7mm in diameter. In extreme cases, there may be so many carbon deposits that the refractory is broken down to a granular material. Fortunately, this destruction occurs only between the temperatures of 400°C and 700°C, being at its severest at 495°C to 510°C.

Before speciality refractories were developed for blast furnaces, it was found that the part of the lining experiencing temperatures above 700°C showed no disintegration. Furthermore, the portion of the lining where the refractory was damaged by carbon monoxide disintegration normally had experienced temperatures between 400°C to 700°C. The cool part of the refractory next to the shell where temperature was lower would again be in good condition. This might be thought of as mechanical spalling, but the cause is so different that in the Refractory Industry, it is considered as an entirely separate destructive service factor.

Factors affecting severity

1. Increasing the concentration of carbon monoxide increase the attack.
2. The temperature of the refractory must be in the destructive range between 400°C to 700°C.

How to achieve improved refractory life

1. Eliminate or reduce the quantity of carbon monoxide, if possible.

2. Use a refractory with low iron oxide content. Users sometimes specify that the refractory must have less than 1% iron oxide.

3. Uses a refractory that has been fired to a high temperature such as jumbo or rhino bricks. This combines the iron oxide with alumino-silicate minerals to form a stable iron aluminium silicate. In this form, the iron oxide cannot be converted to iron carbide, which is the catalyst that causes the destructive reaction to occur.

4. Only a small amount of sulphur or phosphorous in the furnace atmosphere will prevent the reaction as these gases will react with the iron oxide first and prevent the formation iron carbide catalyst.

Due to the improved refractories now available and the inhibiting affect of sulphur and phosphorous, carbon monoxide disintegration does not presently occur very frequently.

C. OXIDISING CONDITIONS

Definition

One in which there is more air (oxygen present than that needed to completely burn the fuel.

Nearly all Refractories give improved lives in oxidizing atmospheres.

The exceptions are carbon and graphite Refractories and those containing additions of carbon or graphite. If carbon or graphite is exposed to air at the furnace's operating temperature, it burns and is quickly destroyed. They can therefore used in reducing conditions, or where the Refractories are protected from exposure to air.

The hearth and bosh (the lower parts) of blast furnaces are often built of graphite Refractories, because of their excellent resistance to chemical attack by iron oxide and slag. As a strong reducing condition exists, the graphite is not destroyed. Electric furnaces for producing calcium carbide or phosphorous use graphite Refractories for the bottom and lower sidewalls, because they will take the extremely high temperature of 2200°C to 2500°C and no air exists in the furnace as the heat is produced by electricity. Electric furnaces for producing ferro-alloys also use graphite Refractories to withstand severe chemical attack by iron and slag.

Fireclay-based Refractories containing graphite additions are used in the foundry industry in runners and ladles to reduce the attack of iron oxide and slag. The composition of these types of bricks causes a glaze to develop on the surface which protects the carbon from exposure to air.

Iscor Refractories' Linmag products for use in basic oxygen process vessel are made of basic granular materials bonded with tar. To prevent excessive burn-out of the carbon introduced in the form of tar, the lining is heated rapidly and the unit is immediately into service. This coats the surface with slag, thereby protecting the refractory lining from the air.

When the graphite lining of a furnace cannot be protected against air during the initial heat-up, as in the case of the hearth and bosh of a blast furnace, it is protected with a thin temporary lining of fireclay bricks, or a castable gunned onto the exposed hot face regions.

Factors affecting severity

1. Only Refractories containing carbon or graphite are affected.
2. A greater percentage of air (oxygen) increases the rate of combustion of carbon.
3. A higher temperature increases the rate of combustion.

How to achieve improved refractory life

1. Operate under reducing conditions
2. Protect the carbon or graphite from exposure to air by means of a glaze coating.
3. Put a temporary fireclay-based refractory in front of the graphite lining I order to protect it from air during the initial heat-up period.

D. HYDRATION

Definition:

This is a chemical reaction between water and free lime or magnesia that causes an increase in volume, resulting in cracking and loss of strength in the refractory. The water may be in liquid, vapour or steam phases.

Description and examples

The product of this reaction is calcium hydroxide (hydrated lime-portlandite) or magnesium hydroxide (brucite). Both have a lower density than the lime or magnesia and must, therefore, occupy a greater volume.

Hydraulically-setting castables use either a calcium silicate or calcium aluminate-type of binder. Calcium silicate binder is usually used only in the less refractory products, whilst calcium aluminate is used in the others. After being heated in the temperature range of 480°C to 870°C, some of the lime (CaO) may be liberated from the calcium silicate binder. This is usually the worst at 650°C, although this can vary from one binder to another. Furthermore, if the furnace is shut down when there is a lot of humidity in the air the lime will hydrate. As the hydrated lime has a greater volume, its expansion destroys the bond of the castable. The depth of destruction is usually no more than 6mm to 25mm. Iscor Refractories' Castables, which use this type of binder, are made with mixes that lessen the severity of the problem.

Castables using calcium aluminate binders are not susceptible to hydration after heating.

Refractories which contain dolomite are composed of a large percentage of free lime and will hydrate from humidity in the air, even though they are coated or impregnated with tar. They must be used in service a few weeks after manufacture or the refractories will disintegrate.

Dolomite refractories hydrate so readily that manufacturers are shipping them to the export market in airtight metal boxes, even though this method of packing is very expensive.

Dolomite Refractories are sometimes used in rotary kilns, making white cement as it does not discolour the cement and withstands the chemical attack very well. However, good life is obtained only if the kiln does not have a shut-down, because the hot face of the dolomite lining is hydrated by moisture in the air and this part of the lining will be lost. If it were not for this destructive factor, dolomite Refractories would be more widely used.

By comparison, other Refractories do not hydrate.

Factors affecting severity

1. Castables using calcium silicate binders are affected only in the temperature range of 480°C to 870°C.
2. A greater amount of water increases the danger of hydration
3. Water in the form of steam increases hydration.
4. Free lime is susceptible to hydration than free magnesia.

How to achieve improved refractory life

1. Use castables with calcium silicate binders at temperatures below 540°C when not protected by installing another refractory in front of them. They can be used at a higher temperature as a back lining, because the moisture does not penetrate into the castable during a shut-down.
2. Install dolomite products within a few weeks of manufacture, or pack them in metal airtight containers.
3. Avoid shutting down a furnace lined with dolomite Refractories.
4. Protect magnesia- containing refractories from water, which will turn to steam when the furnace is heated.

E. ALKALI VAPOUR

Definition

These destroy the refractory by reacting chemically to produce alkaline aluminium silicate or alkaline aluminate minerals that have

lower density and greater volume than the original clay or high alumina minerals. This expansion causes high stresses and cracks the refractory linings.

Description and examples

The alkalies which cause this destruction are sodium and potassium and may occur as chlorides, sulphides, sulphates, carbonates, or other alkaline chemicals.

The alkalies do not create a problem below 815°C, because the rate of reaction decreases rapidly with decreasing temperature. At temperatures above 1200°C, regular slagging occurs as the reaction of the alkalies with the refractory produces new materials which melt.

The alkali vapours in the furnace atmosphere penetrate the refractory until they reach a temperature at which they can condense. It is within this condensation zone that the destructive reaction takes place. The hotter part of the refractory is not harmed, because the alkalies have not been deposited within this region. The cooler part is also not harmed, because the alkalies have condensed before they reach that portion of lining.

The condensation zone is usually 30mm to 40mm thick and endeavours to expand while the refractory on each side maintains its original dimensions. As a result a high stress is set up between the densified zone of condensation and the refractory on either side. This causes a crack to develop along one or both sides of the zone, parallel to the hot face of the lining.

Although some alkali vapours may come from fuel, the usual source is the furnace charge which causes serious alkali vapour attack. For example, a rotary cement kiln using a high alkaline charge, will vapourise the alkalies in the high temperature zone. Some vapour phases penetration into the burning zone lining and increase the slag attack. The remainder travels up the kiln and some penetrates the refractory lining until it reaches the zone where it is cool enough to condense. When there has been sufficient chemical reaction, spalling cracks described earlier occur and the hotter part of the refractory lining spalls away. Then the whole process re-starts itself with a new condensation zone forming further back within the kiln lining.

The alkali vapours can also be produced without there being a high temperature in the furnace, although this is less likely to be a problem. A rather Fluidised bed processing unit had a lining of high fired, superduty bricks in the lower sidewalls. The upper sidewalls were lined with dense castable backed by castable insulation. The unit operated at approximately 950°C.

The feed contains a small amount of sodium chloride (salt) and after a few months of operation, the dense castable began to "peel off" in a layer of 13mm to 20mm thickness. X-ray analysis revealed that considerable sodium aluminium silicate were present in the layer which had peeled away. The expansion that occurred as this mineral was being formed caused the layer of dense castable to break loose. Although not much sodium chloride vapourises at 950°C, the amount of feed passing through the unit hour was great and enough salt vapourised to damage the castable. There was no evidence of damage to the high fired, superduty brick lining.
The amount of growth that occurs can be considerable. A rice mill burnt mangrove wood in its boiler, which had grown in salt water. The salt vapourised in the fire box and condensed in the cooler part of the boiler setting. During the rice harvesting season, burned rice hulls were burnt, which increased the temperature causing very serious reaction. A superduty suspended arch block used in the rear arch of the boiler was originally 4" thick. At the hot face, the expansion of the sodium aluminium silicate minerals caused the arch block to grow to 4¼" thick. Furthermore, the superduty blocks were badly cracked and had to be replaced.
As can be seen, this could be considered structural spalling and it is sometimes referred to as alkali spalling. Due to the rather unusual cause, the refractory industry treats it as a special destructive service factor rather than structural spalling.

It is often difficult to determine whether the cracking is caused by alkali or thermal spalling, because there is little or no difference in the appearance between the portion of the lining which had experienced alkali attack and the part without. The presence of alkalies can be easily determined by analysis in the laboratory.

Factors affecting severity.

1. Increasing the percentage of alkali vapours in the furnace atmosphere worsens the condition.
2. Proper temperature conditions are required.

How to achieve improved refractory life

1. Reduce the amount of alkali vapour phases present.
2. Use a lower temperature, if possible.
3. Avoid use of castable as it is least resistant to this type of destruction.
4. If plastics must be used due to the furnace construction, use phosphate-bonded product because of its lower permeability to alkali vapour phases.

5. Bricks with low porosity give the best performance. High fired superduty bricks also have improved resistance to this type of destruction. Basic bricks are good, but are expensive and may not withstand the spalling conditions.

F. CHLORINE OR HYDROGEN

Chlorine is frequently used in the metallurgical and chemical industries. Less frequently, hydrogen chloride is found in furnace atmospheres.

Definition

Chlorine or hydrogen chloride destruction of a refractory is caused by a chemical reaction which destroys the ceramic bonding.

Description and examples

The first step in the extraction of titanium metal is to treat the ore with chlorine and coke at about 1000°C to produce titanium tetrachloride. Superduty bricks have been taken out of these furnaces which were snow-white and very weak in character. The chlorine had reacted with the iron and other impurities and destroyed the ceramic bonding.

Chlorine is used to remove impurities from molten aluminum. A castable lining becomes weak, because the chlorine combines chemically with the lime in the binder and destroys the bond. Plastic Refractories of bricks should be used in aluminum furnaces where chlorine is employed as a purifying agent.

The action of hydrogen chloride is similar to that of chloride, although not as severe.

Factors affecting severity.

1. The greater the percentage of these gases, the more severe the attack.
2. The effect of temperature is not clearly understood as sometimes the reaction does not occur as expected.

How to achieve improved refractory life

1. Reduce the amount of destructive gas in the furnace atmosphere.
2. Use high fired bricks with the minimum amount of impurities. Do not use basic bricks.

G. FLUORINE OR HYDROGEN FLURIDE

Definition

Fluorine or hydrogen fluoride destruction of a refractory lining is caused by a chemical reaction which destroys the bonding mechanism.

Description and examples
These fluorine are similar in their attack on refractories to chlorine and hydrogen chloride, except that they will combine with silica whereas chlorine and hydrogen chloride cannot.
Generally these gases are found only in very small percentage in the furnace atmosphere and are not harmful to fired brick or plastics. Otherwise, the comments on chlorine and hydrogen chloride are also applicable.

Definition
Sulphur dioxide and sulphur trioxide may cause destruction of the refractory by combining with the lime in its composition

Description and example

Castable are susceptible to this desctruction because of the presence lime in the binder. Fortunately, it is not serious because the amount of sulphur oxides in the atmosphere from burning high sulphur fuel does not harm castables. In addition, a temperature over 1100°C is required.
The conditions under which the sulphur the sulphur oxides will react with castable binders have not yet been fully defined
Some imported 2000°F and 2300°F insulating firebricks contain almost 15% lime. These have shown loss of strength when burning oil. As a result some customers specify low lime content bricks. At higher temperatures, as found in sulphur burners, a high percentage of sulphur oxides in the atmosphere has the effect of a little higher temperature and it is best to use slightly more refractory products.

Factors affecting severity.

1. Increasing the sulphur oxide content increases the severity.
2. Increasing the temperature makes the conditions worsen

How to achieve improved refractory

1. Reduce the percentage of sulphur oxide
2. Decreases the temperature
3. Uses low lime Refractories
4. For high temperature operation, use slightly more refractory products than would be used for conventional fuels.

SPECIAL COMMENTS REGARDING LIQUID ACIDS

Today the high cost of fuel has created much more interest in well-insulated furnace linings. The effect of too much insulation on the hot strength of the Refractories has already been discussed.

Furnaces often have a steel shell on the outside. The more insulation that is used, the cooler the shell becomes. As a furnace lining cannot be made gastight, water vapour from the products of combustion will penetrate to the shell. If the shell temperature is below the dew point, the water vapour will condense in this region.

When the furnace atmosphere contains sizeable amounts of hydrogen chloride, hydrogen fluoride, sulphur dioxide or sulphur trioxide. These gases also penetrate through the refractory lining to the shell. When mixed with the condensed water, they form liquid hydrochloric, hydrofluoric, sulphurous or sulphuric acids. These acids chemically attack the steel and must be replaced. If a 1040°C mineral wool insulation is used next to the shell, it will also be destroyed by the liquid acid. Lighter weight insulting castables may be damaged. Dense castables, plastic refractories, and bricks show no appreciable damage. An exception to this is liquid hydrofluoric acid which will attack the silica in any refractory product.

Factors affecting severity

1. The lower the shell temperature below the condensation temperature, the more condensation will occur. The condensation temperature of sulphuric acid may be well above the condensation temperature of water.
2. The higher the concentration of harmful gases, the greater the amount of acid which will be formed.

How to reduce acid destruction

1. Use less insulation to raise the shell temperature above the condensation temperature.
2. Install some insulation on the outside of the shell in order to raise the shell’s temperature to above the condensation temperature.
3. Reduce the concentration of harmful gases
4. Use an impervious coating on the inside of the shell.

Chapter 7.

COKE OVEN REFRACTORIES

1. INTRODUCTION

Coke is produced by heating of proper coking coal in the absence of oxygen (reducing atmosphere) in a coke oven. During the process, all the volatiles i.e. oils tars etc. are removed from the coal and large lumps of porous coke are the resultant product. The main application of coke is in blast furnace for the production of liquid iron.

2. COKE OVEN CONSTRUCTION

The modern coke oven battery is so complicated as to almost defy description, but the general concept is illustrated in figure 1. Typically it consists of a unit of about 50 ovens arranged side by side like a row of books standing on their long edge. There are various types of oven, the difference being mainly in the detailed arrangements of ducts and flues.

The latest ovens have dimensions of up to 7,5 metres in height 450mm in width and up 16 metres in length, with a coal charge capacity of well over 48m^3. The coal is delivered from a larry car, which discharges its contents through apertures in the oven top, each about 400mm and more in diameter, covered by lids. Normally there are five of these openings per oven.

The two of the oven are closed by doors, the pusher side coke side doors respectively.

Each oven has an accession pipe or pipes, through which the volatile matter is conducted to a common collecting main and then to the by-product plant. A space is left between the top of the charge and the oven roof, the volatile matter escaping through this space to the accession pipe. When the evolution of gas is complete (14 to 30 hours) the oven is taken off mains. The doors are then removed and an electrically-driven ram pushes the coke from the oven into the coke car, which then moves to a tower where the coke is quenched with water for a predetermined time. See figure 2

2.1 Heating wall of coking chamber

The heating wall of a typical Dr Otto coke oven design consists of a multitude of twin flues (**see figure 3**) and a typical coke oven of 16,4m in length has 17 such twin flues or 34 heating flues.

Combustion of fuel gas (coke oven gas, blast furnace gas or lean gases such as producer gas) and air intake takes place in every second heating flue, with the combustion products flowing downward in the adjacent heating flue to the generators. The direction of flow is changed at predetermined intervals by the reversing system. This type of heating with fuel gas and air burning in every second heating flue creates a more uniform distribution of heat input. **See figure 4.**

Temperature in these flues are normally between 1200°C to 1250°C, but can be as high as 1350°C with localized temperature even up to 1400°C. In order to conduct the heats efficiently into the coking chamber, high density silica bricks are used with tongue-and grooves to minimize gas leakage.

For typical coke oven under construction **see figure 5.**

2.2 Regenerators

In modern ovens the regenerators walls are normally built either of silica or with fireclay bricks in the bottom two-thirds and silica in the top third. A special sliding joint (tongue-and-groove) is used to cope with the difference in expansion characteristics. The checker bricks themselves are usually made of fireclay in the form of extruded hollows.

2.3 DOOR LINING

As these doors undergo consistent thermal shock treatment, chamotte castable with or without steel fibres are mostly used.

3. CARBONISATION PROCESS

Perhaps the greatest problem is the choice of the blend of coals to be carbonized. Coals differ greatly in the amount of volatile matter

which increases with decreasing rank. Coals of the lowest and highest ranks do not yield a strong coke, being referred to as non-coking, or weakly coking, whilst coals of intermediate rank show optimum properties in the volatile matter range of 22% to 27%. The usual procedure is to combine a number of coals of different rank to form a blend which gives a strong coke.

The changes which occur in carbonization are extremely complicated. During the early stages, water and absorbed gases are driven off. At a higher temperature the coal becomes plastic and the individual grains form a coherent mass. The gasses evolved from this give rise to a porous structure and also cause swelling. As heating continues, the plasticity passes a maximum and then decreases as a rigid semi-coke is formed.
The coal is charged into the hot oven and that part coming in contact with the walls is rapidly raised to 900°C, while the centre remains relatively cool. As decarbonisation proceeds, the temperature difference drops virtually to zero.

4. HEATING-UP PROCEDURES

As silica makes up most of the refractories in the coking chamber, special care has to be taken in order to achieve at least 20 years service (typical life span 20 to 25years) from a coke oven. About ten weeks is needed for a proper heat-up schedule. See figure 6 for heat-up schedule.

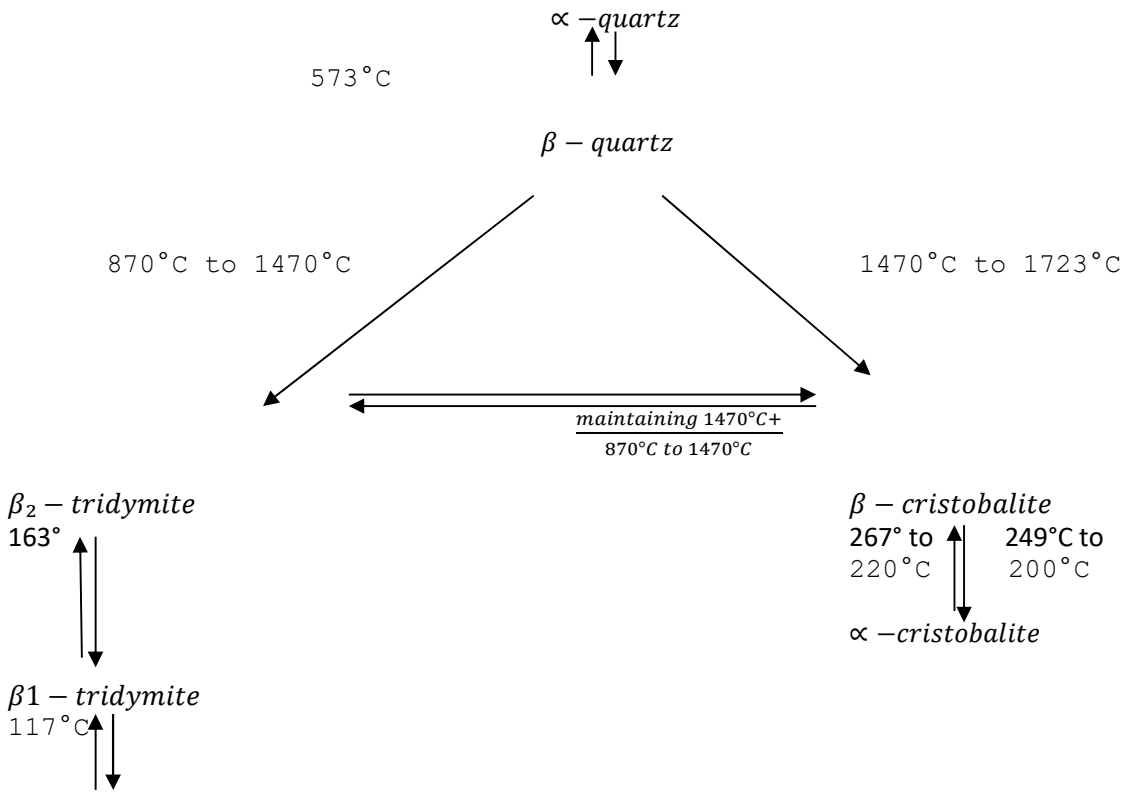
5. SILICA

As silica is the most important refractory in coke ovens, it will be dealt with in more detail. Silica (SiO_2) occurs as a large number of different polymorphs which are stable at specific temperature and pressure ranges. The ones of the importance to refractories are low and high temperature forms of quartz, cristobalite, tridymite and vitreous silica.

5.1 stability relationships of the silica polymorphs

a) The three major modifications of silica are quartz, cristobalite and tridymite.

b) All three exist in high and low temperature forms.



c) Quartz can convert $\beta - cristobalite$ or $\beta_2 - cristobalite$ with the appropriate heat treatment.

d) The conversion of quartz to $\beta_2 - tridymite$ depends on the presence of a liquid phase which may be present as a result of reaction between silica and a flux (impurity).

e) In the absence of a liquid phase, quartz converts to $\beta - cristobalite$.

f) Stability range
Quartz is stable up 870°C $\beta_2 - tridymite$ is stable from 870°C to 1470°C $\beta - cristobalite$ is stable from 1470°C to 1723°C

g) Density at room temperature
Quartz: 2,65 g/cm³
Cristobalite: 2,32 g/cm³
Tridymite 2,26 g/cm³

h) The transformation of quartz to cristobalite is accompanied by a 14,3% increase in volume.
The transformation of quartz to tridymite is accompanied by a volume increase of 17%

However these volume changes are not serious since the transformation from one form to another is sluggish and takes place over a wide range of temperatures.

i) In the absence of a phase quartz does not change to tridymite even when within the stability range 870°C to 1470°C. Instead at about 1250°C the quartz slowly begins to change to $\beta - cristobalite$, the rate of the transformation increasing as the temperature rises. At about 1593°C (within the $\beta - cristobalite$ stability range), the conversion takes place in about one hour.

j) In the presence of a liquid phase or if a liquid phase is developed, the $\beta - cristobalite$ changes to $\beta_2 - tridymite$ at temperatures between 1250°C and 1470°C

k) Each of the three main forms have a high and low temperature modification i.e.:

$\propto$ and β- quartz	(low, high)
$\propto$ and β- cristobalite	(low, high)
$\propto$ and β_1 and β_2 tridymite	(low, low, high)

Changes from one modification to another i.e. $\propto$ - β are rapid and take place at a specific temperature or over a narrow temperature range. They are reversible and are accompanied by volume change.

- $\propto$ β- quartz at 573°C. There is a volume increase on heating of 0,9% with a corresponding decrease on cooling.

  The total reversible expansion occurring between 316°C and 593°C is about 3,2%. When heated or cooled rapidly through the inversion temperature, quartz has a high tendency to spall (crack).

- $\propto$ β -cristobalite. The temperature for the $\propto$ to β (low-high) inversion is 200°C to 267°C. The β to $\propto$ inversion on cooling takes place between 249°C and 200°C.

  The temperature of these inversion is somewhat variable and dependent on both the material from which this cristobalite is formed and the temperature of formation.

  The volume change involved is 2,8%
- Equation

  The total volume changes through the tridymite inversions are small (0,2%) for both) and therefore no cracking occurs when a body consisting mainly of tridymite is cooled or heated through the inversion temperatures.

For coke oven silica bricks, repeated firing below 1470°C is necessary to obtain the maximum amount of tridymite. By determining the amount of quartz, tridymite and cristobalite and glass in silica bricks, the effectiveness of firing can be established.
See table 1 for a typical mineralogical and chemical composition of coke oven silica bricks.
After firing to the required composition, the modifications of concern will be those below 600°C.
See table 2
This implies that silica bricks are thermal shock resistant above 600°C but not below 600°C so that coke ovens hot repair should never be cooled down to below 600°C

5.2 Properties of Silica Bricks

Silica bricks with higher dimensional stability and consistent quality are more suitable for coke ovens than fireclays bricks, furthermore silica bricks are also more creep-resistant than fireclay bricks at high temperatures. The hard-fired silica bricks also have very small after-expansion, which means high volume stability which is necessary for tight oven walls. In comparison with fireclay bricks, silica bricks are more resistant against CO-gas attack (CO-disintegration) and alkali attack as well as fe_2O_3, CaO and MgO (from the coal).

For further properties refer to **table 3**. Another important aspect is that the Al_2O_3 content of the silica bricks should be less than 1%, otherwise low melting liquids will form which are detrimental to the bricks. See attached phase diagram **figure 7.**

6. REPAIR

Typically the life of an oven is 20 to 25 years. The silica bricks in the oven walls change in mineralogical composition with prolonged heating, typically more on the flue side than the oven side, as would be expected. Thermal shock (stresses) and mechanical erosion problems are severe in coke ovens and typical damaged brickwork that may occur (cracking, peeling off) is shown in figure 8.

The presence of adverse economic conditions in industrialised countries made it necessary to extend the countries made it necessary to extend the existing battery life as long as possible, as the capital expenditure to rebuild a coke plant in quite expensive. Prior to the mid-seventies, coke oven management, when faced with serious damage, had no serious alternative to coke rebuilding, as the majority of conventional wet repair techniqiues for coke ovens gave short-term and essentially cosmetic relief. Thus the climate for acceptance of a repair system which not only allowed the near continual use of coke ovens at close to operational temperature, but also satisfied economic requirements was positive.

Ceramic welding was the response to that need which meant that coke producers now had a viable alternative to immediately incurring the heavy costs associated with major oven rebuilds.

The ceramic welding process consists of projecting a dry blend of granular transformed silica, together with metallic silicon and aluminium, in a stream of oxygen through a tabular alloy lance the previously-cleaned repair site. A crystalline bond is developed between the deposited silica repair mass and the silica brick of the weld. (**See figure 8)**. In spite of the high temperatures developed by the reaction, between 2000°C and 3000°C, no crystalline transformations occur in the silica brick material. This can be explained by the high thermal conductivity which prevents overheating and subsequent damage to the silica brick. Up to 1kg of material per minute can be welded onto the damage silica bricks.

Cristobalite is the predominant phase of silica weld whereas for the silica brick it is tridymite. Though there are some differences in the expansion characteristics of the finer crystalline structures, in practice no unfavourable results have been detected as a result of these differences. The deposited materials are physically and chemically almost identical to the refractory under repair. (**See Table 4 and Figure 9a**) and the intimate bond developed not only contributes to long repair life, but eliminates the defect.

Ceramic welding has become a valuable tool in the maintenance of coke oven refractories for which its use continues to expand, with many coke oven operators convinced its application could extend oven life by decades.

There are also other repair methods and materials. In some cases 60% Al_2O_3 bricks are used, but fused silica (**see table 9b** for linear expansion of fused silica) castables either as panel patch repair or pre-cast shapes also find wide application. (**See Tables 5 and 6** for properties and mineralogical composition and **figure 10** for linear thermal expansion of fused silica castables.)

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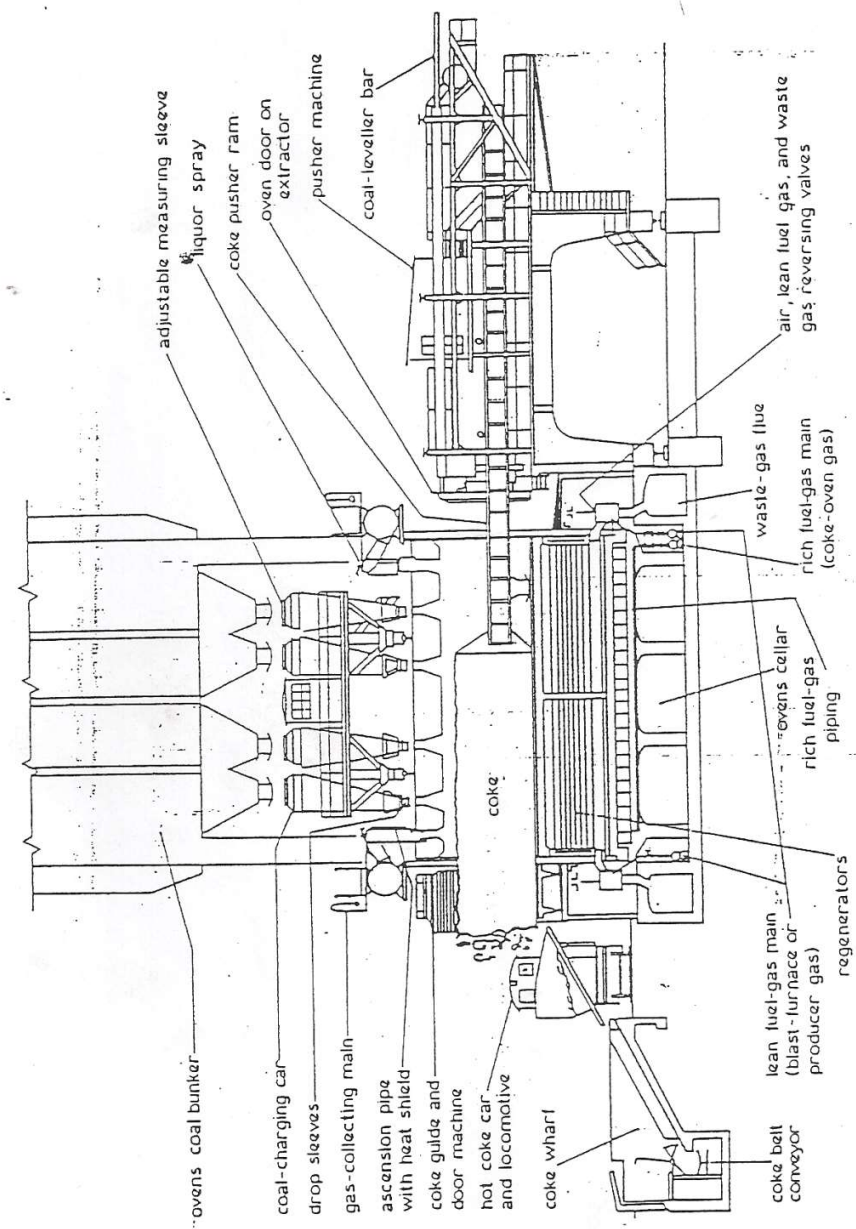
System Steel Times – December 1986

7.4 E William Itell et al – Coke-oven Wall Repairs Using Low Thermal Expansion Fused Silica Iron and Steel Engineer-March 1991
7.5 Fosbel ceramic Welding
7.6 Dr C Otto – Technical Information Brochure
7.7 Dr. H J J Kriek et al – lectures on Refractory materials
7.8 Refractories for Iron and Steel making

FIGURE 1



Cross-section of a typical battery of coke ovens (after BCRA)

FIGURE 2

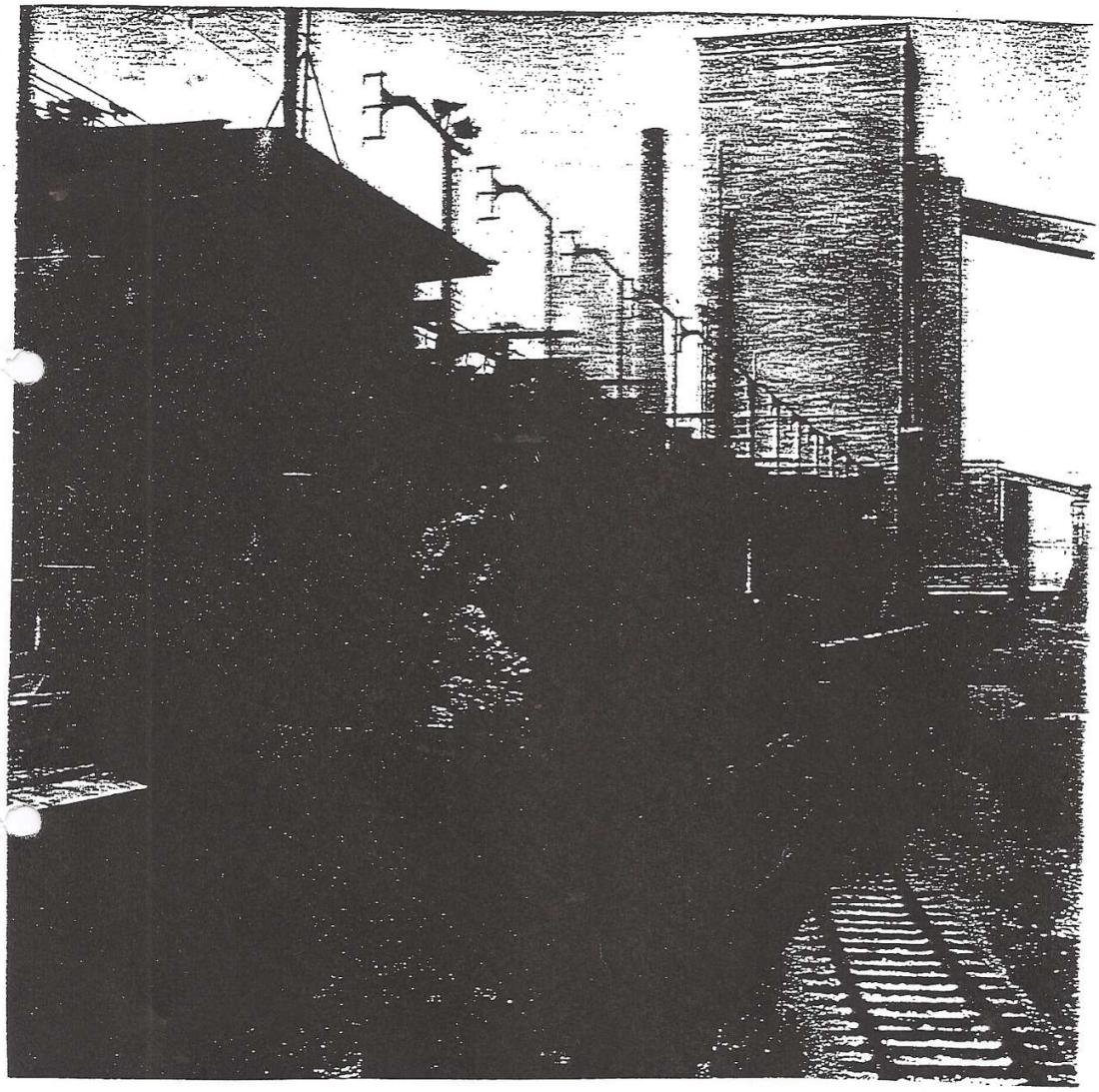


FIGURE 3

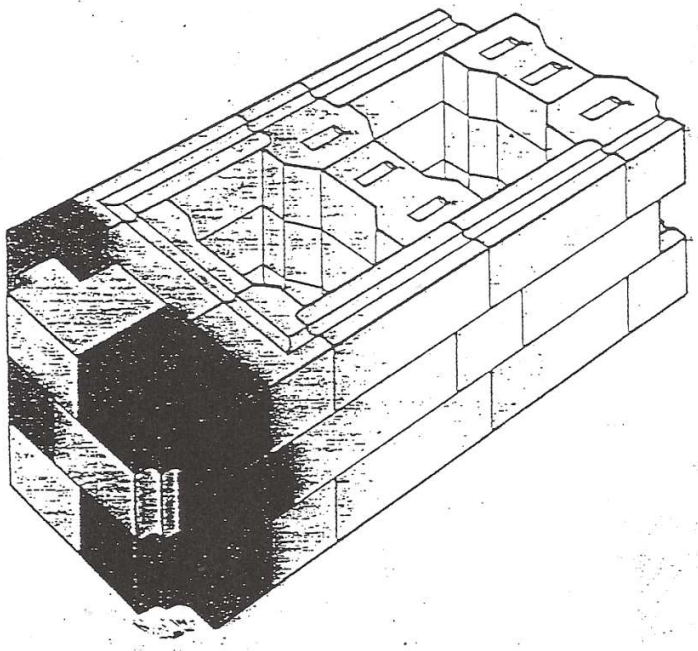
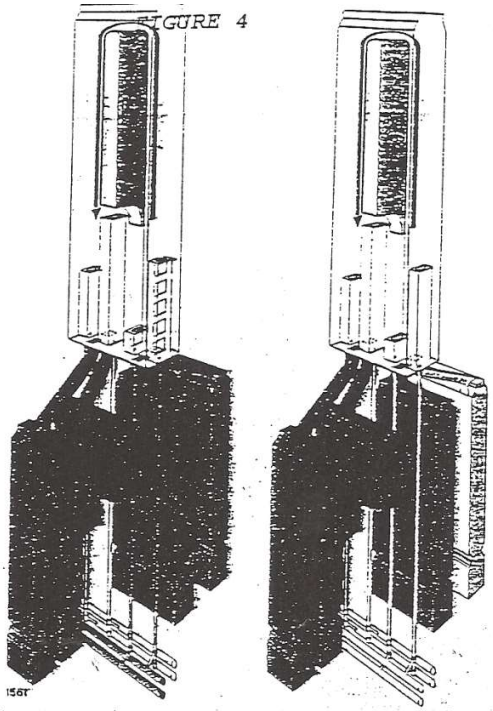


FIGURE 4



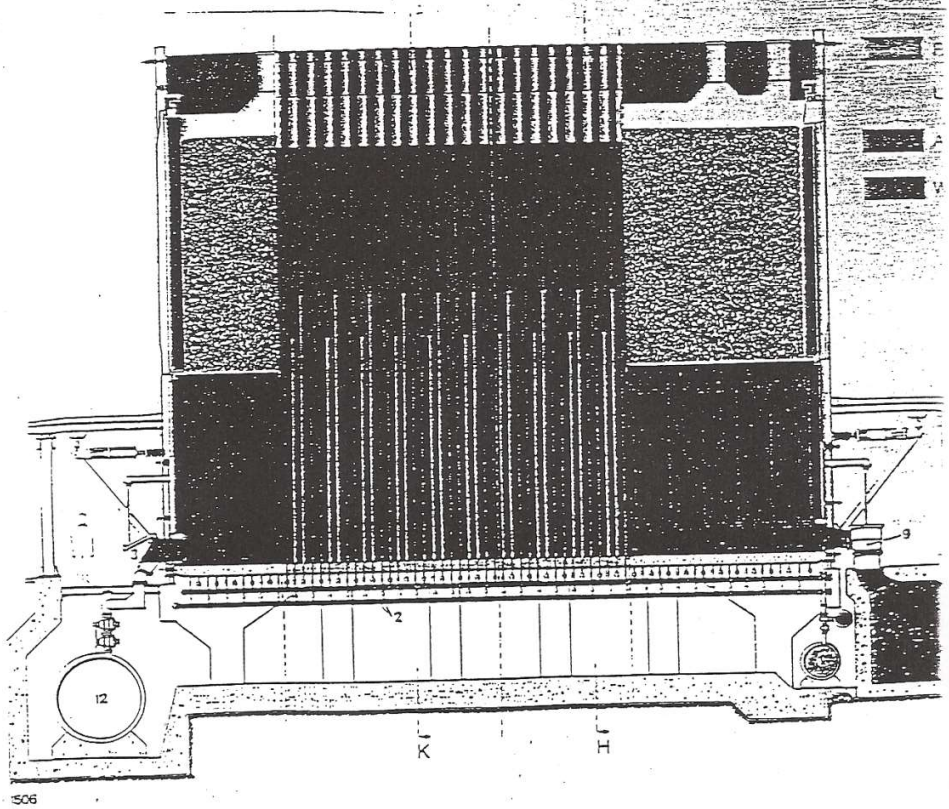


FIGURE 5

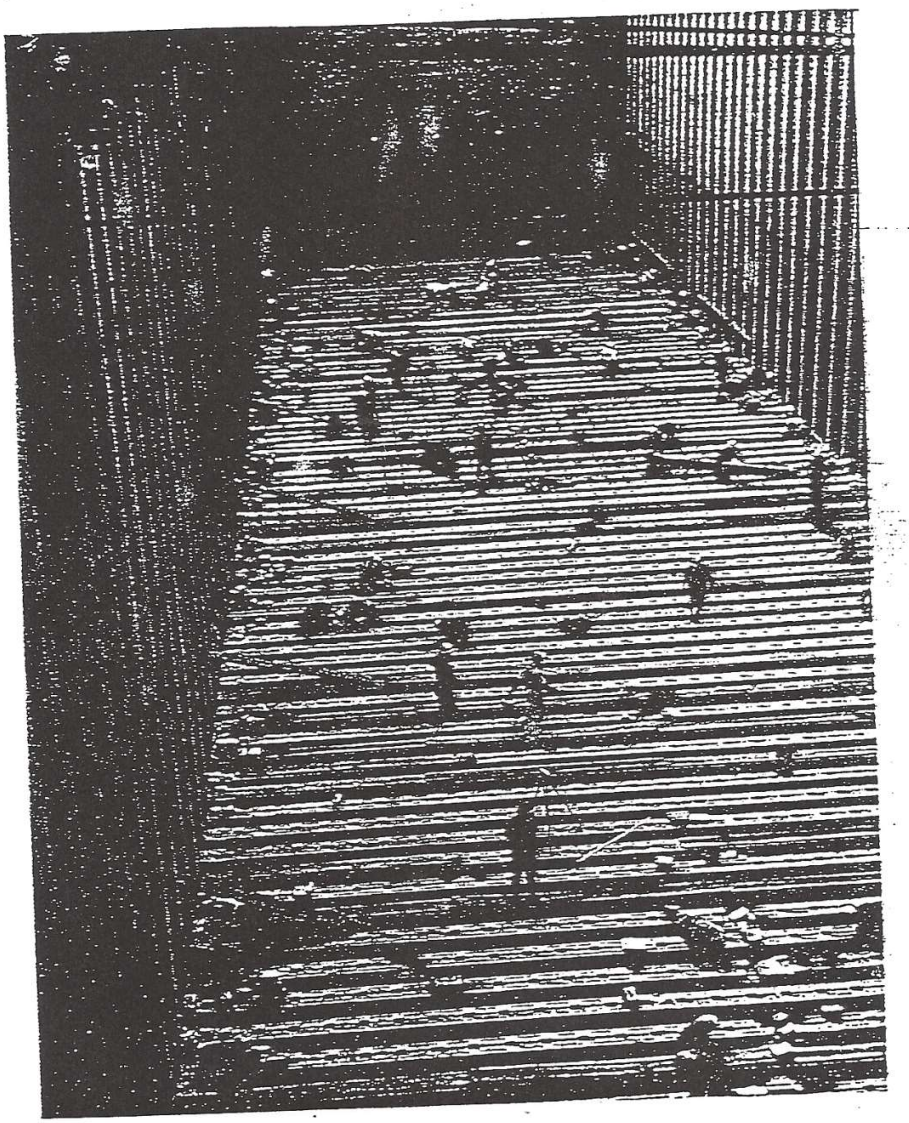
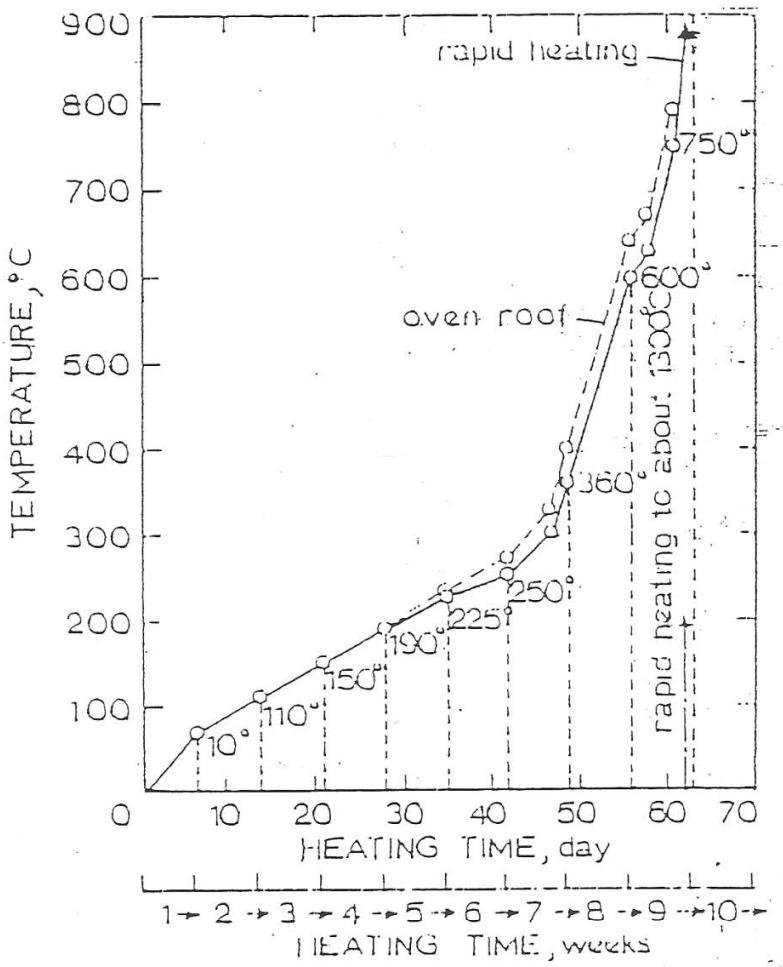


FIGURE 6


rapid heating
oven roof
rapid heating to about 1300°C
TEMPERATURE, °C
HEATING TIME, day
HEATING TIME, weeks
10°
110°
150°
190°
225°
250°
360°
750°
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
1
2
3
4
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6
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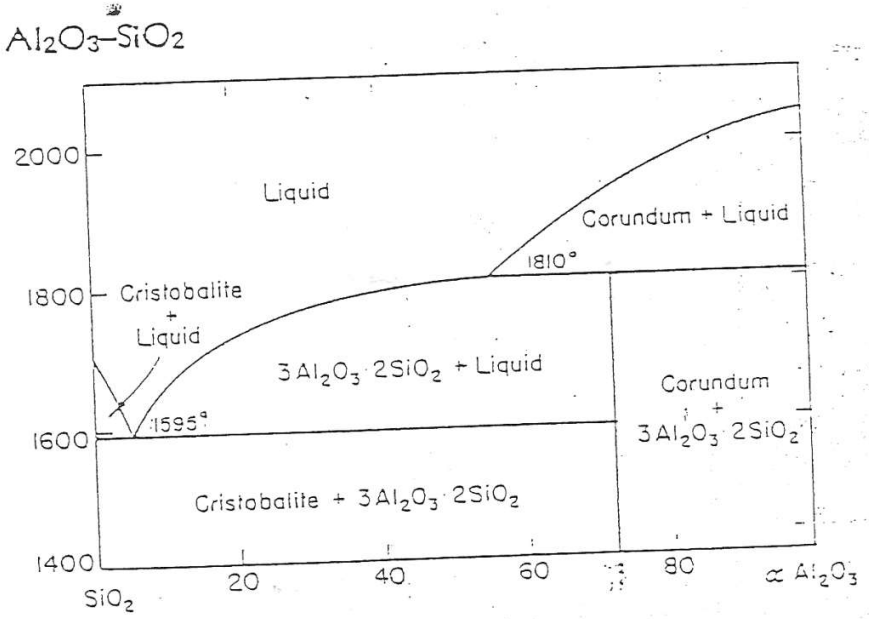
8
9
10

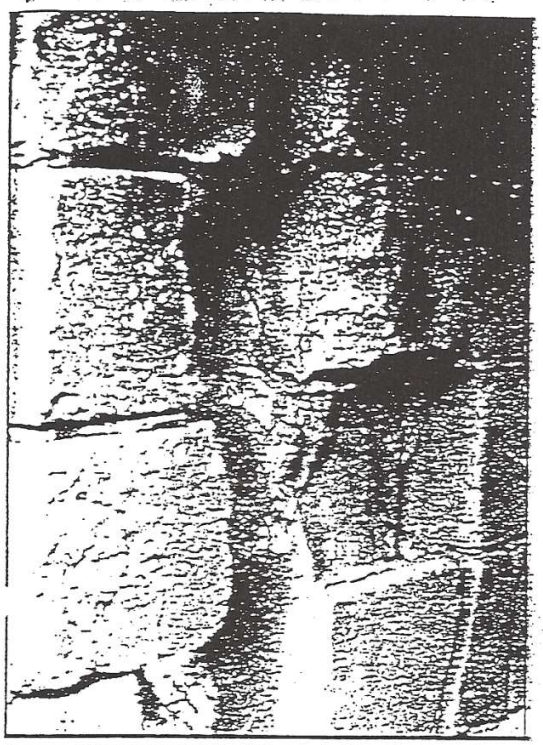
FIGURE 7



—System αAl_2O_3–SiO_2.

N. L. Bowen and J. W. Greig, *J. Am. Ceram. Soc.*, 7 [4] 242 (1924); Eutectic temperature of 1595°C. according to: J. F. Schairer, *ibid.*, 25, 243 (1942).

FIGURE 8



– Typical damaged brickwork in the coke oven.

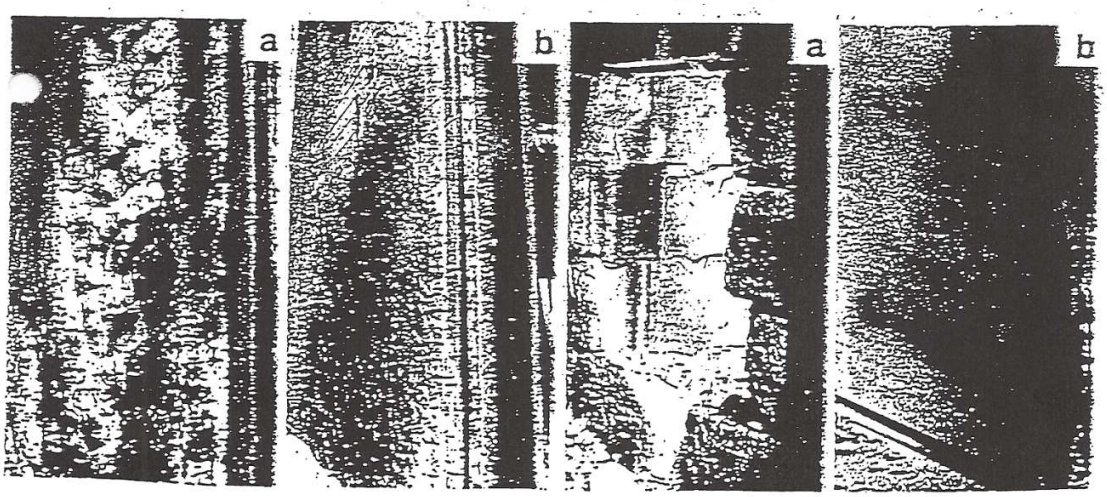


FIGURE 9a

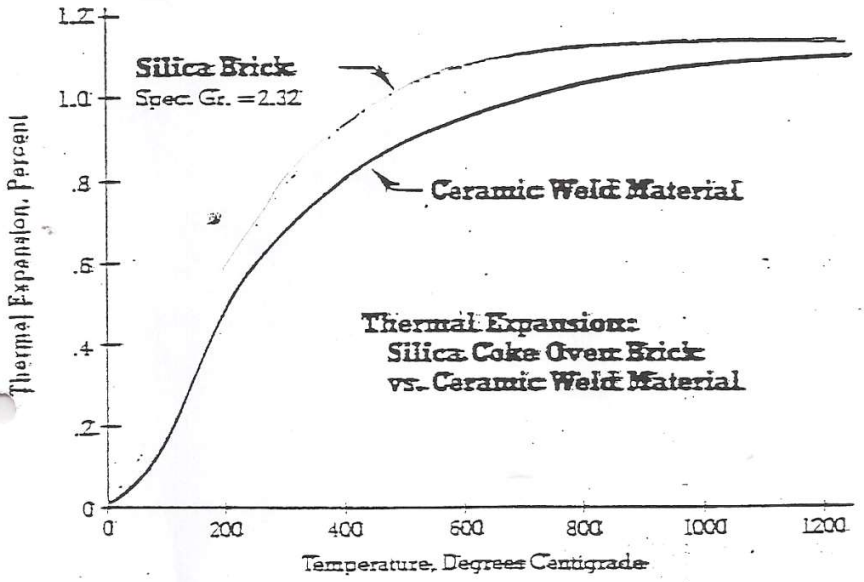
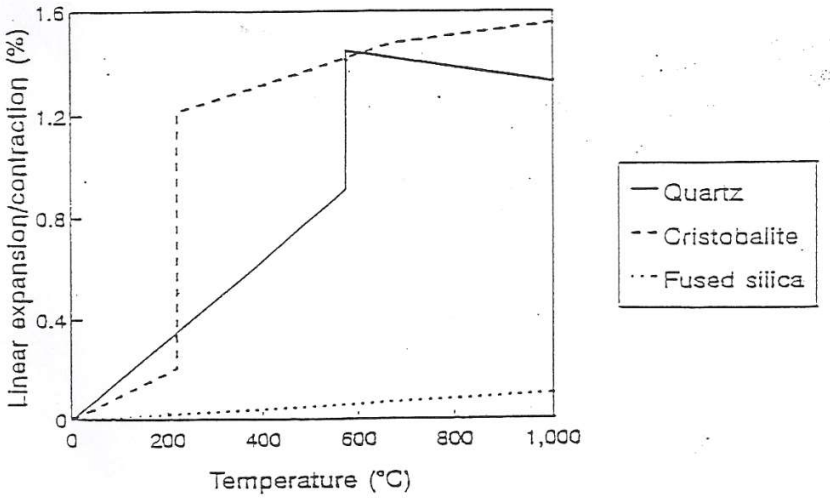


FIGURE 9b



: Linear thermal contraction of silica polymorhs.

FIGURE 10

— Linear thermal expansion of coke-oven quality silica brick and high-purity fused silica castable (no load).

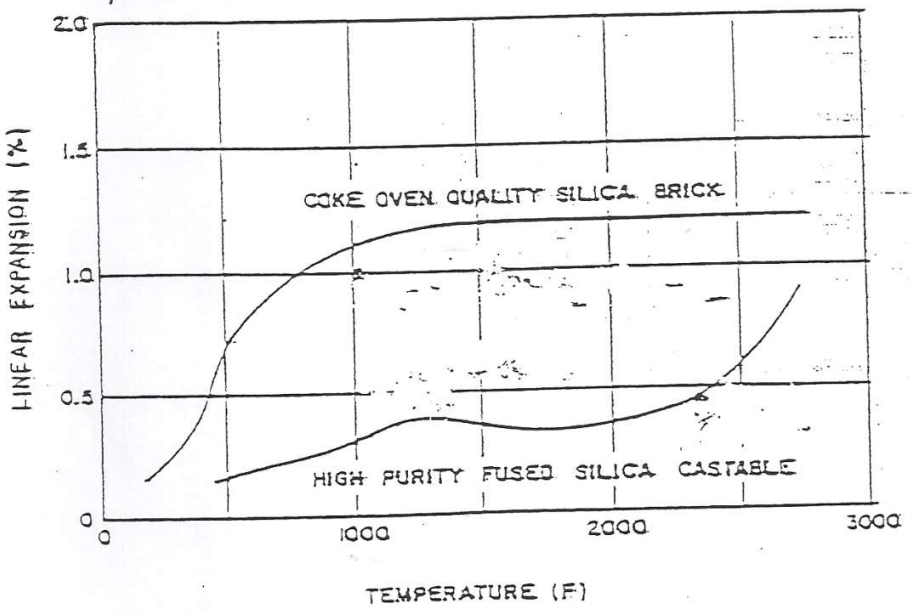


TABLE 1

MINERALOGICAL AND CHEMICAL COMPOSITION OF TYPICAL COKE OVEN SILICA BRICKS

	Type A	Type B
Mineralogical Composition %		
Quartz	1-5	3-5
Tridymite	70-85	60-70
Cristobalite	9-26	25-33
Chemical Composition (%)		
SiO_2	93-94,9	93-94,6
Al_2O_3	0,4-0,8	0,4-0,8
CaO	1,8-2,2	2,1-2,4
MgO	0,2	0,2
TiO_2	0,9-1,6	1,3-1,9
Na_2O	0,05-0,09	0,08
K_2O	0,2 – 0,3	0,2 -0,3
Relative Density	2,30 – 2,33	2,33 – 2,34

TABLE 2

MODIFICATION AND INVERSION TEMPERATURE OF SiO_2

Temp (°C)	Inversion	%linear change	% Volume change	Relative Density
117 to 163	$\propto \leftrightarrow \beta$-tridymite	+0,17	+0,50	2,27
200 to 275	$\propto \leftrightarrow \beta$-cristobalite	+1,00	+2,0 to +2,8	2,33
575	$\propto \leftrightarrow \beta$- quartz	+0,026 to +0,45	+0,86 to +1,3	2,65

TABLE 3

	Regular brick	Dense Brick	Super Dense Brick
Refractories	32½	33	32
True specific gravity	2,31	2,31	2,30
Apparent specific gravity (g/cm^3)	2,30	2,30	2,26
Bulk density (g/cm^3)	1,80	1,85	1,93
Apparent porosity%	21,6	19,5	14,6
True porosity %	22,0	19,9	16,1
Permeability (cc/sec0	0,121	0,103	0,035
Cold crushing strength (kg/cm^2)	600	622	960
Modulus of rupture (kg/cm^2) room temp. 1480°C	190 50	199 55	211 166
Cold elastic modulus (kg/cm^2)	13,0	13,5	17,6
Thermal expansion (at 1000°C)	1,17	1,15	1,18
Reheat change (1450°C x 2hrs,%)	0	0	0
Refractories under load T_1(°)	1620	1630	1630
Thermal conductivity (k cal/mh°C) 350°C 800°C	 1,40 1,62	 1,41 1,71	 1,90 2,15
Chemical composition(%) LOI SiO_2 TiO_2 Al_2O_3 Fe_2O_3 CaO MgO Na_2O K_2O	 0,8 95,60 0,10 0,95 0,55 2,00 0,06 0,06 0,18	 0,14 95,85 0,07 0,96 0,59 2,10 0,06 0,08 0,15	 0,16 96,06 0,07 0,85 0,54 1,96 0,15 0,07 0,14
Mineral composition (%) Quartz Tridymite Cristobalite	 <1 63 18	 <1 61 21	 <1 53 26

TABLE 4

PHYSICAL, CHEMICAL AND CERAMIC PROPERTIES OF THE MASS WELDED ONTO THE SILICA BRICKS OF COKE

	Ceramic Welding Mass	Silica Brick
BULK DENSITY	-1,77	1,73-1,85
Relative density	2,35	2,33-2,38
Open porosity (%)	21,5	<22,0
Reversible thermal expansion at 1200°C (%)	1,10	1,20-1,30
Thermal conductivity at 1000°C (W/km)	1,63	1,70
Cold crushing strength	-18,00	>22,0
Refractories under load as per DIN 1064 ta. (°C)	1645	1650
Chemical Analysis (%)		
SiO_2	94,9	>94,5
Al_2O_3	2,6	0,9
CaO	1,8	3,2
MgO	<0,1	<0,1
Fe_2O_3	0,6	0,065
Cristobalite	Predominant	±6,0%
Tridymite	3,0%	Predominant
Quartz	0	0

TABLE 5

PHYSICAL PROPERTIES OF HIGH PURITY FUSED SILICA CASRABLE AFTER USE

	Physical Properties			
Sample No.	Bulk density (g/cm^3)	Apparent Porosity (%)	Relative Density	Cold crushing Strength (MPa)
1	1,82	21,9	2,34	16,4
2	1,87	20,6	2,36	13,9
3	1,86	20,7	2,35	-
4	1,68	27,9	2,33	-
5	1,79	23,6	2,35	41,3
6	1,78	23,5	2,35	48,4
Typical data (Unused)	1,82	24,5	-	22,8

Sample No.1 heated for 50hrs at 1288°C

Sample Nos.2 and 3 in service for 3 weeks at 1232°C

Sample No.4 in service for 6 months at 1232°C

Sample Nos.5 and 6 in service for 2 years at 1232°C

TABLE 6

MINERALOGICAL OF HIGH PURITY FUSED SILICA CASTABLE AFTER USE

	Mineral Component (%)				
Sample No.	Tridymite (SiO_2)	Cristobalite (SiO_2)	Quartz (SiO_2)	Pseudo-wollastonite ($CaSiO_4$)	Amorphous (SiO_2)
1	6	26	12	4	51
2	6	39	13	4	38
3	21	31	9	4	35
4	52	22	4	4	18
5-flue face	45	28	3	4	20
5-oven face	24	31	2	4	41
6-flue face	32	27	4	4	33
6-oven face	23	26	5	4	42
Typical data (unused)	1	1	15	4	79+
Coke oven quality silica brick (unused)	40-45	28-41	1	2-5	5-24+

Sample No.1 heated for 50hrs at 1288°C

Sample Nos.2 and 3 in service for 3 weeks at 1232°C

Sample No.4 in service for 6 months at 1232°C

Sample Nos.5 and 6 in service for 2 years at 1232°C

Chapter 8

BLAST FURNACE REFRACTORIES

1. INTRODUCTION

The blast furnace is the main source of hot metal and will remain so for at least the next decade. **See figure 1** for general layout.

In principle the furnace is fed from the top with a burden consisting of iron ore, coke limestone and dolomite. The iron ore is either fed as lump ore or sinter. The main impurities in the iron ore are generally alumina, silica and manganese.

The function of the coke is three-fold. Firstly, it provides the heat necessary to reach the temperature at which iron oxide can be reduced by carbon to give metallic iron. Secondly, it yields the carbon monoxide that reacts with the iron oxide to reduce it to metal. Thirdly, it creates a permeable burden through which the hot air through the tuyeres can penetrate to melt the burden from deeper within and not only from the outside, thereby minimizing the effect of the so-called "dead-man".

Manganese and silicon compounds are also reduced to the metallic state and the gangue melted to form slag with the lime and magnesia from the added stone. Given the right basicity, such slug is capable of absorbing much of the sulphur in the burden, yielding to relatively low sulphur iron required for subsequent steelmaking. Where the sulphur is still too high it may be reduced by desulphurization (soda ash, Ca carbide or magnesium). For principal structural elements and flow of materials **see figure 2.**

The blast furnace is characterized by a wide range of temperatures and environmental conditions within it. **See figure 3.**

The hearth must contain liquid iron and slag and withstand erosion when they swirl around the hearth during tapping. In the bosh there is abrasion from coke moving down and grit blasting from coke particles entrained in the blast.

In addition, liquid slags and iron can wash over the refractory and alkalies that have vapourised in the hearth can attack it. There is a progressive change in environment from the bottom of the stack to its top. The environment at the bottom of the stack is much like

that of the bosh, but at the top there are no liquids present and the temperature is low. Here the main wear is by abrasion moving up. Also this is an area of the lining where, under certain circumstances, extensive attack by carbon monoxide can occur. **See figure 4** for the different wear mechanisms in the various zones.

2. BRIEF DESCRIPTION OF THE WEAR MECHANISMS

2.1 Carbon monoxide attack

Carbon from the CO gas is deposited by the reaction $2CO=CO_2+C\downarrow$. This reaction occurs most vigorously at 450°C and is catalysed by the presence of iron. Any iron oxide present is reduced to iron and carbon whiskers grow with a particle of iron in the form of percarbide or cementite at the end of each carbon filament and from which further carbon is deposited. This will eventually result in disintegrating the refractory to a piece of rubble.

2.2 Alkali attack

Alkalies (mostly K_2O) which are charged as impurities in the burden of a furnace (currently at a rate of approximately 2,5 kg/ton of hot metal produced) are evaporated in the high temperature zone near the tuyeres, from whence they are then carried up by the rising gases to condense I the upper bosh and lower stack regions. K-alkalies will react with alumino-silicate bricks to form kaliophilite ($2K_2O.Al_2O_3.SiO_2$), with a consequent volume expansion of about 45%, thereby resulting in cracking of the brickwork.

Although carbon is no longer actually used in the bosh, disruptive attack on refractory carbons can occur by the formation of potassium carbon compounds also called intercalation compounds of the form C_xK (where x is 8, 24, 36 or 60)

2.3 Iron Attack

Carbon can be attacked by the dissolution of carbon into the iron penetration of iron into the carbon (**See figure 5 e**xpansion of iron-containing carbon).
Any carbon in contact with liquid metal at a temperature above 1150°C, the freezing isotherm for pig iron will have a very short life before it is dissolved or eroded away. The success of carbon refractories relies on effective cooling which forms a frozen layer on the surface of the working lining.

2.4 Oxidation

The main source of oxidation is from water coming out of leaking coolers at rates up to hundreds of litres per minute. This can do considerable harm to carbon refractories, where steam reacts with it to form CO_2, CO and hydrogen.

Water falling onto oxide refractories may cause failure by thermal shock.

2.5 Slag attack

Good cooling systems where there is good thermal contact can, under normal operating conditions, reduce slag attack to almost nil provided the protective layer is not scrapped away by the descending burden.

2.6 Stress

Stress applied to refractories can affect their performance and also stresses development in the refractory lining be transferred to the shell and result in splitting. Stresses can be caused by poor design and as a consequence of bad practice. An example of the latter is repeatedly taking a furnace out of service.

3. FURNACE DESIGN AND REFRACTORY CONFIGURATION

Blast furnaces can have various hearth diameters, but for economic considerations they are from 10 to 14 metres and higher, with production between 5000 to 10000 tons or more per day.

For the basic design of the refractory linings there are two schools of thought i.e. "thermal" solution and "refractory" solution, the latter one also known as the 'ceramic cup'.

a) Thermal solution
   The refractory design is based upon high density plate cooling and graphite/semi-graphite high conductivity materials to reduce hot face temperatures to establish freezing of slags into the refractory which will offer protection against any further erosion or corrosion. Furthermore the limit temperatures of aggressive agents will also be lowered. This design requires excellent contact between the various elements forming the wall, including the cooling system, as well as a highly effective cooling system to drain off a high thermal flow.
b) Refractory solution
   This design aims to minimize the thermal losses through the refractory lining. It requires low conductivity products which are able to withstand the different kinds of corrosion even at high temperatures since they are not protected of hot face temperature a in the thermal solution

3.1 Refractory design

There are various configurations which are best illustrated by **figures 6 and 7** see also **figure 8** for a typical example of the thermal solution design, including wear mechanisms.

As can be seen, SiC is widely used even in the bosh region except in the "thermal solution" design where graphite and semi-graphite is used in the bosh.
The Schwelgern No.1 furnace is a typical "refractory solution design.
For the hearth wall, carbon bricks of the micro pore or even super-micro pore quality are used which have more resistance against mechanical abrasion of the liquid iron than graphite or semi-graphite. **See figure 9** for the relative thermal conductivities of carbon-bearing materials.
For the various refractory brick qualities refer to the following tables:
Table 1 – silicon carbide
Table 2 and 3 – carbon –semi-graphite graphite
Table 4 – chamotte (fireclay) and high alumina
Table 5 – Refractories for tuyeres
Table 6 – Refractories for blast furnace bottom – ceramic cup
For a comparison of blast furnace refractory brick properties **see Table 7.**
For a complete (successful) blast furnace operation cast house refractories have to be included (stoves will be omitted from this presentation).

4. BLAST FURNACE TAPHOLE MIXES

When filled in the taphole, the mix forms part of bottom lining of the blast furnace. This means that the taphole mix must function satisfactorily as a taphole filling material. Part of the taphole mix is pushed inside the furnace and serves to protect the bottom lining. When the taphole is opened, it forms a passage through which hot metal is tapped, so it is necessary that the taphole mix can withstand erosion and corrosion by hot metal and slag.

Figure 10 shows the temperature profile obtained. According to calculations (3000m^3 furnace), the taphole mix is heated to 300°C to 500°C within five minutes and 800°C to 1300°C after 30minutes. Sintering and hardening of the mix will take place in these temperature ranges.

General composition of taphole mixes.

a) Main aggregates (grog): fireclay (chammotte),	Andalusite, bauxite, etc.
b) Secondary aggregates	alumina, SiC, zircon
c) Special aggregates:	Fe-Si, metallic Si, Fe-Si_3N_4 etc.
d) Carbonaceous materials:	Coke, carbon
e) Binder:	Coal-tar or resin.

A specific high performance taphole mix can have the following composition.

	%
Fused alumina	15 - 40
Fireclay	10 - 20
SiC	10 - 20
Coke	10 - 20
Metallic Si	0 - 5
Tar or resin	15 - 20

The taphole mix being subjected to the heating effect after closing (filling) of the taphole, is hardened or carburized to form a kind of carbon-bonded structure. Sintering also takes place, particularly amongst the refractory grains.

These mixes have to be designed to have the appropriate properties for a specific application. The following are some of the important properties:

a) Good workability (the ease of pushing the mix 2,0 to 2,5 metres into a ±60mm to 70mm hole)
b) Good setting and sintering properties
c) Sufficient permeability for escape of volatiles
d) Volume –stability
e) Sufficient strength
f) Durability
g) Easy drillability

See table 8 for typical properties of resin- and tar-bonded taphole mixes.

5. BLAST FURNACE RUNNER MIXES (MAIN RUNNER WORKING LINING

Iron troughs include the main trough, iron runner, slag runner, tilting through (tilter) and others, the main trough (runner) being the most important. **See figure 11** for typical layout.

Runners can have the following dimensions

a) Length up to the skimmer block: 14 to 16,5m
b) Width: 1,7 to 2,1m
c) Depth: ±0,9m

Wear factors include oxidation, erosion, corrosion by metal and slag, thermal stresses (cracking) etc. in order to combat these wear

factors the following composition and functions of the different components are applicable:

Components	**Name**	**Function**
Aggregate 80%	Fused alumina Bauxite Andalusite Chamotte	The frame of the product Stable, little or no attack
Binder 2-5%	Fine and ultrafine particles – cement –admixtures.	
Additives 2-25%	SiC Si_3N_4	Function still debated • Anti-oxidant • Improves corrosion resistance • Reacts to produce SiO_2 and C
1-5%	Si Al Mg	Function still debated • Antioxidant • Forms SiC • Improves hot strength
2-10%	C	Different possible types • Graphite • Pitch • Intermediate types Main function: • Prevents wetting • Forms SiC • Reduces the size of pores
0-07%	Anti-explosion agent – metal or organic fibres:	• Allows water to move out when the product is dried • May contribute to water evaporation through exothermic reaction • May help strengthening through exothermic reaction
Fluid 0-10%	Air H_2O	
1-3%	For dry products: Cementing agents at low temperatures	

For a typical wear pattern see **figure 12.**
Properties required of trough materials include the following:
a) Good workability
b) Uniform, high density structure and high strength
c) Wear-resistance to hot metal and slag
d) Resistance to chemical attack by hot metal and slag
e) High temperature volume-stability

f) Oxidation –resistance and thermal shock resistance.

For typical composition and properties of a runner castable material **see table 9.**

The main method of placing the runner materials is by vibrating-casting, although ramming, dry vibratables and free-flowing castables are also used.

6. Refrences

6.1 Refractories for iron steelmaking

6.2 M.O. Warman – Combating a changing blast Furnace Environment by Examination, Testing and Selection of refractories.

6.3 Dr H.J.J. kriek et al – lectures on Refractories

6.4 Development of Refractories For BF Troughs. Refractory seminar – steel Times May 1986.

6.5 Dr K. Sugita et al – Refractories technology for Blast Furnace Tapholes and Troughs.

6.6 Mr. A Matsuo – SiC Refractories for the Blast furnace.

6.7 J.M. bauer – Technical Trends in European Blast Furnace Refractory linings.

6.8 K. Hiraguishi – Current Concept of Blast Furnace Refractories above the Tuyere Belt in Japan

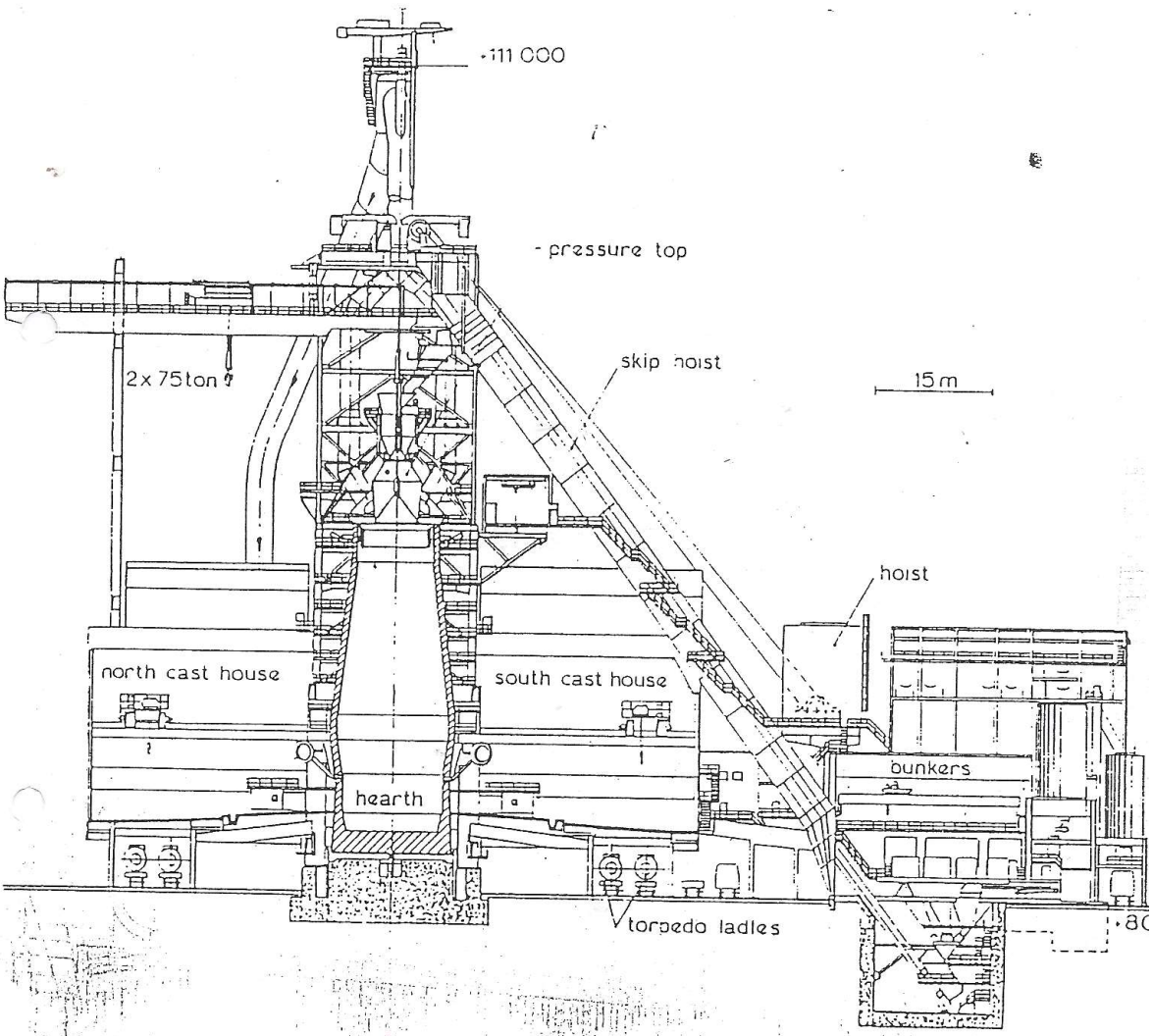
6.9 K. Lechthaler – Various Lining Concepts in the Construction of Blast Furnaces

6.10 Dr. K. Sugita et al – Improvements in blast furnace Refractories in Japan.

6.11 Dr. J. van Laar, et al Blast Furnace Refractories and cooling Systems – The Hoogoven solution

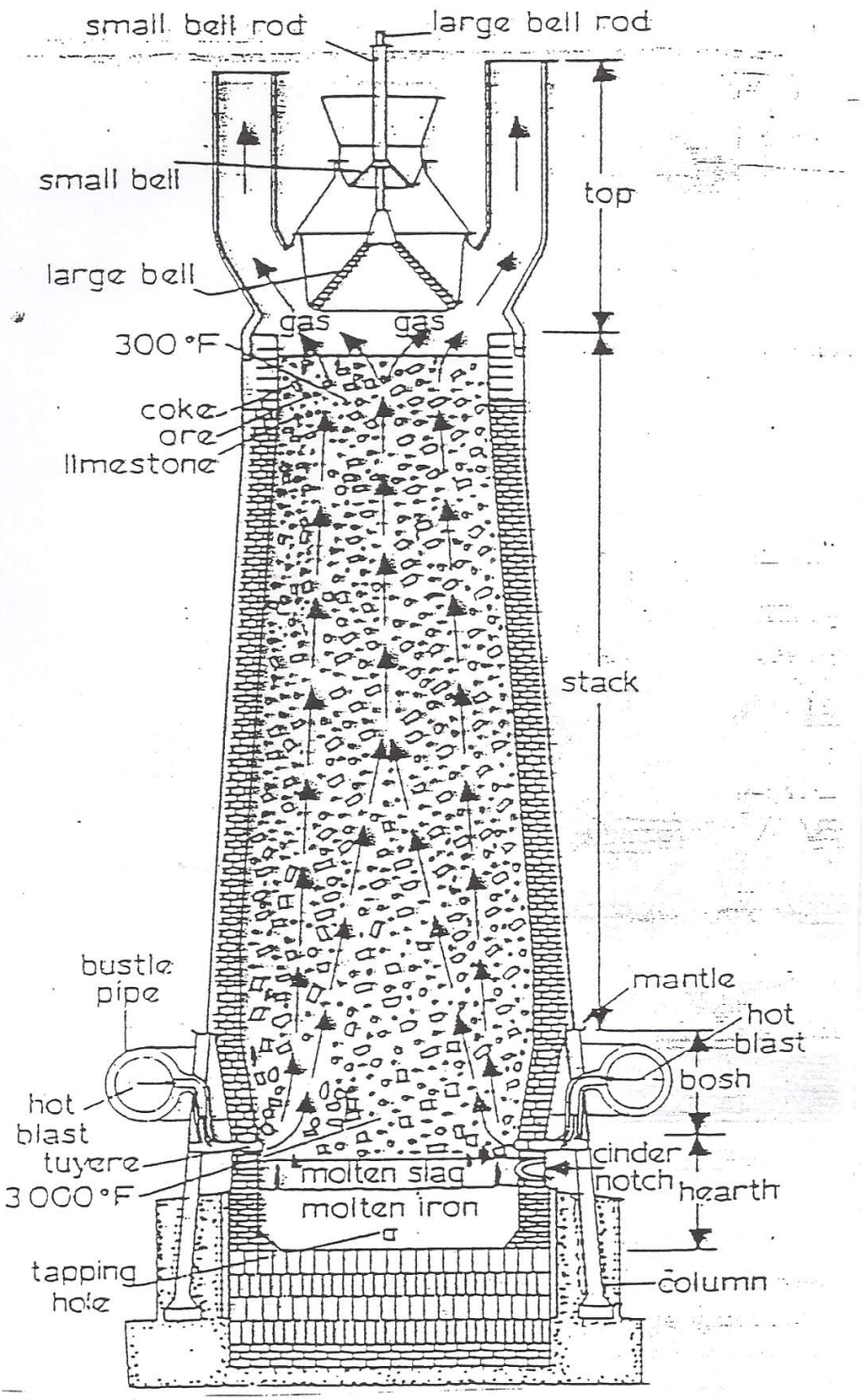
6.12 Dr. J. Mittag – Modern Blast Furnace – from Wear mechanism to solution.

FIGURE 1



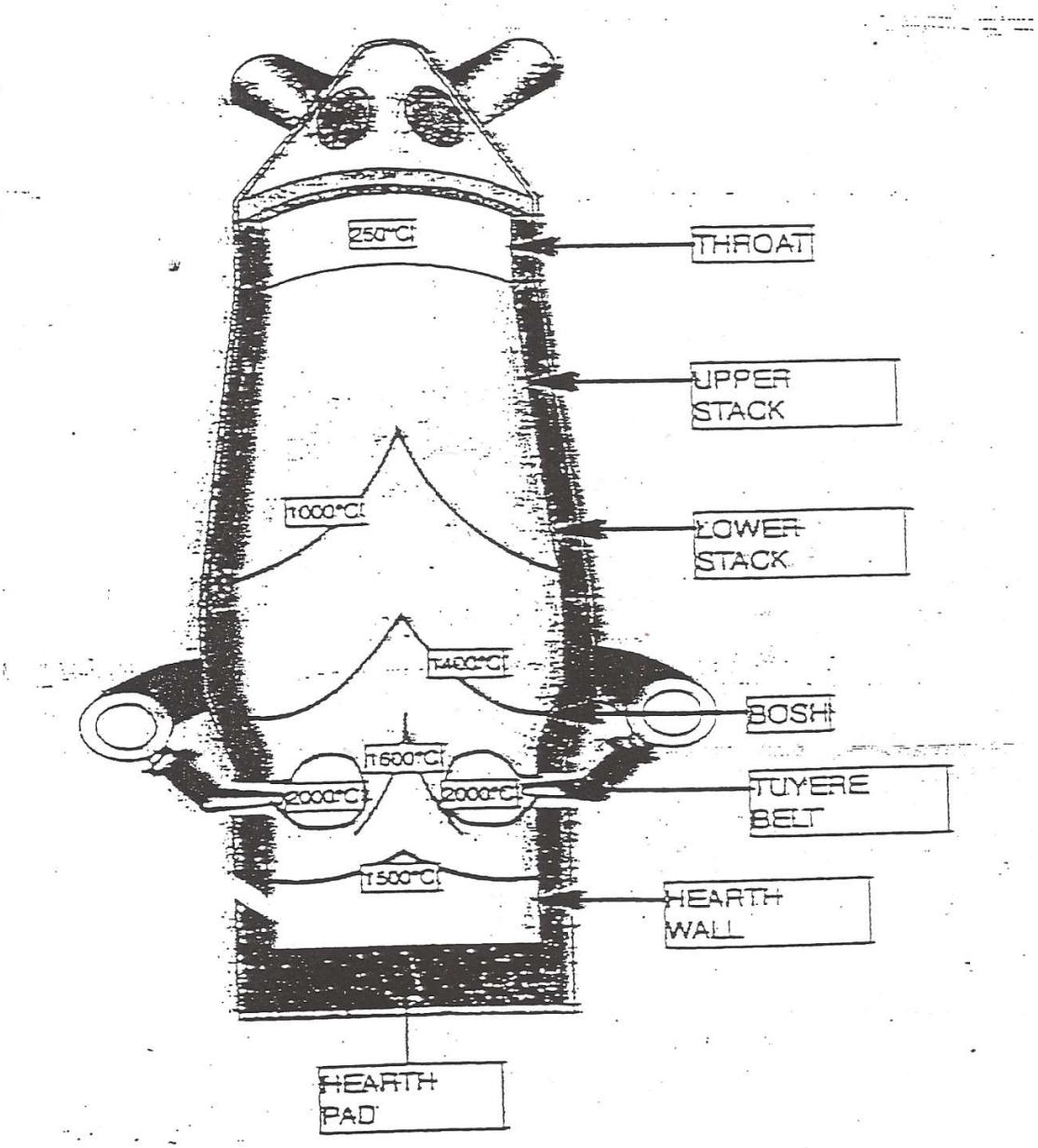
Schematic of new Hoogovens 10 000 t/day ironmaking plant (courtesy of Hoogovens)

FIGURE 2

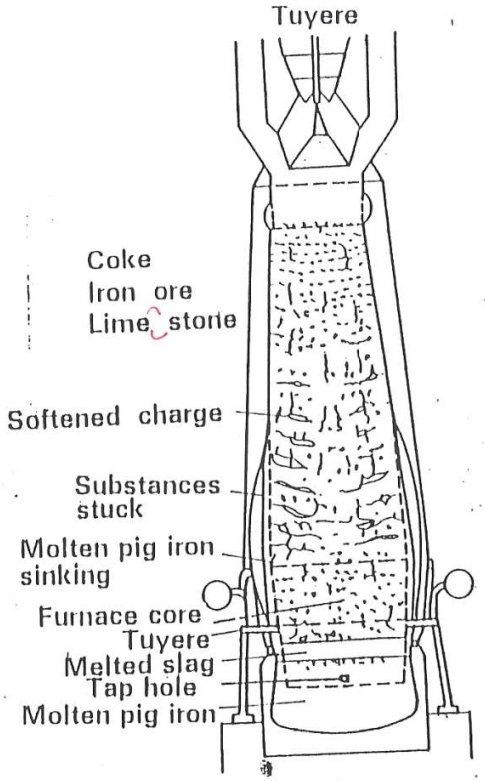


Principal structural elements and flow of materials in the blast-furnace process (after USSC)

FIGURE 3



Temperatures in Various Zones of the Blast Furnace

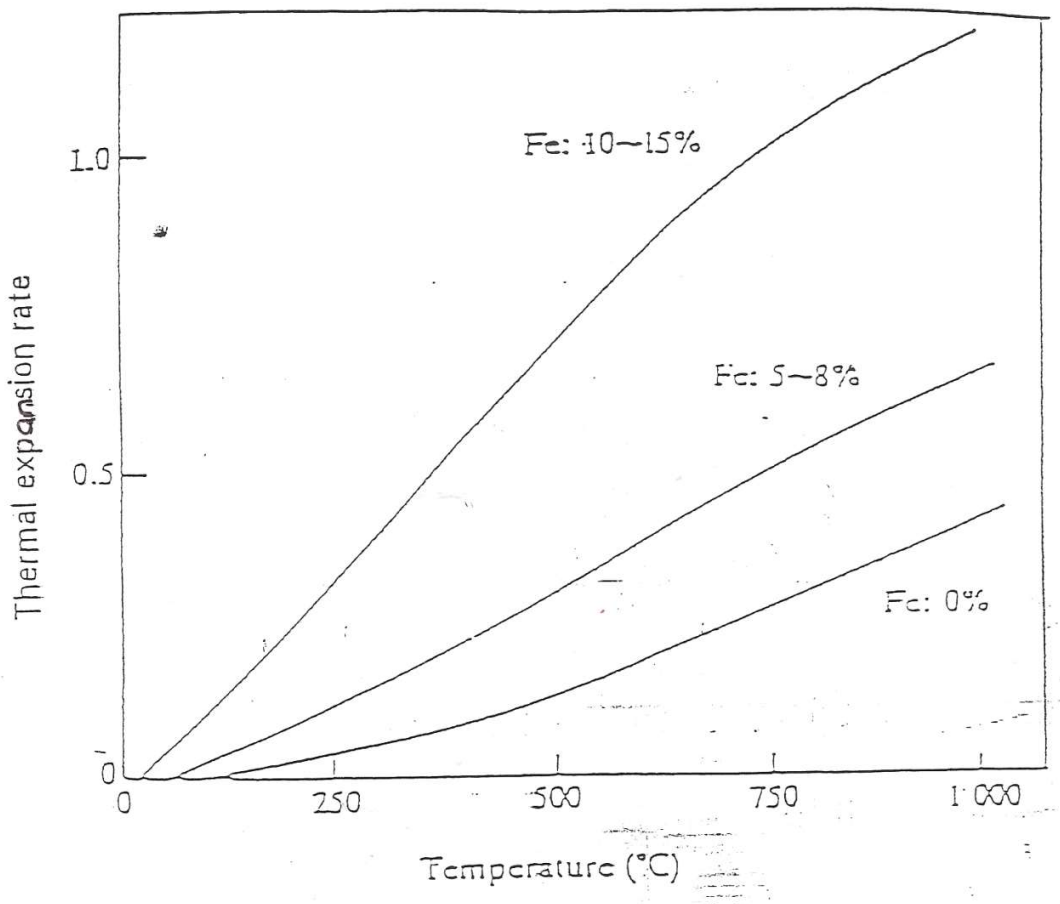


	Temperature within furnace	Reaction within furnace	Furnace materials wear: Cause	Furnace materials wear: Mechanism
Lump zone	300°C		Charge drops	Abrasion
		Indirect cause		
	500	Indirect cause	Zinc depositing	Expansion
	800	Direct reduction		
Softening zone		Reduction of iron oxide by CO_2	Alkali gas phase reaction	Expansion, Cracking, Increase in pores Strength decrease
		Carbon oxidation by CO_2		
		Water gas reaction		
	1,000	Carbonated dissolution	Carbon depositing	
		Carbon addition to spongy iron		
	1,400	Completion of ore reduction	Alkali slag	Softening, melting
Melting zone		Manganese reduction		
		Slag formation	Slag	
		Melting & sinking		
	2,500	CO_2, H_2 formation by hot blast		
		CaS formation		
Molten pig iron	1,500		Molten pig iron reaction High temperature	Solution into (Carbon molten iron brick) Softening and (Clay melting brick)

FIGURE 4

Blast furnace temperature distribution and reaction inside furnace.

FIGURE 5



Thermal Expansion of Iron infiltrated Carbon.

FIGURE 6

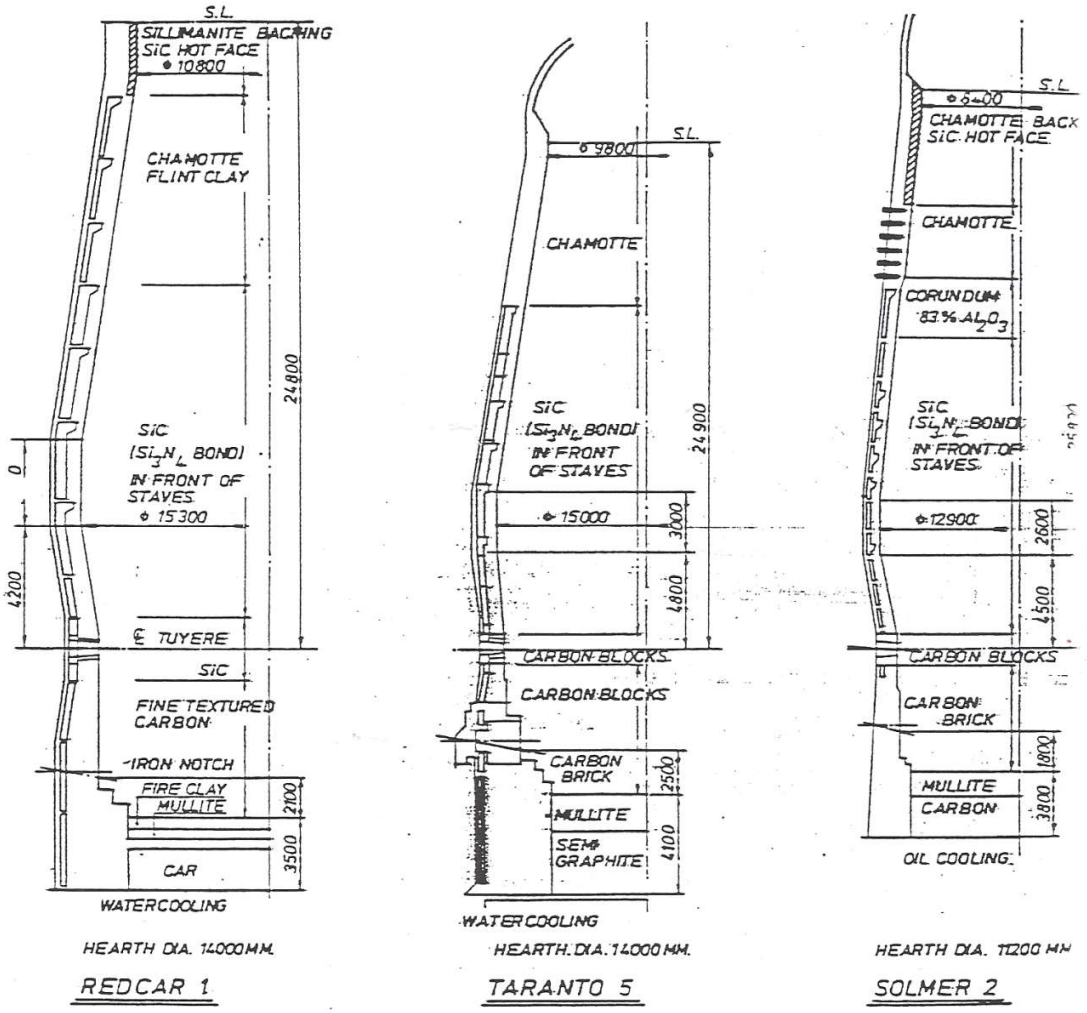

S.L.
SILLIMANITE BACKING
SiC HOT FACE
Φ 10800
CHAMOTTE
FLINT CLAY
24800
SiC
(Si3N4 BOND)
IN FRONT OF
STAVES
Φ 15300
0
4200
℄ TUYERE
SiC
FINE TEXTURED
CARBON
IRON NOTCH
FIRE CLAY
MULLITE
2100
3500
CAR
WATERCOOLING
HEARTH DIA. 14000 MM.
REDCAR 1
S.L.
Φ 9800
CHAMOTTE
SiC
(Si3N4 BOND)
IN FRONT
OF STAVES
24900
Φ 15000
3000
4800
CARBON BLOCKS
CARBON BLOCKS
CARBON
BRICK
2500
MULLITE
SEMI
GRAPHITE
4100
WATER COOLING
HEARTH DIA. 14000 MM.
TARANTO 5
S.L.
Φ 6400
CHAMOTTE BACK
SiC HOT FACE
CHAMOTTE
CORUNDUM
83% Al2O3
SiC
(Si3N4 BOND)
IN FRONT OF
STAVES
Φ 12900
2600
4500
CARBON BLOCKS
CARBON
BRICK
1800
MULLITE
CARBON
3800
OIL COOLING
HEARTH DIA. 11200 MM
SOLMER 2

FIGURE 7

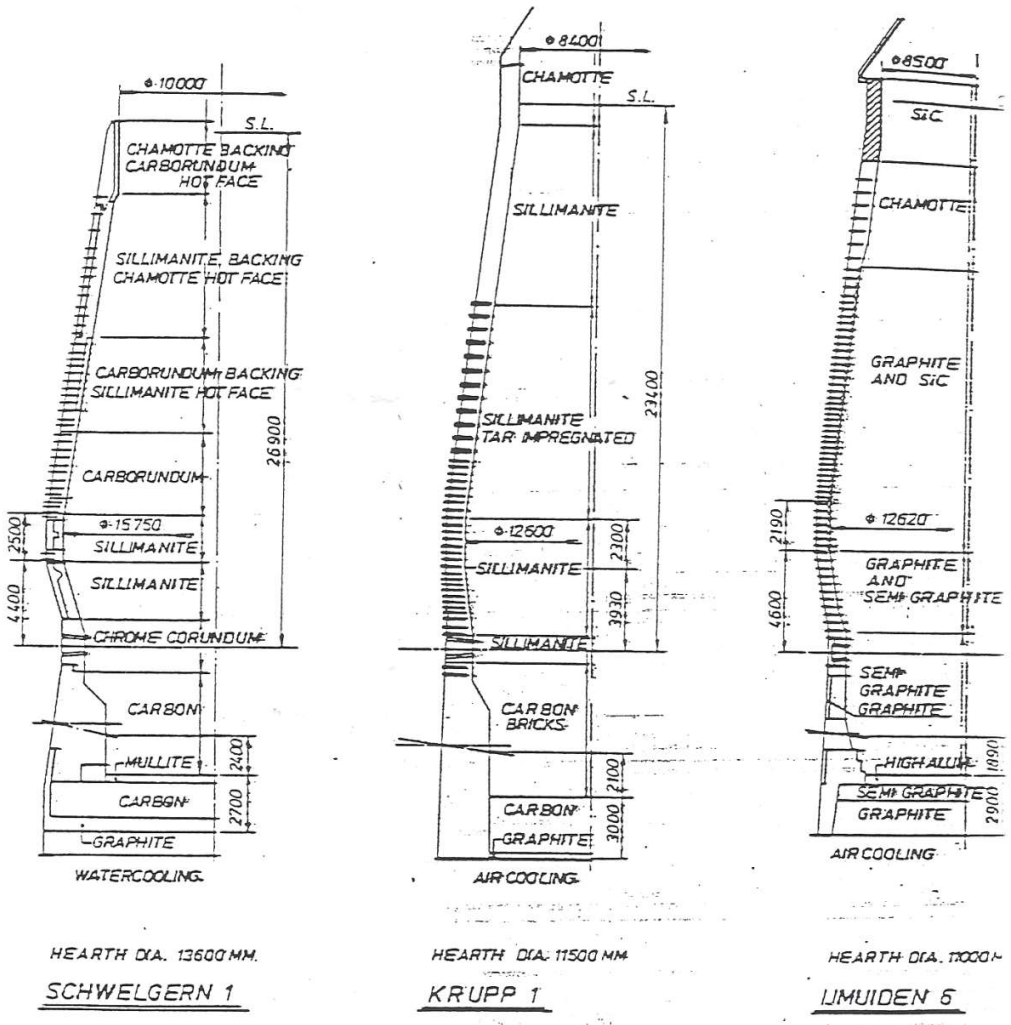
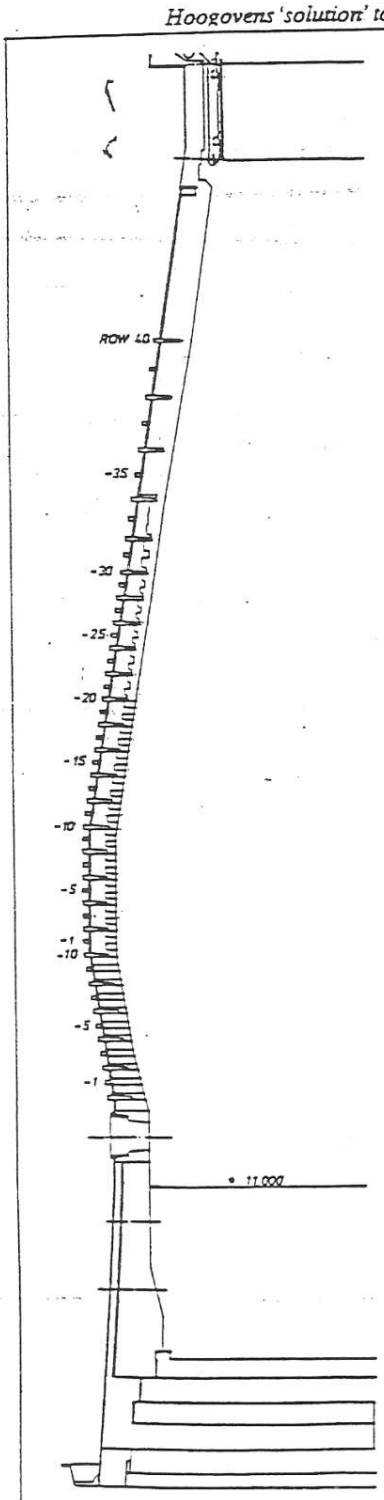

⌀ 10000
S.L.
CHAMOTTE BACKING
CARBORUNDUM
HOT FACE
SILLIMANITE, BACKING
CHAMOTTE HOT FACE
CARBORUNDUM BACKING
SILLIMANITE HOT FACE
CARBORUNDUM
26900
2500
⌀ 15750
SILLIMANITE
4400
SILLIMANITE
CHROME CORUNDUM
CARBON
MULLITE
2400
CARBON
2700
GRAPHITE
WATERCOOLING
HEARTH DIA. 13600 MM.
SCHWELGERN 1
⌀ 8400
CHAMOTTE
S.L.
SILLIMANITE
23400
SILLIMANITE
TAR IMPREGNATED
⌀ 12600
2300
SILLIMANITE
3930
SILLIMANITE
CARBON
BRICKS
2100
CARBON
3000
GRAPHITE
AIR COOLING
HEARTH DIA. 11500 MM
KRUPP 1
⌀ 8500
SiC
CHAMOTTE
GRAPHITE
AND SiC
2190
⌀ 12620
4600
GRAPHITE
AND
SEMI GRAPHITE
SEMI
GRAPHITE
GRAPHITE
HIGH ALUM
1090
SEMI GRAPHITE
GRAPHITE
2900
AIR COOLING
HEARTH DIA. 11000 M
IJMUIDEN 6

FIGURE 8

Hoogovens 'solution' to blast furnace refractories and cooling for extended campaign life



Area	Principle attack phenomenon	Resulting damage	Hoogovens integrated cooling/refractory design	Selected construction
Upper stack	Abrasion	Abrasive wear	High abrasion resistance	SiC wear surface
	Medium temperature fluctuations		Plate cooler spacing for adequate support of refractory	Alumina brick backing (42-44%) Al_2O_3
	Impact	Loss of bricks	Profile friction	
Middle stack	Abrasion	Abrasive wear	Cooling water design (Quantity, Velocity) to cope with local peak loads	
	Heavy/medium temperature fluctuations	Spalling	Medium dense to dense plate cooler spacing	SiC + graphite gradually decreasing SiC-graphite surface area ratio
	Gas erosion	Wear	High/medium spalling resistance	
	Oxidation	Deterioration	Medium/high oxidation resistance	Spalling resistant lining construction
	Alkali attack		Medium/high abrasion resistance	
Lower stack	Heavy temp. fluctuations	Severe spalling	Cooling water design (Q, V) to cope with extreme peak loads	Dense plate cooler spacing
	Erosion by gas jets	Wear	Very high spalling resistance	SiC + graphite
	Abrasion			
	Alkali	Deterioration	High chemical resistance	Spalling resistant lining construction, panel construction
	Oxidation			
	Thermal fatigue	Shell damage and cracks	Proper expansion allowance	
Belly	Medium temperature fluctuations	Spalling	Cooling water design (Q, V) to cope with local peak loads	
	Alkali	Deterioration	Resistance against gas erosion	SiC + graphite
	Oxidation		Medium dense plate cooler spacing	Spalling resistant lining, construction, panel construction
	Abrasion and gas erosion	Wear	Medium spalling resistance	
	High temperature		High slag/chemical resistance	
Bosh	High temperature	Stress cracking	Cooling water design to cope with medium heat load	
	Slag attack	Deterioration, wear	Medium spalling resistance	Alternating rings of semi-graphite and graphite
	Alkali		Low abrasion resistance	
	Medium temp. fluctuations	Spalling	High temperature resistance	Expansion allowance by panel construction
	Abrasion	Wear	High chemical resistance	
Raceway and tuyere zone	Very high temperature	Stress cracking and wear	High temperature resistance	
	Temperature fluctuations	Spalling	Stress reduction	Special densified graphites
	Oxidation (water and O_2)	Deterioration	Spalling resistance	
	Slag attack	Wear	Slag and chemical resistance	Oxidation resistance is not the first priority
	Erosion		Spalling resistant tuyere blocks	
	Damage from scabs	Loss of plate coolers and tuyeres	Oxidation resistance	
		Break out risk		
Hearth	Oxidation (water)	Wear	Stress elimination	
	Zn + alkali	Deterioration	Oxidation protection	Dense semi-graphite
	Slag attack			
	High temperature	Stress build up and cracking	Chemical resistance	Refractory design with metal gas seals
	Erosion from hot liquids	Break out risk	Expansion allowance	
Iron notch	Heavy temp. fluctuations	Spalling	Spalling resistant taphole block	Semi-graphite door
	Erosion (slag and iron)	Taphole wear	Oxidation protection (H_2O)	Graphite taphole cylinder
	Zn + alkali attack	Deterioration	Chemical resistance	
	Gas attack	Wear and deterioration	Gas leakage reduction	Alumina magnesia brick
	Oxidation (water attack)			
Bottom/hearth connection	High temperature	Stress build-up and cracking	Stress reduction by:	
	Zn + alkali	Deterioration	1 – Expansion allowance 2 – Proper cooling	Semi-graphite cooled by graphite resulting in suppressing of inverted mushroom effect
	Hot metal erosion	Inverted mushroom effect	Increased chemical resistance	
	Slag attack			
	Ferrostatic pressure	Iron penetration in pores	Selected thermal conductivity resulting in local freezing	
		Salamander formation		
Bottom	High temperature	Stress build up and cracking	Stress elimination by:	
	Slag attack	Deterioration	1 – Expansion allowance 2 – Proper cooling 3 – Sandwich construction	Sandwich construction:
	Zn + alkali + Pb		Increased chemical resistance	High alumina top
	Ferrostatic pressure		Thermal conductivity based on isotherm calculations	semi-graphite
	Solution in iron	Salamander formation		graphite
	Erosion from hot metal			carbon
				graphite

FIGURE 9

Thermal conductivity of carbon materials vs. temperature

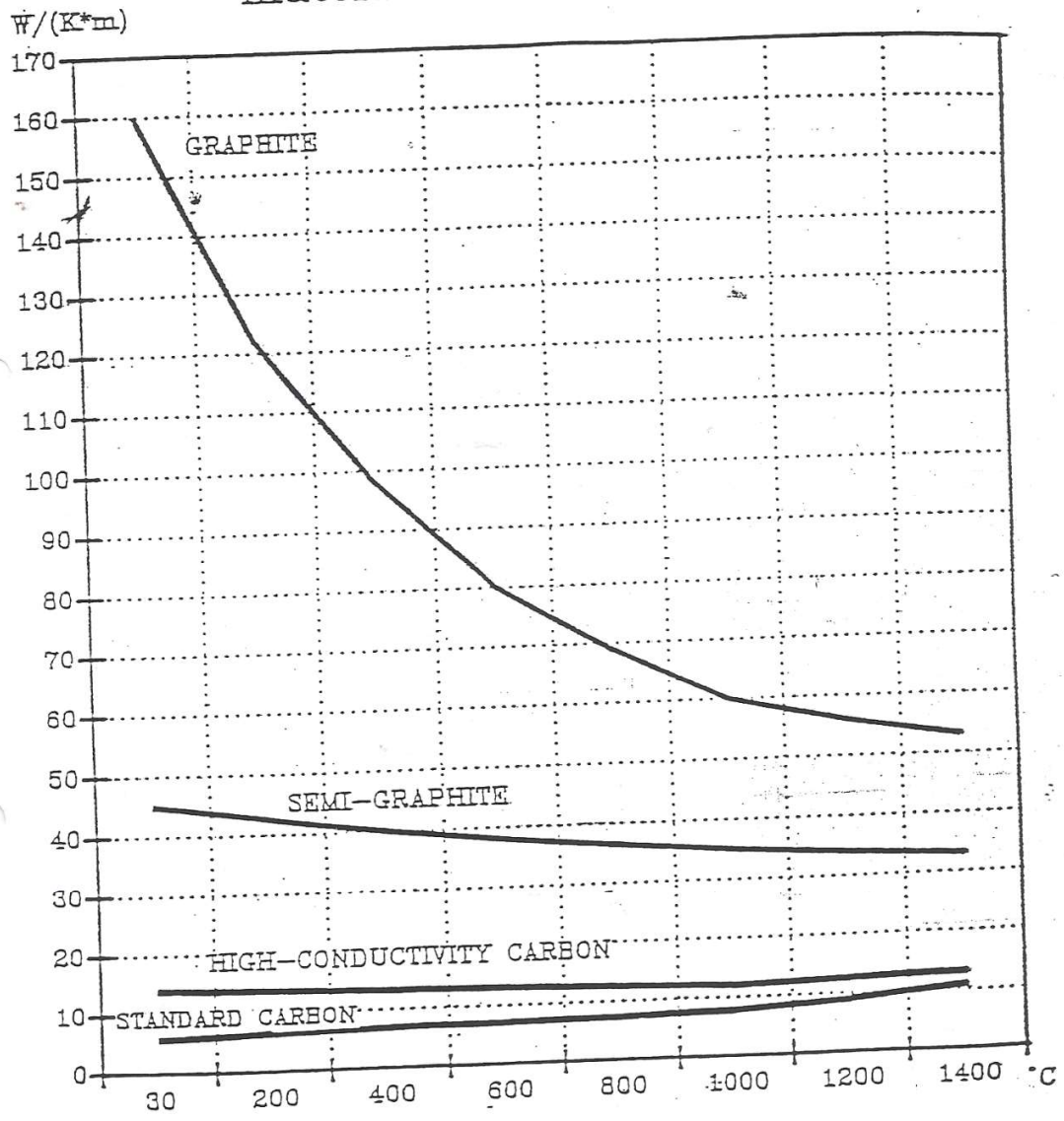
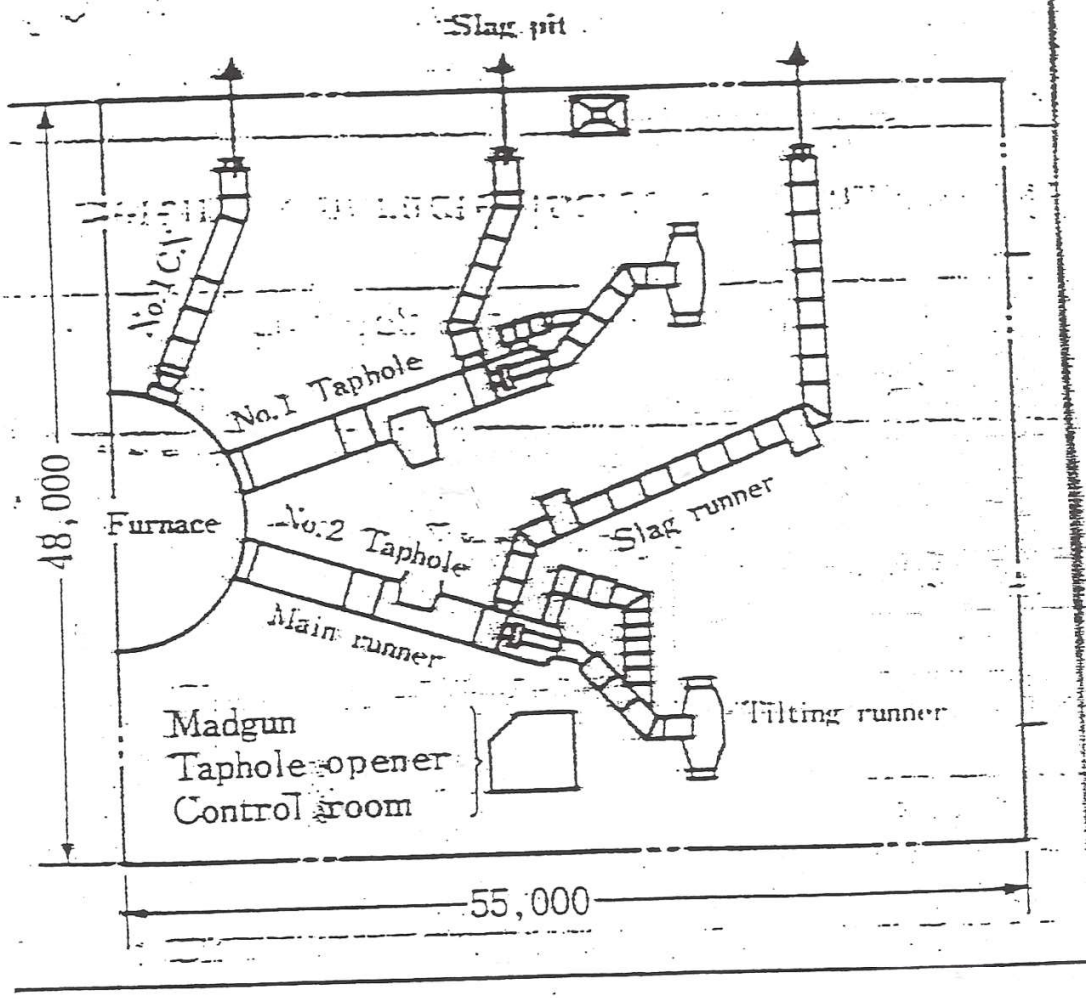


FIGURE 10

Temperature Profile in Taphole

FIGURE 11



Casthouse Layout

FIGURE 12

Lining Arrangement of Trough and Its Typical Wear Pattern

Table 1

SILICON CARBIDE BRICKS FOR LOWER STACK

	SiC –C	**Self bond SiC**	**Nitride Bond Sic**	**Sialon bond SiC**
Chemical compositon (%)				
Fixed Carbon	≥ 50	≤ 4	-	-
SiC	≥ 20	≥ 80	≥ 73	72
Si_3N_4	-	-	≥ 18	9
AlN	-	-	-	6
Al_2O_3	-	-	-	9
Bulk Density	1,97	2,67	2,66	2,89
Apparent porosity (%)	15,0	15,8	14,8	9,6
MOR (Kg/cm^2)	205	469	510	791
Thermal Expansion (%) At 1000°C	0,45	0,46	0,45	0,69
Thermal Conductivity At 400°C (Kcal/mh°C)	40,1	27,8	20,3	-
Alkali Vapour test (%)	-0,04	+0,17	+0,65	+0,17
CO gas test (%)	+1,89	+3,69	+2,26	-

	standard carbon Carbural R	**Microporous-carbon Carbural A/G**	**Carbon with different additives carbural A/1**	**Semigraphite Carbural TG**	**Graphite Carbural G**	**Semigraphite with diffferent additives Carbural TG/1**
Cold Crushing strength (N/mm²)	40	50	60	25	15	48
Thermal conductivity (1000°C) (W/mK)	8	11	11	19	51	22
Additives		Si	Si Al_2O_3			Si Al_2O_3
E- Module (at 20°C) (N/mm²)	3700	11400	12400	2900	2100	5900
Pig iron infiltration Vol%)	33,9	0	1,4	9,2	17,6	3,3
Alkali resistance (Internal test) (%)	5,1	1,6	1,6	5,2	3,5	0,3
Dissolution in pig iron (%) (internal test)	3,0	4,2	0,5	4,2	4,6	1,0
Slag/pig iron rotary kiln test (residual brick thickness in%)	26,	55,6	57,1	10,5		56,8

TABLE 3

PROPERTIES OF BLAST FURNACE CARBON BRICKS

Grade	**R**	**With Al_2O_3**	**A**	**With Sic/ Al_2O_3**	**AE**	**With Sic/ Al_2O_3**	**Tg**	**With Sic/ Al_2O_3**
Area of installation	**Bottom**	**Bottom**	**Hearth**	**Bottom hearth**	**Hearth**	**Hearth**	**Bosh**	**Bosh belly**
Bulk density(g/cm^3)	1.54	1.59	1.52	1.6	1.5	1.6	1.65	1.73
Open porosity (%)	16	15	15	16	16	18	22	25
Cold crushing strength (N/mm^2)	35	30	40	55	24	42	22	44
Thermal conductivity (HLF) (W/mK)								
100°C	3	3	5	6	9	10	23	20
400°C	5	5	7	8	11	12	21	27
Dissolution of pig iron (Fe %)	3	0,5	3,6	0,5	3,7	0,6	4,2	1
Alkali expansion	5,5	5,5	4,2	1,6	2,3	1,6	5,2	0,3
Abrasion (mm/15 min)	0,13	0,13	0,1	0,1	0,26	0,24	0,1	4,6
Residual wall thickness	26	28	35	64	23	65	31	72
Pore size distribution %								
>1µ	9	6	8	1	11	3	13	4
>10µ	4	3	3	0,5	3	1	3	2

TABLE 4

PROPERTIES OF Al_2O_3 - SiO_2 BRICKS FOR SUPPER STACK

Refractories (SK)	35	38	36
Chemical composition (%) Al_2O_3 MgO	 44,3 -	 63,2 -	 67,7 2,5
Bulk density(g/cm²)	2,38	2,54	2,51
Apparent porosity (%)	12,8	15,0	13,3
Apparent specific gravity (g/cm³)	2,72	2,99	2,90
Thermal expansion (%) At 1000°C	 0,63	 0,61	 0,35
Cold crushing strength (MPa)	105	107	76
RUL T1 (°C)	1402	1521	1420
Thermal expansion shock test I(cycle)	9	17	>20
R" ($x10^{-4}$)*	6,5	7,6	17,2

*R" = S.K/(1-γ) (E.p.c) γ=0,25

TABLE 5
PROPERTIES OF REFRACTORY BRICKS FOR TUYERES

	High alumina I	Silicon Carbide
Refractories (SK)	37	-
Chemical composition (%) Al_2O_3 SiC	 73,7 -	 - 90,8
Bulk density (g/cm^3)	2,64	2,61
Apparent Porosity (%)	15,5	15,6
MOR (MPa)	25	45
Thermal expansion (%) At 1000°C	 0,53	 0,46
Thermal shock conductivity (kcal/mh°C) At500°C	 1,8	 20,0
Thermal shock test I cycle	>20	>20
Alkali vapour test (%)	5,30	0,35

TABLE 6
PROPERTIES OF REFRACTORY BRICKS
FOR BLAST FURNACE BOTTOM

	HIGH ALUMINA
Chemical composition(%) Al_2O_3	71
Bulk Density (g/cm^3)	2,80
Apparent porosity (%)	16
Cold crushing strength (MPa)	115
Thermal expansion (%) At 1000°C	1,5
Alkali vapour test (%)	8
Av. Pore size (µ)	2,0
Slag test II (Index)	100

COMPARISON OF BLAST FURNACE REFRACTORY BRICK PROPERTIES

Thermal stress fracture resistance	♦	♦	○	▲	
Cooling effect	○	♦	○	▲	
Alkali resistance	♦	▲	▲	○	
Iron penetration resistance	♦	♦		○	▲
FeO corrosion resistance	○	○	▲	▲	▲
CaO corrosion resistance	○	♦	♦	○	▲
Abrasion- resistance	♦	▲	▲	♦	▲
Oxidation- resistance	○	▲		♦	♦

♦: Ecellent ○: Good ▲: Fair Poor

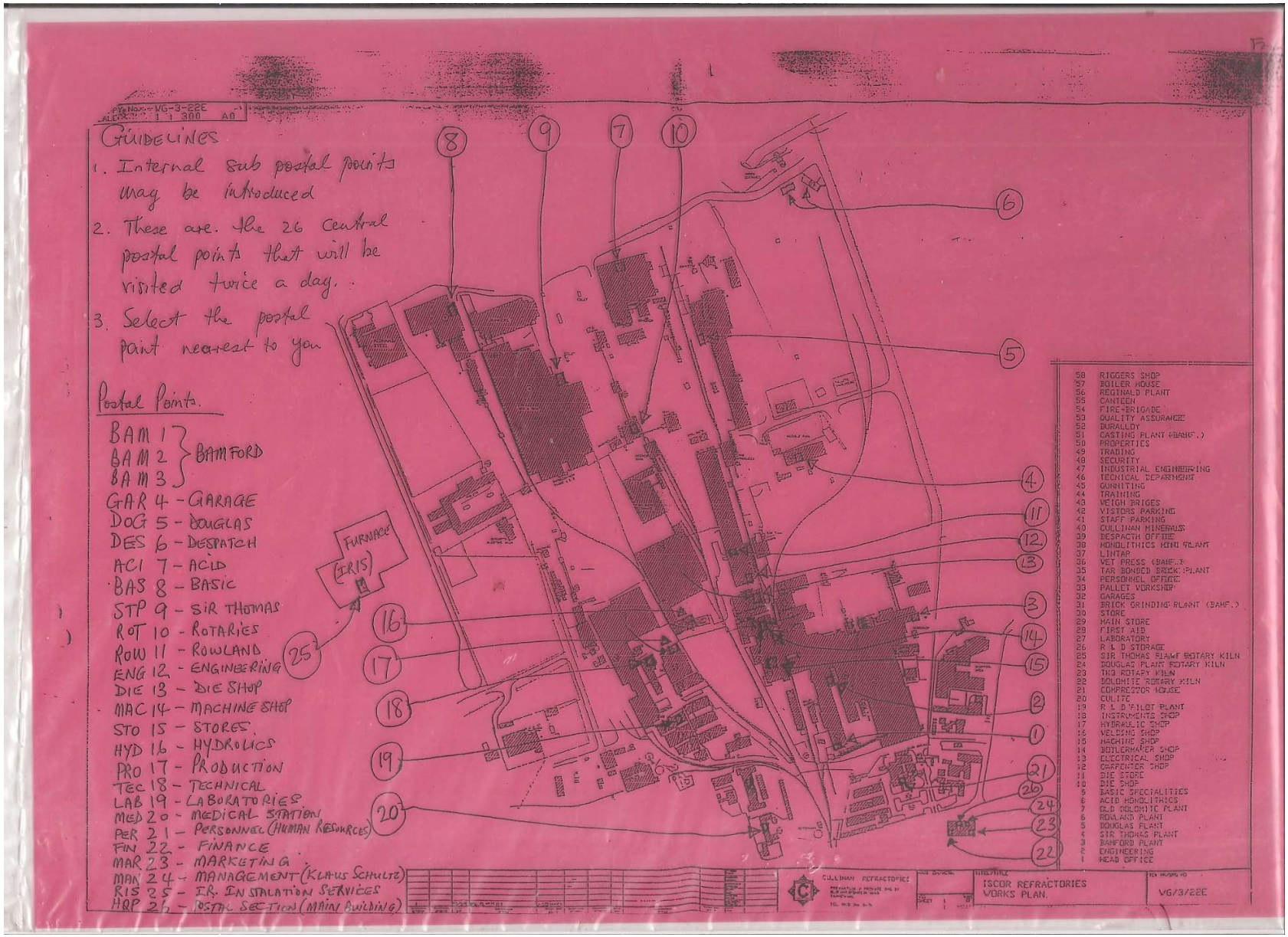
Table 8

PROPERTIES OF RESIN-BONDED AND TAR-BONDED MIXES

		Baking temperature	Resin-Bonded	Tar-Bonded
Bulk density (g/cm³)		1200	1,71	1,71
Apparent porosity		1200	27,2	29,6
Cold crushing strength		1200	22	10
MOR Mpa		1200	4	2
Hardening	5 min	600	2,5	0
	10 min	600	25	0
	15 min	600	52,5	0
Hot MOR (MPa)		1200	12	4
Erosion index		1200	0,59	1

TABLE 9
PROPERTIES OF TROUGH LINING MATERIAL
(N-CAST PROCESS)

Chemical composition (%)	SiO_2 Al_2O_3 SiC Fixed C	3-4 67-68 17-18 5-6
Water Content (%)	X	9,0
Bulk density (g/cm³)	110°C x 24hrs 1450°C X 2hrs	2,63 2,62
Apparent porosity (%)	110°C x 24hrs 1450°C X 2hrs	21,8 25,3
Modulus Of rupture (MPa)	110°C x 24hrs 1450°C X 2hrs	1,5 4,0
Cold crushing strength (MPa)	110°C x 24hrs 1450°C X 2hrs	15 21
Permanent linear change (PLC)(%)	1450°C x 2hrs	0,0


GUIDELINES
1. Internal sub postal points may be introduced
2. These are the 26 central postal points that will be visited twice a day.
3. Select the postal point nearest to you
Postal Points.
BAM 1 } BAMFORD
BAM 2
BAM 3
GAR 4 - GARAGE
DOG 5 - DOUGLAS
DES 6 - DESPATCH
ACI 7 - ACID
BAS 8 - BASIC
STP 9 - SIR THOMAS
ROT 10 - ROTARIES
ROW 11 - ROWLAND
ENG 12 - ENGINEERING
DIE 13 - DIE SHOP
MAC 14 - MACHINE SHOP
STO 15 - STORES
HYD 16 - HYDROLICS
PRO 17 - PRODUCTION
TEC 18 - TECHNICAL
LAB 19 - LABORATORIES
MED 20 - MEDICAL STATION
PER 21 - PERSONNEL (HUMAN RESOURCES)
FIN 22 - FINANCE
MAR 23 - MARKETING
MAN 24 - MANAGEMENT (KLAUS SCHULTZ)
RIS 25 - I.R. INSTALLATION SERVICES
HRP 26 - POSTAL SECTION (MAIN BUILDING)
FURNACE (IRIS)
58 RIGGERS SHOP
57 BOILER HOUSE
56 REGINALD PLANT
55 CANTEEN
54 FIRE-BRIGADE
53 QUALITY ASSURANCE
52 DURALLOY
51 CASTING PLANT (BAMF.)
50 PROPERTIES
49 TRADING
48 SECURITY
47 INDUSTRIAL ENGINEERING
46 TECNICAL DEPARTMENT
45 GUNNITING
44 TRAINING
43 WEIGH BRIGES
42 VISTORS PARKING
41 STAFF PARKING
40 CULLINAN MINERALS
39 DESPACTH OFFICE
38 MONOLITHICS MINI PLANT
37 LINTAP
36 WET PRESS (BAMF.)
35 TAR BONDED BRICK PLANT
34 PERSONNEL OFFICE
33 PALLET WORKSHOP
32 GARAGES
31 BRICK GRINDING PLANT (BAMF.)
30 STORE
29 MAIN STORE
28 FIRST AID
27 LABORATORY
26 R & D STORAGE
25 SIR THOMAS RAMM ROTARY KILN
24 DOUGLAS PLANT ROTARY KILN
23 TH3 ROTARY KILN
22 DOLOMITE ROTARY KILN
21 COMPRESSOR HOUSE
20 CULITE
19 R & D PILOT PLANT
18 INSTRUMENTS SHOP
17 HYDRAULIC SHOP
16 WELDING SHOP
15 MACHINE SHOP
14 BOILERMAKER SHOP
13 ELECTRICAL SHOP
12 CARPENTER SHOP
11 DIE STORE
10 DIE SHOP
9 BASIC SPECIALITIES
8 ACID MONOLITHICS
7 R&D DOLOMITIC PLANT
6 ROWLAND PLANT
5 DOUGLAS PLANT
4 SIR THOMAS PLANT
3 BAMFORD PLANT
2 ENGINEERING
1 HEAD OFFICE
CULLINAN REFRACTORIES
ISCOR REFRACTORIES WORKS PLAN.
VG/3/22E

PRODUCTION CAPACITY

Sir Thomas Plant	200	tons/day
Bamford	200	tons/day
Tar bonding	50	tons/day
Rowland	60	tons/day
Culite	5	tons/day
Acid monolithic	160	tons/day
Basic Monolithics	160	tons/day
	TAOTAL 839/tons/day	

Dolomite – slag conditioner	1000	tons/day

Plus Casting and Ramming:

Used material produced from above plants ±15 tons/day