

MINERALOGICAL CHANGES IN MAGNESITE AND
CHROME-MAGNESITE REFRACTORIES DUE TO
VARIATIONS IN SLAG COMPOSITION

by

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ABSTRACT

During the refining of steel by basic processes, a multitude of mineralogical reactions take place in the refractories with which the furnace is lined. The reactions are caused by an influx of material from the slag and are a function of the composition of the slag and of the refractory. The flow of material from the slag into the refractory resembles the process of metasomatism encountered in nature.

The reactions between slags of different composition and magnesite- and chromite-containing refractories could be studied systematically as a result of a series of four experiments. During each of the experiments four different refractories were subjected to the influence of a slag having a specific composition for a considerable length of time. The experiments were conducted in a rotating furnace at 1700°C.

Mineralogical reactions in the refractories used in these experiments can be divided into two main categories, viz. reactions involving the oxides and reactions involving the silicates.

The relevant oxides are periclase, the sesquioxides and spinel.

Periclase is found to undergo reactions like grain growth, resorption and elongation normal to the hot face of the refractory. These reactions are dependent on the composition of the refractory and of the metasomatised components.

Reaction between periclase and sesquioxides yield spinel, provided there is no excess of lime. Exsolution of bodies of spinel from periclase is governed by the crystal-chemistry of both minerals.

At elevated temperature, spinel, and more specifically chromite, acts as a source of sesquioxides in general, and of ferric oxide in particular. The stability of chromite depends on the molecular ratio between lime and silica of both the refractory and the slag. This ratio determines the amount of sesquioxides present, but not in spinel or in periclase, i.e. in the matrix of the refractory.

The postulation of the reactions involving the silicates is possible because of the tendency of the refractory to reach equilibrium with the composition of the slag.

The silicates present in acid slags are not in equilibrium with magnesia in the refractory, and consequent reaction yields the minerals

monticellite and merwinite. These minerals are not in equilibrium with the bonding silicates of magnesite refractories which have high molecular lime/silica ratios and also not with the bonding silicates of chromite-containing refractories having very low molecular lime/silica ratios. Reaction between metasomatic and autochthonous silicates result in a new set of silicates.

The silicates present in basic slags are in equilibrium with magnesia of the refractories as well as with the bonding silicates of magnesite refractories having high molecular lime/silica ratios. Consequently, no reaction results. Reaction does, however, take place between the silicates supplied by basic slags and the bonding silicates of chromite-containing refractories.

Ultrabasic slags react mildly with magnesite and drastically with chrome-magnesite bricks. The reason is that in the former reaction, only monticellite and merwinite are not in equilibrium with the composition of the melt, but these minerals have a relatively high mobility, and migrate deeper into the refractory. In chromite-containing refractories, however, neither of the minerals chromite, monticellite or forsterite are in equilibrium with the composition of the slag. Reaction results in the formation of an association of minerals in the area of contact between the slag and the refractory which differs completely from the original minerals of the refractory.

The conclusion arrived at is that chromite has a beneficial influence on refractories used in contact with less basic slags, because of the textural superiority of chromite-containing refractories over magnesite refractories. In contact with basic slags, however, metasomatism leads to the formation of components which have low melting points and low viscosities. During the refining of steel by basic processes, ultrabasic slags are preferred and magnesite refractories having high molecular lime/silica ratios are better suited for use in contact with the liquid slag.

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1. INTRODUCTION

Units producing basic steel use basic slags and consequently basic refractories as containers for the metal. Basic refractories consist mainly of the principal oxides of calcium and magnesium. Initially MgO-refractories were used, but the bricks made of this material suffered from two main defects viz. a low mechanical strength at elevated temperatures and a low resistance to the damaging effects of thermal fluctuations.

During the period 1930-1940 it was found that the addition of chrome ore as a coarse fraction (+28 mesh) to periclase in the ratio 40 parts chromite to 60 parts periclase yielded a chrome-magnesite brick which had definitely superior load-bearing and thermal-shock properties. As a result of these properties it was possible to use the chrome-magnesite bricks extensively in basic open-hearth furnaces and particularly in their roofs. It was also possible to produce more steel per time unit as higher operating temperatures were possible. One roof of a furnace of this kind gave an all-time record life of 2205 heats at Bilston, England, and this gave a fresh impetus to the research on these types of bricks.

With the advent of the oxygen-blowing steel-making processes like the LD, Kaldo and Rotor, the open-hearth furnaces had to operate at faster rates in order to be competitive. This was achieved through the use of oxygen and the results obtained with the traditional chrome-magnesite roofs were disastrous. Considerable attention was accordingly paid, particularly in England, to the composition and the mineralogical make-up of the bricks obtained from the Bilston roof, which had shown a record life. This work resulted in the evolution of the direct-bonded chrome-magnesite brick which gave on the average 30 per cent better lives than the ordinary chrome-magnesite bricks. In order to obtain this direct bonding between the chromite and the magnesia fractions it was necessary to reduce the silica content of the bricks and to fire them at high temperatures. The factors influencing the degree of direct bonding were determined principally at Sheffield University.

In practice, however, it was found that as the rate at which oxygen is blown is increased, the amounts of chromite and silica present in the brick must be produced. This reduction in the chromite content results in a reduction of the number of direct contacts between chromite and

periclase and consequently in the strength at high temperatures. Despite this reduction in strength better results were obtained in practice and this resulted in conflicting statements and views.

At Iscor a unique laboratory furnace was constructed and the results obtained by means of a more fundamental approach to the effect of the constitution of both the slag and the refractory on the durability of the refractories, led to considerable improvements in practice, especially with the Rotor furnace. With this experimental furnace it is possible to test a number of refractories simultaneously under controlled conditions, thereby eliminating the uncertainty that prevails when similar tests are conducted in a furnace while in production. In view of the information gained with experiments on magnesite refractories and the resulting improvements in practice, it was decided to tackle the problem of the durability of chrome-magnesite and magnesite-chrome refractories along the same lines.

While perusing this work, it will become evident to the reader that with so many factors which influence the rate of wear of refractory materials used in the steel-making industry, only limited improvement can be obtained without the aid of intensified research on the causes and effects of the changes occurring in the refractories during use. The importance of improving the durability of the materials cannot be over-estimated. This statement can best be explained by means of a hypothetical example:

'A furnace which has a high consumption of refractory linings produces (say) 2,000 tons of steel per day, and has to be relined after a service of 14 days. It takes 7 days to cool the furnace, reline it, and heat it back to production temperature. Taken over one year, the furnace would be out of production for 122 days. If by improving the refractories the period between relinings is improved to 21 days, the furnace would be out of production for only 91 days per annum. In this way 31 days are saved during which time steel can be produced, i.e. a gain of 62,000 tons of steel.'

Apart from breakdowns as a result of mechanical failure, or other unforeseen circumstances, the most regular stoppages in production are caused by failure of the refractories. This may be due to a concentration of excessive heat in a small area. The temperature in this area rises far above that which the refractory is able to withstand.

The major cause of lining wear, however, is chemical alteration of

the original minerals which make up the refractories. The driving force is the difference in oxide concentration between the refractory and the slag, which results in metasomatism and pneumatolysis i.e. addition of liquid and gaseous components because of the concentration gradient. These processes depend not only on the porosity, permeability and temperature gradient of the refractory but also on its composition and the composition of the slag.

2. DEFINITIONS AND TERMINOLOGY

To the student of the Geological Sciences there is a multitude of anomalies in the nomenclature and terminology pertaining to refractories. This necessitates a definition of the terms most widely used.

2.1. Magnesite Refractory

A magnesite refractory is a refractory consisting mainly of periclase.

2.2. Chrome-magnesite Refractory

A chrome-magnesite refractory consists mainly of chromite and periclase. The periclase fraction of the brick can be less, equal to or even slightly higher than the chromite fraction.

2.3. Magnesite-chrome Refractory

A magnesite-chrome refractory consists mostly of periclase and subordinate chromite, and is normally composed of 70 parts periclase and 30 parts chromite, although these ratios are not strictly adhered to.

2.4 Slag

This term refers to the oxides which combine with suitable fluxes to form a liquid layer on top of the liquid metal. The oxides originate either from the gangue associated with the ore during the extraction of the iron or from non-volatile impurities during the refining of the steel.

2.4.1. General Discussion of Basic Slags

As basic refractories are utilized in the refining of steel something more should be said about 'basic' slags.

Steel-makers have been aware of the fact for a long time that steel-making is in reality slag-making and the adage 'make a good slag and the steel will look after itself' is really axiomatic.

The refining of scrap and pig-iron by basic processes consists of the controlled oxidation of the metalloids Si, Mn, P, C and S which are soluble in molten iron, to insoluble oxides. This process is possible since the oxides of iron are chemically more unstable than the oxides

SiO_2 , MnO and CO at the melting temperature of steel. In the presence of CaO , which is added as a flux, FeO is also less stable than P_2O_5 and S combined as Ca-phosphates and Ca-sulphides. It is evident that some Fe will be oxidized to iron oxides, which also form a prominent part of the slag. The CO , being gaseous, escapes through the slag. This CO may be oxidized to CO_2 with the liberation of further heat (e.g. in the open-hearth and Tandem processes) or may be drawn off as waste gas without being oxidized. Owing to the insolubility of the oxides formed and the differences in density between the oxides and the metal, the oxides are precipitated and segregate into a separate layer called the slag layer (Rösch, 1965, p. 1).

Because of the vast difference in surface tension, the metal does not usually wet the refractory with the result that the former has no detrimental effect on refractories. The slag on the other hand acts as mineralizer which gives rise to a multitude of mineralogical changes in the refractory. These reactions, as will be explained presently, are dependent to a large extent on the molecular ratio of lime to silica (henceforth referred to as the C/S ratio) of both the refractory and the slag.

Although it is not standard practice, the author will henceforth use the following classification of slag basicity.

TABLE I

DESIGNATIONS ATTACHED TO SLAGS WITH DIFFERENT C/S RATIOS

C/S ratio of slag	Designation
<1	Ultra-acid
>1 <1.5	Acid
>1.5 <2	Basic
>2	Ultrabasic

In a normal oxygen-blowing process the metalloïd impurities in the iron which are oxidized to SiO_2 , MnO , FeO , P_2O_5 and CO , come in contact with CaO and the consequent chemical reaction produces relatively acid compounds like CaSiO_3 and Fe_2SiO_4 . This relatively acid slag comes in contact with the refractory and more lime. The basicity of the slag is increased owing to increased solution of and reaction with lime and compounds richer in lime are formed. Lime is normally charged to the furnace in order to obtain a final slag having a C/S ratio of 3:1 or higher.

2.5. Basic Refractory

There seems to be no clear definition of this widely used term. 'Basic' refers most probably to the fact that the refractories (magnesite-, dolomite-, chrome-magnesite- and magnesite-chrome) consist predominantly of the basic oxides of the elements of Groups II and III of the Periodic Table. The chemical and mineralogical composition of these materials are discussed briefly below.

2.5.1. Chemical Composition of Basic Refractories

Dolomite refractories will not be considered as they are outside the scope of this thesis.

The range in chemical composition of the most common magnesite- and chromite-containing refractories are listed in table II.

TABLE II

VARIATION IN CHEMICAL COMPOSITION OF BASIC REFRACTORIES

Components (Wt. %)	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	B ₂ O ₃
Magnesite refractories	85-98	.4-8	.8-4	.1-5	.2-.6	-	0-.5
Chromite-containing refractories	40-85	.5-3	1.4	5-16	2-12	5-35	0-.5

These values are intended to give a general indication of the possible composition of these refractories and are not claimed to be altogether comprehensive.

2.5.2. The Mineralogical Composition of Basic Refractories

The mineralogical composition can best be explained by a study of the phase diagrams CaO - MgO - SiO₂ (Fig. 1) in the case of magnesite, and MgO - MgAl₂O₄ - Mg₂SiO₄ - Ca₂SiO₄ (Fig. 2) in the case of chrome-magnesite refractories.

2.5.2.1. Magnesite Refractory.- A melt of a magnesite refractory of composition (say) 90 per cent MgO, 6 per cent SiO₂ and 4 per cent CaO would on cooling yield periclase from $\pm 2680^{\circ}\text{C}$, periclase and forsterite from $\pm 1520^{\circ}\text{C}$ and periclase, forsterite and monticellite at the ternary eutectic at 1502°C (Fig. 1). In its solid state this particular refractory would consist mainly of periclase, but also of the silicates forsterite and monticellite. This example demonstrates the relationship between the C/S ratio of the refractory and the final crystalline

silicates. The influence of the C/S ratio on the silicate constitutions of magnesite refractories can be gauged from the phase diagram (Fig. 1), but is tabled below for the sake of brevity.

TABLE III
RELATIONSHIP BETWEEN C/S RATIOS OF REFRACTORIES AND
RESULTING SILICATE PHASES

C/S ratios	Silicate phases
0	Mg_2SiO_4
$>0 <1$	$Mg_2SiO_4 + CaMgSiO_4$
1	$CaMgSiO_4$
$>1 <1.5$	$CaMgSiO_4 + Ca_3MgSi_2O_8$
1.5	$Ca_3MgSi_2O_8$
$>1.5 <2$	$Ca_2SiO_4 + Ca_3MgSi_2O_8$
2	Ca_2SiO_4
>2	$Ca_2SiO_4 + Ca_3SiO_5$

During the industrial manufacturing of refractories these same assemblages are obtained by mixing the raw materials in the required ratio, and then heating them to the temperature required to obtain stable equilibrium. Phase equilibrium can of course be obtained through solid-state reactions without the actual formation of liquid phases.

Macroscopically the above-mentioned refractory consists of discreet angular aggregates of periclase in a ground-mass of refractory oxides and silicates. Microscopically the aggregates consist of well to partly rounded grains of periclase bonded by forsterite and monticellite. These aggregates will henceforth be referred to as grog-units. The bonding of periclase grains can thus be either direct (i.e. periclase against periclase), or can consist of silicates.

2.5.2.2. Chromite-containing Refractories.— In the case of chrome-magnesite or magnesite-chrome refractories, a large number of trivalent cations (Al^{3+} , Fe^{3+} and Cr^{3+}) are present. They are grouped together as a R_2O_3 -component. The resulting MgR_2O_4 (spinel)-phase is considered to be analogous to $MgAl_2O_4$. The crystallization can therefore be considered as analogous to that depicted in the $MgO - MgAl_2O_4 - Mg_2SiO_4 - Ca_2SiO_4$ -phase diagram, as pointed out by Hayhurst and Laming (1963, p. 1000).

In a refractory with a composition of melt x in the quaternary phase diagram $MgO - MgAl_2O_4 - Mg_2SiO_4 - Ca_2SiO_4$ (Fig. 2), consolidation during cooling will start with precipitation of periclase. When the melt has the composition a , spinel (or for that matter chromite) crystallizes together with periclase. On reaching composition b , forsterite will crystallize together with periclase and spinel. At the peritectic point γ , with the temperature at $1380^\circ C$, the remaining liquid will crystallize as periclase + spinel + forsterite + monticellite.

As in the case of magnesite refractories, chromite-containing refractories are manufactured by heating mixtures of the components in the required proportions. It is also clear that, as in the case of magnesite refractories, the composition of the silicate phases is determined by the C/S ratio of the mixture.

By decreasing the CaO and SiO_2 -contents and subjecting these chromite-containing refractories to high temperatures, bonding of the components is not only done by silicates, but on account of reactions in the solid state, as well as precipitation of secondary spinels, periclase is welded on to chromite and other periclase grains. The latter process gives rise to the so-called direct-bonded refractories.

2.6. The Temperature Gradient

The operating temperature of a furnace determines the temperature of the brick in immediate contact with the slag.

The temperature (T) inside a refractory in use (at any point) is directly proportional to the operating temperature (T_{op}), and inversely proportional to the distance (S) of the said point from the hot side.

$$\begin{aligned} \text{i.e. } T &\propto \frac{T_{op}}{S} \\ &= \frac{c \cdot T_{op}}{S} \end{aligned}$$

Where c = constant, equal to the specific conductivity of the particular refractory.

Hence, by differentiation:

$$\begin{aligned} dT &= \frac{-c \cdot T_{op} \cdot dS}{S^2} \\ \therefore \frac{dT}{dS} &= \frac{-c \cdot T_{op}}{S^2} \\ &\propto -\frac{1}{S^2} \end{aligned}$$

This means that the rate of change in temperature with corresponding change in distance from the hot side is inversely proportional to the square of the distance from the hot side.

Neely (1967, p. 581) published a curve (Fig. 3) of the approximate thermal gradients in a number of refractories subjected to a certain given temperature for 55 hours. According to this curve, the greatest distance from the hot face of a refractory at which liquids can be expected is approximately 5 ± 2 cm from the hot face. At this depth, the temperature is approximately 1365°C , which is the quaternary monticellite-merwinite-spinel-periclase eutectic melting point (Fig. 2). This is in good agreement with the values obtained in refractories used experimentally, as well as industrially.

2.7. Porosity

The porosity of a refractory can be defined as that part of the material which does not consist of solid matter. The porosity of refractories, coupled with their permeabilities (the degree of interconnection between the voids which make up the porosity) play an extremely important part in their relative rates of wear. It is evident that a refractory with a high porosity and permeability will be more accessible to infiltration by liquid slags. The porosities of the refractories used during the experimental work to be described, range from 17.0 per cent to 20.1 per cent.

2.8. Pneumatolysis and Metasomatism

In nature pneumatolysis and metasomatism provide large and complicated fields of study, in so far as most of the changes are effected in open systems. Tentative but calculated risks have to be taken in deciding on which components are allochthonous and which are autochthonous. Furthermore, temperature ranges and temperature gradients within rocks have to be decided on, using theoretically sound, but not absolute geological thermometers.

In the examples under discussion, however, where basic refractories are used as linings in the steel-making industry and are infiltrated and impregnated with various oxides, several changes take place. These changes not only resemble natural metamorphic ones but are also closely related to them. These processes take place in closed systems which are completely under control. As a very definite temperature gradient exists within the brick, gradual changes at different temperatures can be studied and compared with the original brick of which the exact

chemical and mineralogical composition is known.

2.9. Abbreviations

In order to limit the continuous use of lengthy names and chemical formulae like monticellite (CaMgSiO_4), merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), brownmillerite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$), etc., cement chemists have worked out abbreviations which, once one is accustomed to them, are very handy. The author proposes to keep to these conventional notations which are used internationally in the refractory science (Table IV).

TABLE IV
COMMON ABBREVIATIONS

Chemical or Mineralogical Name	Chemical Formula	Notation
Calcia (Lime)	CaO	C
Magnesia (Periclase)	MgO	M
Ferric oxide (Hematite)	Fe_2O_3	F
Ferrous oxide (Wüstite)	FeO	F'
Alumina (Corundum)	Al_2O_3	A
Chromic oxide	Cr_2O_3	K
Sesquioxide	$(\text{Fe,Al,Cr})_2\text{O}_3$	R
Silica (Quartz)	SiO_2	S
Tricalcium silicate (Alite)	$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium silicate		
(α - = Glaserite		
α' - = Bredigite	$2\text{CaO} \cdot \text{SiO}_2$	C_2S
β - = Larnite		
γ - = Shannonite)		
Merwinite	$3\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	C_3MS_2
Åkermanite	$2\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	C_2MS_2
Monticellite	$\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2$	CMS
Forsterite	$2\text{MgO} \cdot \text{SiO}_2$	M_2S
Rankinite	$3\text{CaO} \cdot 2\text{SiO}_2$	C_3S_2
Wollastonite	$\text{CaO} \cdot \text{SiO}_2$	CS
Diopside	$\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$	CMS_2
Chromite	$(\text{Fe,Mg})\text{O} \cdot (\text{Cr,Al,Fe})_2\text{O}_3$	(MF')KAF
Magnesioferrite	$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	MF
Spinel	$\text{MgO} \cdot (\text{Fe,Cr,Al})_2\text{O}_3$	MR
Magnetite	$\text{FeO} \cdot \text{Fe}_2\text{O}_3$	F'F

Chemical or Mineralogical Name	Chemical Formula	Notation
Dicalcium ferrite	$2\text{CaO} \cdot \text{Fe}_2\text{O}_3$	C_2^{F}
Brownmillerite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4^{AF}

3. PREVIOUS WORK

During the 1930's Lynam and Rees (1937, p. 137-172) developed the chrome-magnesite brick. Although a tremendous amount of work was done on chrome ores and spinel since then, no real advance was made until approximately 1958. However, in 1953 Parnham (p. 513-535) had pointed out that chrome ores containing between 3 and 5 per cent SiO_2 , more than 40 per cent Cr_2O_3 , less than 15 per cent FeO and less than 1 per cent CaO are most suitable for bricks that should have a strength at high temperature. This now appears to be due to the forsterite bond prevalent in a chrome-magnesite brick. Following on the excellent results obtained by the Bilston roof, the bricks from this roof were examined exhaustively. Cockbain and Johnson (1958, p. 511-525) published the results obtained by means of X-ray and petrological techniques and suggested that a zonary structure results from an attempt by the brick to reach equilibrium with the composition of the atmosphere of the furnace. The zonal structure which is caused by chemical and mineralogical changes, results in the composition of the hot face being more or less independent of the original composition of the brick. This reconstruction was considered to be a major factor in brick failure. In the same year Greaves and Mackenzie (p. 195-197) found a good correlation between high-temperature strength, creep characteristics and service performance in open-hearth furnace roofs. Although limited results were available there also appeared to be a correlation between decreasing silica content of the chrome ore, higher firing temperature of the brick and improved performance. Laming (1959, p. 116) indicated that volume stability at high temperature could be correlated with the silica content of the brick i.e. low silica materials produced bricks with better volume stability. He favoured the direct bond i.e. the periclase-spinel bond rather than the forsterite, i.e. silicate bond and indicated that the development of the spinel bond was promoted by a low silica content and firing to a high temperature.

The work of Laming was of particular importance as it showed that

after firing to temperatures of between 1150°C and 1550°C the silicates in the chrome ore formed "haloes" around the chromite grains. These "haloes" disappeared after firing at higher temperatures (1550-1600°C) leaving gaps between the chromite grains and the periclase matrix. On firing at 1800°C periclase was found to recrystallize, become opaque in thin section and form a direct bond with chromite grains. These opaque grains of periclase appear as a dark zone around the chromite grains. In 1961 Ford, Hayhurst and White pointed out that this direct bond consists of a layer of periclase crystals bonded directly to the surface of the chromite grains. The silicates appear disseminated and fill the interstices between the recrystallized periclase crystals. Periclase was found to contain a larger amount of exsolved spinel than in the case of chrome-magnesite refractories subjected to lower temperatures. The silicate phase was noted to contain a relatively large number of small angular crystals. These crystals were obviously spinel and were described as secondary spinel. The authors mentioned that the mechanical properties of direct-bonded refractories at high temperatures were superior to those of refractories fired to lower temperatures. By means of electron-probe work they proved that Fe_2O_3 and Cr_2O_3 had diffused into the periclase matrix from the chromite grains. Richardson, Fitchett and Lester (1960) pointed out that additives like Fe_2O_3 , Cr_2O_3 and TiO_2 which enhance the formation of spinel, improve the formation of direct bonds.

According to Cockbain (1962) the changes occurring in a basic refractory during service resemble those undergone by rocks during metasomatism. He also suggested that recrystallization of periclase crystals and of iron rich spinel crystals in the Bilston brick to a mosaic could have been instrumental in avoiding any disruptive effect which might have resulted from continued growth in one direction. A brick composed of a dense packing of recrystallized periclase and spinel and little silicates was therefore considered to be the optimum. This type of structure is obtained by firing chrome-magnesite bricks at approximately 1800°C and allowing them to cool slowly. In 1963 Hayhurst and Laming indicated that periclase was also precipitated from the silicate phase during slow cooling from 1700°C. It was therefore concluded that precipitation of material from the liquid phase during cooling gave rise to an interlocking structure of original chromite grains, a secondary angular spinel phase and periclase grains. These components constitute the "direct bond". Of major importance, however, was that these authors indicated that the direct bond does not exist at temperatures of the order of 1500-1600°C and that the silicates are disseminated at these

temperatures.

One striking feature of the bricks which possess a direct bond is the isolation in pockets of the silicates present in the brick. This isolation is due to the ability of the silicates to wet the refractory and is a function of the dihedral angle. The dihedral angle is the angle which is formed when two crystals of one mineral meet with one crystal of a second mineral, and can be constructed by drawing a tangent to the interface of the different minerals at the point of contact of the like minerals. The size of the dihedral angle is a function of the interfacial tensions. The bigger this angle, the smaller the ability to wet the refractory and the bigger the isolation. Jackson, Ford and White (1963) described the influence of Cr_2O_3 and Fe_2O_3 on the dihedral angle of compressed mixtures of 85 per cent periclase and 15 per cent monticellite. They found that Cr_2O_3 increased, and Fe_2O_3 decreased the dihedral angle. Ford and Whiteley (1964, p. 209) proved by means of the tensile-loading test that addition of Cr_2O_3 increased the cohesive strength of the mixtures mentioned above, whereas the addition of Fe_2O_3 decreased the cohesive strength.

In a summary of the work done in his department, White (1966) states that an alternative possibility (to the impossibility of using reagent-grade material for large-scale manufacture of heavy-duty refractories) is to minimise the harmful effects of constituents having low melting points. This can be achieved by controlling the composition of refractories. Continuing, White describes how replacement of Fe_2O_3 and Al_2O_3 by Cr_2O_3 in a refractory can be expected to raise the temperature of initial formation of a melt in the systems $\text{MgAl}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{Ca}_2\text{SiO}_4$, $\text{MgFe}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{Ca}_2\text{SiO}_4$ (El Shahat and White, 1964) and the pseudosystems $\text{MgAl}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{CaMgSiO}_4$, $\text{MgFe}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{CaMgSiO}_4$ and $\text{MgAl}_2\text{O}_4 - \text{MgFe}_2\text{O}_4 - \text{CaMgSiO}_4$ (El Shahat and White, 1966). The author adds that the same phenomenon can be expected in the system $\text{MgAl}_2\text{O}_4 - \text{MgFe}_2\text{O}_4 - \text{MgCr}_2\text{O}_4 - \text{Ca}_3\text{MgSi}_2\text{O}_8$. Consequently, addition of Cr_2O_3 , either as the oxide or as chrome ore, could be expected to improve the refractory properties of many commercial magnesite refractories. It is mentioned, however, by White that additions of Cr_2O_3 to magnesite refractories which contain silicates but little or no sesquioxides would not necessarily have a beneficial effect on melt formation in unused refractories although it might have a beneficial effect in service where pick-up of sesquioxides occurs. He concludes by pointing out the spatial (textural) superiority of chromite-containing refractories over pure

magnesite refractories.

Although these facts are stated with magnificent clarity, they give no indication as to the nature of the eutectics thus formed, and especially not of the reason for the phenomena pointed out by Pickering and Ford (1964, p. 493). These authors, also in Prof. White's Department of Refractory Materials at Sheffield University, found that the strength of direct bonded chrome-magnesite refractories at 1450°C is reduced by increasing the C/S ratios. The temperatures of formation of initial liquids are respectively 1380°C , 1366°C , 1387°C and 1418°C for the periclase-spinel-silicate composition with C/S ratios 0-1, 1-1.5, 1.5-2 and 2 i.e. they pass through a minimum and then rise again. El Shahat and White (1964) pointed out that by replacement of Al_2O_3 by Cr_2O_3 the temperature of initial melting at a C/S ratio of 2 would be raised from 1418°C to 1480°C . Further work by El Shahat has shown that replacement of Al_2O_3 by Fe_2O_3 reduced the temperature. This loss of cohesion in the tensile test is in sharp contrast with the high stability under a compressive load at 1650°C of C_2S -bonded chrome-magnesite refractories found by Rigby and Richardson (1957, p. 22-36) for bricks from the Bilston roof, and it is also at variance with the temperatures of liquid formation.

In view of the complexity of the problem, and the conflicting results obtained at times as shown in this section, it was decided to reinvestigate the problem on a more fundamental basis. The following aspects received attention:

1. The effect of the C/S ratio on the mechanical strength at high temperatures of chromite-containing refractories as measured in torsion.
2. The effect of the C/S ratio of the slag on the relative rates of wear of magnesite, magnesite-chrome and chrome-magnesite refractories.
3. The mineralogical changes occurring in bricks during the various experiments.

4. EXPERIMENTAL PROCEDURE

4.1. Material Used

4.1.1. Refractories

The experimental work was carried out in the course of four tests in an experimental rotor during which time four types of refractories were exposed to various slags.

The refractories, together with their relevant properties are listed in Table V.

TABLE V
PROPERTIES OF REFRACTORIES USED DURING THE EXPERIMENTAL WORK

Chemical composition (Wt.%)	Refractories			
	V	B ₁	N	O
SiO ₂	1.3	2.5-4.0	5.0	3.9
CaO	2.4	3.9-5.0	1.6	1.0
MgO	95.7	87.5-90.0	64.4	43.2
Al ₂ O ₃	0.2	0.6-0.9	7.3	10.3
Fe ₂ O ₃	0.4	2.5-2.6	8.0	13.5
Cr ₂ O ₃	0.0	0.0	13.7	28.1
Porosity (%)	18.1-20.1 [‡]	16.5-19.4	17.3-18.4	17.0-18.5
Permeability (c.g.s. units)	0.0346-0.1106	0.2946-0.3100	0.1418-0.2468	0.0800-0.2043
Thermal shock (cycles)	30+	30+	30+	30+

V = Veitsch Anker PV15 (Magnesite refractory)

B₁ = V.B.T. Experimental Fired Mk B₁ (Magnesite refractory)

N = V.B.T. Experimental Mk N (Magnesite-chrome refractory)

O = V.B.T. Experimental Mk O (Chrome-magnesite refractory)

[‡] As the original Veitsch Anker PV15 refractories were impregnated with tar, the porosity was determined after firing the specimens for two hours at 1500°C.

The chemical composition and the other characteristics provided in Table V reflect average values. All the refractories, except Mk B₁, are very consistent in composition and general make-up; this factor facilitated considerably the standardization of the results.

4.1.2. Slags

The composition of the different slags used is given in Table VI.

TABLE VI
COMPOSITION OF SLAGS USED IN CAMPAIGNS 40 - 43

Campaign No.	Average composition of slag							C/S ratio	C/(S+P ₂ O ₅) ratio
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅		
40	15.9	30.2	27.4	23.8	1.0	1.0	0.7	1.18	1.17
41	10.3	41.4	23.2	21.7	1.2	1.6	0.6	1.91	1.89
42	9.4	43.7	18.8	23.9	1.7	1.8	0.7	2.50	2.46
43 A	8.4	39.0	28.2	21.9	0.7	0.8	1.0	1.48	1.46
B	6.9	45.8	23.4	21.1	0.7	0.9	1.2	2.10	2.10
C	7.7	48.6	17.9	21.8	1.0	1.6	1.4	2.91	2.82

The slags (Table VI) were prepared synthetically by mixing limestone, high-purity sand, hematite and tricalcium phosphate in the correct proportions. The amounts of each component were calculated by taking into account their chemical composition. The above analyses are those of slags that were tapped from the rotor and the components MgO, Al₂O₃ and Cr₂O₃ were added to the slag as a result of refractory wear. The last column shows the molecular ratio of CaO : SiO₂ + P₂O₅, as P can take the place of Si in silicate structures. It can be seen that the P₂O₅ content is minimal in that the C/S ratios of the slags remain within the same categories.

The slag used in campaign 43 was periodically changed in basicity in order to determine the composite effect of changes in slag basicity during the refining of steel on refractory wear. The slags of campaigns 40, 41 and 42 were of one basicity throughout in order to determine the effect of one specific basicity on the rate of wear.

4.2. The Experimental Rotor

4.2.1. The Experimental Rotor and the Installation of the Material

The experimental rotor, henceforth briefly referred to as the rotor, is a rotating furnace having a slag capacity of about 0.5 ton (Fig. 4). The rotor is lined with refractories and heated to the required temperature. By careful control of the composition of the slag, the same minerals are synthesized in the refractories as during steel-making processes, but under controlled conditions and at elevated rates.

The rotor is composed of three components viz., a burner cone, a barrel and a tap cone.

The two cones are detachable and are first rammed with Romag ramming magnesite, slightly damped with a saturated solution of magnesium sulphate.

Before the bricklaying process commences, the rammed tap cone is bolted tightly on to the barrel. The rotor is now tilted into a vertical position. The first row of bricks is laid on top of the rammed portion of the tap cone. Because of the tapered shape of the refractories, they describe a circle when placed side by side. A space of ± 15 cm is left open between the backs of the bricks and the wall of the rotor. This space is filled with damped high-magnesia Romag and rammed tight. This is done for the dual purpose of securing the refractories tightly in their positions, and for added heat insulation. One circular row of bricks usually consists of 17 ± 1 bricks. Bricks of similar constitution are placed on top of one another, so that eventually, the cylindrical brick-structure consists of four sections (V, B₁, N and O in the case under consideration) about seventeen bricks high.

When the bricklaying is completed, the rammed burner cone is replaced. The small gap between the top of the brick structure and the rammed portion of the burner cone is now filled with MR9 refractory cement. This cement is allowed to dry before rotation and the heating up procedure commences. The weight of the refractories used during each campaign was about 3.5 tons, and the total weight of the refractory materials (bricks plus ramming material) was about 4.5 tons.

4.2.2. Heating Procedure

In order not to subject the refractory materials to too great a thermal shock, the initial heating is accomplished with a 'pilot burner' using producer-gas and oxygen as fuel. After about 5 to 6 hours, this burner is replaced by the main Rotovac burner which uses a mixture of furnace-oil, producer-gas, oxygen and compressed air as fuel. For the next 12 hours, the burner is fed with a lean mixture of oxygen, producer-gas and compressed air, so as not to exceed 800°C. From 800°C up to the working temperature of 1700°C, heating is carried out according to a fixed rate of 50°C per hour.

On reaching 1700°C, the furnace is kept at this temperature for approximately 10 hours in order to obtain thermal equilibrium. Material which has spalled from the refractories during the heating up procedure is removed by tilting the furnace. The surface of the white-hot refractories rotating at ± 1 rev./min is covered with a thin layer of

slag. The experiment commences 30 minutes after completion of the above operation.

4.2.3. Experimentation

Each charge of approximately 800 lbs of slag is loaded in three equal portions over a period of three hours. The first and the last charge are tapped after two hours. The other charges are left in the rotor for five hours at a time before tapping. The temperature which is measured with an optical pyrometer, is regulated at 1700°C , except during those periods when charging is in progress. During these periods absorption of heat by the cold, added material, forces the temperature down to $1550 \pm 50^{\circ}\text{C}$. A constant watch is kept on the fluidity of the slag, because a considerable amount of corroded refractory material might raise the melting point of the bulk slag to an extent that slag-freezing sets in. The barrel temperatures are also recorded by means of thermocouples.

After tapping the final charge, the rotor is cooled down to 800°C at a rate of 50°C per hour. The pilot burner is then inserted, and when the temperature reaches 600°C , it is extracted and the refractories are allowed to cool normally. After two more days, the temperature is low enough to allow demolition of the material.

4.3. Sampling and Sample Preparation

4.3.1. Sampling

After taking off the burner cone, the bricks are broken out one by one. Each brick is measured accurately to the nearest sixteenth of an inch (0.159 cm). For mineralogical and chemical examination one sample of each type of refractory is taken approximately at the centre of the stack (row 9). Each of these samples are divided into three portions, one portion of mineralogical examination, one for chemical analysis and one for safe-keeping. The portion which is used for chemical analysis is sawn into sections parallel to the hot face, with thicknesses ranging from $\frac{1}{2}$ " (1.27 cm) at the hot face, to 2" (5.08 cm) at the unaltered cold end.

4.3.2. Sample Preparation

The portion of the brick which is examined mineralogically is first photographed. It should be noted that the Mk B₁ refractories used during campaign 42 were not examined. The reason is that these refractories disintegrated completely during cooling as a result of the transformation

of larnite into shannonite at 675°C, which is accompanied by a voluminal expansion of 10 per cent (Plate 1). Most of the Veitsch refractories also disintegrated, but a few remained intact.

A section, approximately 1 cm x 1 cm x the total length is sawn from each refractory specimen, and cut into 1 cm x 1 cm x 1 cm portions. These specimens are mounted in perspex mounting powder, carefully indicating their position in the brick as well as the direction of the hot face.

The specimens are impregnated with epoxy resin mixed with one tenth of its volume of hardener. The impregnation is carried out in a vacuum oven at 25 mm Hg and 50°C (so as to obtain the lowest viscosity resin). After impregnation, the samples are removed from the oven and allowed to harden for 24 hours. The thin layer of resin covering the specimen is removed on a grinding wheel and the specimen is roughly flattened. The samples are now secured in a Buehler Automet sample holder from which they are not removed until they are finally polished. The surfaces to be polished are ground on a series of wet waterproof carborundum grinding papers mounted on a brass disc. The papers are kept well wet so as not to break out any of the periclase (which has an excellent parting). In the case of refractories where dicalcium silicate might be one of the phases present, the grinding papers are kept damp with alcohol, as this mineral is slightly unstable in the presence of water.

Polishing is carried out on a lead wheel impregnated with an emulsion of Tonerde No. 3 in Redex lubricating oil. It can take up to two days to polish one series of five samples. As can be seen from the photomicrographs, sections polished according to this method have practically no relief, which is of the utmost importance when using etching techniques for identification.

4.3.3. Identification of Components

4.3.3.1. Microscopic Identification.— It is extremely difficult to identify the minerals present in used refractories by means of transmitted light. The reason for this is the fine-grained texture, the multitude of opaque inclusions and contamination by ferric oxides. The problem can best be visualized when looking at fig. 5. It represents an edge-wise view of a hypothetical thin section of a used refractory. In transmitted light, portion a reveals the actual structure only approximately. Portion b is opaque and portion c increases in transparency

from left to right. The pit in the surface at d will not show up. The small opaque inclusions at e may appear to be in the mineral f. The two transparent minerals finely intergrown (as at g) cannot be distinguished as the optical properties of neither can be determined accurately (Schouten, 1951, p. 131). It is thus obvious why identification by means of the technique of reflected light is preferred. Transmitted light was, however, used in the case of powder mounts in order to obtain the refractive indices and the optical properties of the silicates. Polished thin sections were also examined to ascertain the degree of contamination by ferric oxides.

The identification of the minerals is facilitated by a knowledge of the chemical composition and by a process of elimination, as minerals unstable at high temperatures can be excluded. The most effective method of identification, however, is by making use of etching techniques as described by Steyn (1965, p. 108) and Snow (1947, p. 2167). The author followed the procedure presented in Table VII. As it is a difficult and long procedure to repolish a section, an attempt was always made to identify all the minerals in one operation without repolishing the section. This was achieved by starting off with the weakest etchant, and keeping to the order outlined in Table VII.

The success of the method is dependent on the quality of the polishing. The samples should be free from relief, which is not easily acquired with the range in hardness and polishing susceptibility of the minerals under consideration. By applying the polishing method described by the author, relief can be eliminated almost completely. The value of etching in identifying the minerals can be gauged from Plate 2. The reliability of the method was constantly checked by means of X-ray diffraction.

4.3.3.2. Chemical Data.- The portion of the used refractory set aside for chemical analysis is ground to -100 mesh and analysed chemically for SiO_2 , CaO , MgO , Al_2O_3 , Fe_2O_3 , Cr_2O_3 and, in the case of magnesite refractories, also for P_2O_5 . The chemical analyses, listed in Table VIII, furnish by far the most accurate indication as to which components were added to the refractory during use, as well as to the amounts of added material.

TABLE VII
IDENTIFICATION OF MINERALS BY ETCHING TECHNIQUES

Etchants	Time	Components								
		M	MR	C ₂ F	C ₄ AF	C ₃ S	C ₂ S	C ₃ MS ₂	CMS	M ₂ S
1% Borax Soln.	10 m	-	-	-	-	S +++	T ⁻ ,S ++	-	-	-
5% NH ₄ Cl	60-90 s	-	-	-	-	++++	+++	T ⁺ ,S ++	-	-
10% HCl	10-15 s	-	-	-	-	++++	++++	+++	S,G ++	-
5% HF	3 s	-	-	+	+	++++	++++	++++	ST ⁺ ++	-
Saturated Soln. of (NH ₄) ₂ S _x	60 s	-	-	ST ⁺ +++	ST ⁻ ++					-
Polished on dry canvas cloth	3 m									
then boiled in water	10 m	G	-							-

Key: The number of crosses gives an indication of the degree of attack of the minerals by the etchant, viz. (+) - etched weakly, (++++) - very strongly etched, etc.

S - scratched.

T⁻ - sometimes twinned.

T⁺ - mostly twinned.

ST⁻ - sometimes stained.

ST⁺ - mostly stained.

G - grain boundaries etched out.

TABLE VIII
CHEMICAL ANALYSES OF REFRACTORIES USED DURING
THE EXPERIMENTAL WORK

Sample No.	Components.							C/S ratio
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅	
C40 V ₁ & V ₂	76.7	7.6	6.3	8.8	0.4		0.2	1.30
C40 V ₃	82.2	8.8	6.5	2.0	0.3		0.1	1.45
C40 V ₄	84.3	8.2	6.0	1.0	0.4		0.1	1.47
C40 V ₅	87.7	6.3	4.5	0.7	0.6		0.1	1.51
C40 V ₆	49.9	2.8	1.4	0.5	0.2		0.1	2.17
C40 V ₇	95.5	2.4	1.3	0.5	0.2		0.0	1.95
C40 V ₈	95.6	2.4	1.3	0.5	0.2		0.0	1.95
C40 V ₉	95.6	2.5	2.3	0.4	0.2		0.0	2.05
C40 B ₁	59.3	8.8	7.4	23.8	0.5		0.2	1.28
C40 B ₂	75.4	10.0	7.9	6.0	0.6		0.1	1.36
C40 B ₃	73.3	11.7	8.8	5.5	0.6		0.1	1.42
C40 B ₄	74.7	11.1	8.3	5.0	0.8		0.1	1.44
C40 B ₅	77.6	9.9	7.3	3.0	2.1		0.1	1.45
C40 B ₆	88.4	5.0	3.0	2.7	0.9		0.0	1.78
C40 B ₇	89.8	4.5	2.4	2.7	0.6		0.0	2.00
C40 B ₈	90.9	4.3	2.5	2.7	0.6		0.0	1.83
C40 B ₉	89.9	4.3	2.6	2.6	0.7		0.0	1.79
C40 N ₁	50.2	9.4	11.4	13.6	4.2	11.2		0.88
C40 N ₂	58.8	5.0	9.4	7.5	6.1	13.2		0.57
C40 N ₄	59.8	4.7	10.2	7.1	5.8	12.5		0.49
C40 N ₅	60.2	4.4	9.2	7.1	5.9	13.2		0.52
C40 N ₆	64.7	2.0	6.2	7.7	5.3	14.1		0.35
C40 N ₇	65.9	1.4	5.6	7.2	5.1	14.8		0.27
C40 N ₈	66.8	1.3	5.3	7.2	5.2	14.2		0.26
C40 O ₁	35.3	8.0	7.9	21.7	5.5	21.7		0.84
C40 O ₂	40.9	5.1	7.2	14.8	9.5	22.5		0.76
C40 O ₃	40.9	4.1	8.3	14.3	9.3	23.1		0.53
C40 O ₄	40.3	5.1	8.9	13.9	9.1	22.7		0.62
C40 O ₅	41.4	3.8	7.3	13.9	9.4	24.2		0.56
C40 O ₆	43.4	1.5	4.7	14.2	9.8	26.5		0.35
C40 O ₇	43.6	1.1	4.4	14.0	10.0	26.9		0.27

Sample No.	Components							
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅	C/S ratio
C40 O ₈	43.8	1.1	4.5	14.1	9.9	26.6		0.27
C40 O ₉	42.7	1.1	4.4	14.3	10.4	27.1		0.27
C41 V ₁	69.4	9.3	6.6	13.1	1.4		0.2	1.51
C41 V ₂	68.3	13.5	8.6	8.2	1.1		0.2	1.66
C41 V ₃	77.7	11.5	6.7	2.9	1.0		0.2	1.83
C41 V ₄	81.1	9.5	6.4	1.5	1.4		0.1	1.59
C41 V ₅	81.7	9.7	6.5	0.9	1.0		0.1	1.60
C41 V ₆	83.6	8.0	6.5	0.6	1.2		0.1	1.32
C41 V ₇	85.5	7.1	5.5	0.6	1.1		0.1	1.38
C41 V ₈	88.0	5.8	4.4	0.5	1.2		0.1	1.43
C41 V ₉	95.6	2.5	1.3	0.5	0.1		0.0	2.05
C41 V ₁₀	95.7	2.4	1.3	0.4	0.2		0.0	1.95
C41 V ₁₁	95.7	2.3	1.3	0.5	0.2		0.0	1.86
C41 B ₁	66.0	10.4	7.0	14.8	1.6		0.2	1.59
C41 B ₂	72.1	12.7	7.2	7.5	0.3		0.2	1.89
C41 B ₃	73.6	12.5	7.5	6.0	0.3		0.2	1.81
C41 B ₄	74.6	12.1	8.5	4.3	0.4		0.1	1.52
C41 B ₅	76.3	11.3	7.7	3.6	1.0		0.1	1.58
C41 B ₆	78.6	9.3	7.2	2.9	1.7		0.1	1.38
C41 B ₇	83.7	6.8	5.0	2.7	1.5		0.1	1.48
C41 B ₈	87.9	4.9	3.4	2.6	0.9		0.1	1.54
C41 B ₉	87.1	5.1	4.0	2.6	0.9		0.0	1.36
C41 N ₁	50.9	8.4	7.3	17.5	3.4	12.5		1.23
C41 N ₂	52.5	8.0	6.3	15.6	4.9	12.7		1.36
C41 N ₃	56.7	7.2	7.5	8.2	7.3	13.1		1.03
C41 N ₄	57.9	5.6	9.1	7.9	7.1	12.4		0.66
C41 N ₅	58.9	4.9	8.6	7.6	7.2	12.8		0.62
C41 N ₆	64.7	1.6	5.3	7.5	6.7	14.1		0.33
C41 N ₇	65.6	1.2	5.2	7.6	6.4	14.0		0.24
C41 N ₈	65.6	1.1	5.1	7.5	6.5	14.2		0.24
C41 O ₁	38.3	10.7	7.7	16.5	4.3	22.5		1.49
C41 O ₂	38.4	7.6	5.7	17.0	7.4	23.9		1.43
C41 O ₃	39.5	6.5	6.0	14.1	10.0	23.9		1.16
C41 O ₄	40.3	5.1	7.7	13.9	9.7	23.3		0.71
C41 O ₅	40.5	4.7	7.4	14.0	9.2	24.2		0.68

Sample No.	Components							
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅	C/S ratio
C41 O ₆	43.1	1.8	4.6	14.4	9.7	26.5		0.42
C41 O ₇	43.4	1.1	4.2	14.5	9.7	27.1		0.29
C41 O ₈	43.6	1.1	4.0	14.3	9.8	27.2		0.30
C41 O ₉	38.0	0.8	3.7	14.7	11.3	32.1		0.23
C42 V ₁	73.9	8.5	4.6	11.3	1.7		0.1	1.98
C42 V ₂	77.4	11.5	5.7	4.3	0.9		0.2	2.16
C42 V ₃	80.0	9.7	5.1	3.7	1.4		0.1	2.04
C42 V ₄	81.9	9.3	5.1	2.3	1.3		0.1	1.95
C42 V ₅	83.6	8.4	5.3	1.3	1.3		0.0	1.70
C42 V ₆	85.0	7.4	5.0	0.7	1.8		0.1	1.59
C42 V ₇	88.7	6.0	3.2	0.5	1.5		0.1	2.02
C42 V ₈	94.7	2.9	1.3	0.5	0.5		0.0	2.36
C42 V ₉	95.7	2.4	1.3	0.4	0.2		0.0	1.95
C42 V ₁₀	95.8	2.3	1.3	0.4	0.1		0.0	1.86
C42 B	not done because of "dusting"							
C42 N ₁	52.2	11.0	7.2	14.3	4.2	11.1		1.64
C42 N ₂	55.7	8.0	6.6	9.3	7.5	12.9		1.30
C42 N ₃	57.4	5.8	8.0	8.2	7.7	12.9		0.78
C42 N ₄	56.8	5.5	8.7	8.2	7.9	13.0		0.68
C42 N ₅	60.0	4.7	7.1	7.6	7.2	13.4		0.71
C42 N ₆	63.1	1.7	4.4	8.1	7.4	15.3		0.41
C42 N ₇	63.2	1.3	4.5	8.1	7.4	15.5		0.31
C42 N ₈	63.5	1.3	4.4	8.0	7.3	15.5		0.31
C42 N ₉	64.4	1.6	5.0	8.0	7.3	13.7		0.35
C42 O ₁	44.5	10.4	6.7	13.5	5.3	19.6		1.66
C42 O ₂	40.5	7.5	4.9	15.5	7.8	23.7		1.63
C42 O ₃	41.6	5.8	6.7	13.4	9.5	23.0		0.93
C42 O ₄	42.3	5.1	7.7	13.1	9.1	22.7		0.71
C42 O ₅	43.8	2.6	5.7	13.4	9.4	25.1		0.48
C42 O ₆	44.9	1.2	4.3	13.6	9.7	26.3		0.29
C42 O ₇	45.8	1.1	4.2	13.6	8.7	26.6		0.29
C42 O ₈	43.2	1.0	3.9	13.5	10.3	28.1		0.28
C43 V ₁	68.0	16.0	7.1	7.9	0.4		0.5	2.42
C43 V ₂	79.2	10.9	5.6	3.7	0.4		0.2	2.10

Sample No.	Components							
	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅	C/S ratio
C43 V ₃	81.8	9.4	6.0	2.2	0.5		0.1	1.68
C43 V ₄	82.3	9.2	5.9	2.0	0.5		0.1	1.67
C43 V ₅	84.7	7.8	5.6	1.0	0.8		0.1	1.50
C43 V ₆	88.7	5.5	4.0	1.1	0.6		0.1	1.46
C43 V ₇	94.9	2.5	1.5	0.8	0.2		0.0	1.80
C43 V ₈	95.5	2.5	1.3	0.5	0.1		0.0	2.05
C43 V ₉	95.7	2.3	1.3	0.5	0.1		0.0	1.86
C43 V ₁₀	95.3	2.4	1.4	0.5	0.3		0.0	1.87
C43 B ₁	67.0	15.4	6.9	9.9	0.3		0.5	2.39
C43 B ₂	73.2	13.2	6.9	6.4	0.4		0.2	2.11
C43 B ₃	75.4	11.4	7.0	5.5	0.6		0.2	1.74
C43 B ₄	not done							
C43 B ₅	79.2	8.8	8.2	2.7	1.0		0.1	1.15
C43 B ₆	81.9	7.4	6.5	2.6	1.5		0.1	1.22
C43 B ₇	89.6	3.9	3.2	2.4	0.7		0.0	1.32
C43 B ₈	89.9	3.8	3.2	2.4	0.2		0.0	1.30
C43 B ₉	89.3	4.0	3.4	2.5	0.7		0.0	1.25
C43 N ₁	51.0	14.9	6.6	14.9	2.0	10.6		2.42
C43 N ₂	57.7	8.4	7.1	7.9	6.4	12.4		1.27
C43 N ₃	60.2	5.3	8.0	7.4	6.6	12.5		0.71
C43 N ₄	58.7	5.5	9.3	7.3	6.5	12.7		0.63
C43 N ₅	63.7	2.8	6.1	7.6	6.3	13.5		0.49
C43 N ₆	65.5	1.8	5.1	7.6	6.7	13.3		0.38
C43 N ₇	65.6	1.8	5.3	7.6	6.0	13.7		0.36
C43 N ₈	65.1	1.9	5.0	7.8	6.5	13.7		0.41
C43 N ₉	65.0	1.8	5.2	7.7	6.6	13.8		0.37
C43 O ₁	36.4	13.2	5.8	15.1	2.8	26.7		2.43
C43 O ₂	35.4	8.8	5.5	16.8	9.5	24.0		1.71
C43 O ₃	38.4	5.3	7.7	13.7	10.0	24.9		0.74
C43 O ₄	39.4	4.9	8.1	13.5	9.6	24.5		0.65
C43 O ₅	40.8	2.0	4.9	14.0	10.6	27.7		0.44
C43 O ₆	41.4	1.1	3.8	14.3	10.8	28.6		0.32
C43 O ₇	41.3	1.1	4.1	14.2	10.5	28.8		0.29
C43 O ₈	41.0	1.0	4.1	14.4	10.8	28.7		0.27

Analysts: S.J.L. van der Linde and P.J. Botma.

Analyses recalculated so that $\Sigma = 100.00$

The analyses, however, give no indication of the mineralogical composition of the refractories. A method was, however, developed by Rigby, Richardson and Ball (1947, p. 313-329) according to which the mineralogical phases present at equilibrium conditions can be calculated from the chemical analyses. In all specimens investigated the calculated composition was found to show excellent agreement with the microscopical and diffractometric determinations. As the method of Rigby, Richardson and Ball was originally worked out for pure magnesite refractories, certain conversions had to be made in order to incorporate chromite-containing refractories. According to this conversion, chromite is taken to be a solid solution of $MgAl_2O_4$, $MgFe_2O_4$ and $MgCr_2O_4$, which is, as will be shown later, not too rough an approximation. The ratio of the different spinels depend on the amount of available Al_2O_3 , Fe_2O_3 and Cr_2O_3 . The mineralogical composition of the refractories as calculated by means of the above method are presented in Fig. 6. It will be noted that only variations with regard to the silicate components and solid solution between dicalcium ferrite and brownmillerite are indicated. The reason is that the remaining phases apart from magnesioferrite, are combinations of periclase and chromite which show no marked variation in concentration.

Another advantage of a chemical analysis, is that it furnishes the investigator with the possibility of calculating the amount and the composition of the liquid phases present in the refractory at different temperature levels. The calculation is carried out according to the method described by Solacolu (1960, p. 266).

4.4. The Mineralogical Composition of Basic Refractories and Slags

The minerals constituting the basic refractories and slags in the examples under consideration, fall within the compositional polyhedron $MgO - (FeO) - CaO - SiO_2 - P_2O_5 - Al_2O_3 - Fe_2O_3 - Cr_2O_3$. The compositional polyhedron can be simplified to a compositional tetrahedron by grouping the components into units possessing similar chemical characteristics. The components which are grouped together, are:

1. SiO_2 and P_2O_5 , as P can take the place of Si in silicate structures. An example is the nagelschmidite ($7CaO.P_2O_5.2SiO_2$) - larnite solid-solution series.
2. MgO and FeO as in the periclase - wüstite solid-solution series.

3. Fe_2O_3 , Al_2O_3 and Cr_2O_3 as in the multitude of spinels and in the dicalcium ferrite - brownmillerite solid solution series.
4. Al^{3+} can also take the place of Si^{4+} in most of the silicate structures.

In Fig. 7, $\text{R}_2\text{O}_3 = \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3$, $\text{SiO}_2 = \text{SiO}_2 + \text{P}_2\text{O}_5$ and $\text{MgO} = \text{MgO} + \text{FeO}$. The minerals found in the refractories are underlined; the stippled mineral phases were found in specimens where equilibrium was not obtained.

5. MINERALOGICAL CHANGES IN MAGNESITE AND CHROME-MAGNESITE REFRACTORIES DUE TO CHANGES IN SLAG COMPOSITION

It is virtually impossible to keep a strict order in dealing with the subject of mineralogical changes. The reason is that there is an intricate intermingling of components, causes and effects. An attempt has, however, been made to maintain some order.

The author has deviated from the customary method of dividing a refractory into zones, like hot face zone, iron oxide zone, silicate zone and unaltered zone or cold portion. The reason for this deviation is that it is not the author's intention to deal in this thesis with the constitution of a used refractory, but rather to try and explain the reactions taking place in a refractory whilst in use, and their effects.

Since refractories consist of oxides and silicates, the possible reactions are divided into two main categories, viz.

1. Reactions involving the oxides.
2. Reactions involving the silicates.

5.1. Reactions involving the Oxides

This is a wide and complicated field of study. An attempt will, however, be made to keep to those aspects which are relevant to the subject under discussion.

5.1.1. Reactions involving Periclase

5.1.1.1. Grain Growth.— Periclase grains in those portions of the refractories which are exposed to the highest temperature, will tend to grow larger. The reason for this is the difference in total areas of

the grain boundaries and hence the total boundary energy between a substance having a large grain size and one having a small grain size. Phenomena like "peeling" and poor resistance to thermal shock have been ascribed previously to the growth of periclase crystals. Growth of periclase grains will, however, not take place under all circumstances. For instance, it has been found during the present investigation that the growth of periclase grains varies inversely with the concentration of Ca^{2+} associated with the ferric oxides in the liquid phase surrounding the periclase grains. With the C/S ratio high enough to produce C_2S , but not so high as to bind the available Fe_2O_3 as C_2F , periclase grains still tend to decrease their radii of curvature and hence grow larger. The Fe_2O_3 may be present in the melt or as exsolutions of MF in periclase. If, however, the C/S ratio is so high that after all the Fe_2O_3 present in the liquid phase is bound as C_2F , there is still an excess of CaO, then growth of grains is inhibited to a very large extent. In fact, in a matrix of $\text{C}_2\text{S} - \text{C}_2\text{F} - \text{C}_4\text{AF}$, periclase reveals no obvious grain growth. Mention of, or an explanation for this phenomenon could not be found in the literature. The reason could probably be that a lime-rich liquid is an extremely good acceptor of the oxides Fe_2O_3 , Al_2O_3 and to a lesser degree Cr_2O_3 . If there is an excess of CaO over that which is necessary for the formation of C_2F and C_4AF , and a deficiency of (mainly) Fe_2O_3 in the liquid for ferrite formation, the excess CaO will exert a blotting-paper effect on the sesquioxides present as solid solutions in periclase. In this way Fe_2O_3 will be extracted from periclase until a stage is reached when all the CaO is bound as the stable phase C_2F . The extraction of sesquioxides from periclase causes a diffusion of material having a specific volume out of the periclase phase. The result is a reduction of its grain size. It has in fact been found that slowly-cooled periclase embedded in a ground-mass consisting of the phases $\text{C}_2\text{S} - \text{C}_2\text{F} - \text{C}_4\text{AF}$ is relatively free from inclusions of exsolved spinel (Plates 3 and 4) which is rather uncommon considering the Fe_2O_3 content. The Fe_2O_3 which is present in relatively large amounts should result in abundant MF, exsolved from the periclase (Plate 5). The extraction of Fe_2O_3 will not take place when sufficient Fe_2O_3 is present in the liquid phase for the formation of a $\text{C}_2\text{F} - \text{C}_4\text{AF}$ solid solution (Plate 6), which is invariably the case with chromite-containing refractories.

The affinity of Fe_2O_3 for lime-rich liquids, like those supplied by the slag used during campaign 43 (C/S = 2.91) is so great, that only an

excess of Fe_2O_3 over CaO , after formation of C_2S and $\text{C}_2\text{F} - \text{C}_4\text{AF}$, combines with Mg^{2+} in the solution to form MF. The latter mineral crystallizes autectically with $\text{C}_2\text{F} - \text{C}_4\text{AF}$ as a final phase interstitial to primary periclase (Plate 7).

5.1.1.2. Resorption of Periclase.- Resorption of periclase grains takes place in all the various silicate slags used (Plates 6 and 17). This is interesting as viscous liquids like silicate melts from thick boundary layers and cause a slow transfer of material, which implies a slow rate of solution. It can be reasoned that in the regions immediately adjacent to the hot faces the turbulent motion of the slag could be the cause of resorption. Inside the refractory there could be a fluid flow caused by the density differences between the saturated solution and the bulk solution (Kingery, 1963, p. 333). This question will receive attention at a later stage, but for the present suffice it to mention that Kienow and Seeger (1964, p. 503) found that the rate of solution of periclase decreases with an increase in the C/S ratio of the silicates.

An interesting problem which now arises is: what happens to all the Mg^{2+} that goes into solution. Considerable amounts are obviously washed into the slag. Large concentrations of CMS, C_3MS_2 and secondary MF in the bricks exposed to the relatively acid slags (Fig. 6) prove that considerable amounts of dissolved Mg^{2+} remain in the refractory. In the examples of basic to ultrabasic slags, practically no trace of secondary minerals containing Mg^{2+} could be found in lime-rich regions. The only examples of secondary minerals containing Mg^{2+} are growths of periclase tongues on to the surfaces of primary periclase grains (Plate 9). This brings us to the phenomenon of Mg^{2+} drifting towards the colder portion of the refractory, where we would expect a concentration of Mg-rich minerals (Fig. 6, Veitsoh, Campaign 41, 42 and 43, and Plate 10). In other words, although a basic slag in itself is poor in MgO (MgO -free at the initial stage) Mg^{2+} is picked up by the liquid supplied by the slag on its way into the refractory, and there concentrated as a silicate zone possessing a low melting point. It is evident that with the temperature in this region being low, phase equilibrium will not always be attained, as is explicitly shown in Plate 10.

5.1.1.3. Elongation of Periclase Grains Perpendicular to the Hot Face.- Although the reason for this well-known phenomenon (Plate 11) is not clear it might possibly be another result of periclase resorption parallel to the direction of flow of metasomatised constituents. As in certain regional-metamorphic aureoles, it is not impossible to envisage

some of the dissolved MgO being reprecipitated in the non-fluid areas, more or less in accordance with the principle of Riecke.

5.1.1.4. Reaction between Periclase and Sesquioxides.- The sesquioxides are both of ^{introduced} allochthonous and ^{in situ} autochthonous origin, being both a primary constituent of slags and of chromite-containing refractories.

Before discussing these reactions, it would perhaps be advantageous to make some comments on the crystal-chemical aspects.

1. Periclase has a NaCl-type of structure, having O^{2-} arranged in cubic close packing, and Mg^{2+} nestled in the octahedral holes, each surrounded by six oxygen anions. For solid solution to take place between periclase and R_2O_3 , R^{3+} cations have to displace Mg^{2+} cations. By comparing the ionic radii of the components for sixfold co-ordination, viz. $Mg^{2+} = 0.66 \text{ \AA}$, $Fe^{2+} = 0.74 \text{ \AA}$, $Fe^{3+} = 0.64 \text{ \AA}$, $Cr^{3+} = 0.63 \text{ \AA}$ and $Al^{3+} = 0.51 \text{ \AA}$, it is obvious that only Al^{3+} renders an ionic-radius ratio with oxygen which lies outside the limit considered necessary for sixfold co-ordination. Alper et al (1962, p. 264), however, showed that considerable solid solution of Al^{3+} in periclase is possible (Fig. 8). For the conservation of electrical neutrality, one should accept that three of the divalent ions are displaced by two trivalent ions, with the creation of one cation vacancy per pair of displacing ions.
2. Bowen and Schairer (1935) found a complete solid-solution series to exist between periclase and wüstite (Fig. 9). These results are confirmed by the findings of Hahn and Muan (1962) that the dimensions of the unit cell increases from MgO to FeO. The phase diagram $Fe_2O_3 - MgO$ (Fig. 10) illustrates two important facts. Firstly, liquidus and solidus temperatures increase drastically when MgO is added to iron oxide, both at low and at high oxygen pressures. Secondly, MgO has a strong stabilizing effect on phases in which iron is present predominantly or partly in the divalent state (wüstite and magnetite) relative to phases in which practically all the iron is present in the trivalent state (Muan and Osborn, 1965, p. 81).
3. According to Alper et al (1964, p. 30) MgO can take 12 per cent by weight of Cr_2O_3 into solid-solution at $1600^\circ C$ (Fig. 11). They also pointed out (1958) that in the system periclase - chromite - olivine (periclase - Transvaal chrome ore), a maximum of ± 45 per cent by weight of chromite will go into solid solution with

periclase at 2060°C.

Considering the above data, it is evident that reaction will take place when periclase and sesquioxides are brought into contact at elevated temperatures. This reaction is of great interest, because, judging from phase equilibrium data, one would expect these reactions to take place without the formation of a liquid phase, i.e. in the solid state. The original sesquioxides could of course have been part of a liquid phase. The conservation of crystalline structures and textures confirms the contention of reaction in the solid state. This reaction would therefore be critically dependent on the relative rates of diffusion of the relevant trivalent ions.

In vicinities where the C/S ratio is low, R^{3+} exhibits a much greater affinity for periclase than for the liquid silicate ground-mass. The relative distribution of MR between the ground-mass and the periclase phase (Plate 12) proves this. This phenomenon can be used to determine the depth of impregnation of allochthonous ferric oxides. The depth to which MF is found exsolved from periclase in a refractory which is free of chromite therefore gives an indication of the depth of intrusion of allochthonous ferric oxides. This holds true if the C/S ratio of the slag is low, and was found to agree with values obtained by chemical analysis (Table VIII). In the case of autochthonous sesquioxides, the oxides are supplied by chromite as a result of diffusion of the relevant components from chromite into periclase. The diffusion coefficients of the sesquioxides have been found to increase in the order $Cr_2O_3 < Al_2O_3 < Fe_2O_3$.

5.1.1.4.1. The Mechanism of Formation of Exsolutions of Spinel from Periclase.— The spinel and the periclase structures, both of which are cubic, have oxygen atoms arranged in similar positions. Coherent precipitate-particles can thus form which have common (100)-planes, and all the precipitate-crystals will have the same crystallographic orientation. With this kind of precipitate, the oxygen ions do not have to migrate, and small rearrangements of the cations in the anion lattice can give rise to stable nuclei (Kingery, 1963, p. 321). The interface energy for nucleation of a new phase depends on the interface structure and orientation. In a coherent precipitate, planes of atoms are continuous across the interface, so that only the second co-ordination of individual atoms is changed, similar to a twin boundary. The interface energy of a coherent boundary is of an order of magnitude less than that of an incoherent boundary, where the planes of atoms or some of

them are discontinuous across the interface, giving rise to dislocations or a random structure in the boundary layer (Kingery, 1963, p. 319, 320).

It is therefore evident that new phases with a definite structural relationship to the mother matrix are strongly preferred (Plates 13 and 14).

When growth is rapid, dendritic crystals will result with the radius of curvature of the growing tip remaining small, and side arms developing to form a tree-like structure (Plate 15). Depending on the conditions prevailing during exsolution, different structures arise, viz. (i) platelets // (100) of periclase (Plate 16); (ii) dendrites (Plate 15); (iii) small spheroidal precipitates (Plate 9), in which the total surface energy is a minimum and strain energy may be relieved by plastic flow after long periods at high temperatures (Kingery, 1963, p. 322).

Exsolution of spinels from periclase can take place to such an extent that a vast amount of original periclase is seemingly transformed into spinel (Plate 16). In this example, "transformation" of original periclase into MR starts along the (100)-planes of periclase and eventually penetrates the whole periclase lattice. In some examples even euhedral spinel is formed in periclase (Plate 16).

As implied by the term "exsolution bodies", these textural features originate during the cooling period. During cooling the sesquioxides, soluble in periclase at high temperatures, are precipitated along crystallographic directions of the periclase lattice so as to render a configuration corresponding with a state of minimum free energy within the system. This would imply that, whilst there is not a complete randomness in atomic arrangement at high temperatures, it can be reasonably suggested that of the atoms in solid-solution, the oxygen atoms are the more stationary components. This can be seen by quenching samples containing sesquioxides and periclase from high temperatures. Little or no exsolved spinels will be observed, and periclase is found to exhibit a high reflectivity (Plates 22b, 23b and 24b).

It should now be clear that in multicomponent systems, reactions cannot be defined simply in terms of reagents and reaction products. For these there are too many independent variables viz. fluctuations in composition of the liquid phases associated with the reagents, differences in affinities of components for one another and temperature ranges. The reader should bear this in mind when the following reactions are

described.

5.1.2. Reactions involving the Spinel

Apart from the exsolved spinels discussed above, which are by nature of their origin secondary spinels, two other spinel-types occur, viz.

1. Original spinels, i.e. chromite, which is a primary constituent of chrome-magnesite and magnesite-chrome refractories.
2. Spinel which have crystallized from a melt.

5.1.2.1. Original Spinel.- Chromite is a primary constituent of chrome-magnesite and magnesite-chrome refractories. Mineralogically this mineral is a solid solution having a general formula AB_2O_4 where A denotes Mg^{2+} and Fe^{2+} and B denotes Fe^{3+} , Al^{3+} and Cr^{3+} . When subjected to high temperatures, chromite is found to expand appreciably. An explanation for this phenomenon of "bursting expansion" that is widely accepted, is that the various atoms diffuse at different rates, so that the well-known Kirkendall effect applied to metal diffusion occurs. Small holes left behind by the diffusing atoms, coalesce to form pores and room has to be made on the opposite side of the diffusion barrier for the excess atoms that have reached this area. These atoms are accommodated by an expansion in the system (Richardson, 1965, p. 116). The addition of periclase and silicates cushion this expansion effect, most probably on account of their ability to accommodate the excess of sesquioxides. Even so, slight expansion effects during the initial heating-up procedure renders the hot face area of a chromite-containing refractory more brittle and more accessible to slag attack than pure magnesite refractories. This effect, however, is negligible when compared with that of slag composition on the ultimate behaviour of these refractories.

It has already been shown that, when in contact with periclase, chromite will act as a source of sesquioxides. A very interesting aspect of the diffusion of sesquioxides is that in the areas immediately adjacent to the areas of contact of the grains, there is a slight change in the appearance of both chromite and periclase (Plate 17). In the former, a thin rim which has a high reflectivity can be observed, and in the latter an area exhibits a marked difference in the amount of exsolved MR, as well as in reflectivity. This could indicate a reverse movement during cooling of especially Fe_2O_3 (judging by the higher reflectivity of the thin zone around the chromite border) towards chromite, followed

by its deposition in the area of contact between the grains. The cause of the deposition in the area of contact is most probably that atoms in solid solution can fit into the disorientated boundary layer more easily than into the bulk phase, since the elastic energy required to expand a lattice is not necessary at the disorientated boundary. This could be the cause of the direct bond advocated by so many authors. Therefore, apart from the fact that direct bonds can originate as a result of precipitation of spinel from a liquid phase [Hayhurst and Laming (1963, p. 1003) and Jackson, Ford and White (1963, p. 577)], they can result without the actual participation of a liquid phase.

Zubakov and Yusupova (1964, p. 31) made some very interesting observations on the properties of original and secondary spinels, formed with different degrees of completion of the reaction between chromite and periclase (Table IX).

TABLE IX
PROPERTIES OF ORIGINAL AND SECONDARY SPINELS FORMED DURING
REACTION BETWEEN CHROMITE AND PERICLASE

Properties		Secondary spinel formed during the completion of the reaction	
		Partial	Complete
Chemical Composition (Mol. per cent)	Original chrome spinel		
MgO	34.1	48.3	50.0
FeO	15.9	1.7	0.0
Fe ₂ O ₃	1.6	33.3	8.2
Cr ₂ O ₃	39.9	13.7	34.6
Al ₂ O ₃	8.5	3.0	7.2
Mol. Groups (per cent)			
FeO.Cr ₂ O ₃	28.6	3.4	0.0
FeO.Fe ₂ O ₃	3.2	0.0	0.0
MgO.Cr ₂ O ₃	51.2	24.0	69.3
MgO.Fe ₂ O ₃	0.0	66.6	16.3
MgO.Al ₂ O ₃ (?)	(17.0)	(6.0)	(14.4)

It is interesting to note the transformation of FeO into Fe₂O₃ when the reaction between chromite and periclase is completed.

The chemical composition of chromite (Table X) in unused refractories (Plate 18) is most informative, as will be shown presently.

TABLE X
CHEMICAL COMPOSITION OF ORIGINAL CHROMITE
IN UNUSED REFRACTORIES

Components	Weight per cent
MgO	19.80
FeO	9.28
SiO ₂	1.31
Fe ₂ O ₃	4.88
Al ₂ O ₃	16.23
Cr ₂ O ₃	48.49

Analyst: T.L. Sandrock

In order to obtain the chromite for chemical analysis, a sample of an unused portion of a chrome-magnesite refractory (Mk 0) was crushed to a workable mesh. The chromite grains were picked out under a stereoscopic microscope, boiled in concentrated HCl, and finally all the visible impurities were removed. A random portion of the sample which was ground to a fine powder yielded an until-cell dimension of $8.279 \pm 0.002 \text{ \AA}$. This value corresponds with that of other chromite particles drilled out with a diamond tipped objective.

In order to calculate the mineralogical composition, the author assumed the chromite to consist of solid solutions of FeCr_2O_4 , MgFe_2O_4 , MgCr_2O_4 and MgAl_2O_4 (Table XI). The silicate was taken to be forsterite which could not be separated from chromite.

If MgO (periclase) and forsterite are taken as impurities that could not be separated from chromite, the chromite would have the composition $(\text{Fe}_{3.1}\text{Mg}_{6.9})\text{O} \cdot \text{Fe}_{0.7}\text{Cr}_{6.9})_2\text{O}_3$. This composition agrees with the unit cell value of 8.279 \AA .

The values calculated reveal interesting facts concerning the diffusion of Fe_2O_3 from chromite even in the absence of metasomatised minerals, as the process must have taken place during the final firing in the manufacturing process. There is namely a discrepancy with regard to the FeO- and Fe_2O_3 -content of this chromite and that of the bulk chemical composition of the unused refractory from which the chromite

was obtained (Table XII).

TABLE XI
CALCULATION OF THE MINERALOGICAL COMPOSITION OF
CHROMITE FROM AN UNUSED CHROME-MAGNESITE REFRACTORY

Components	MgO	FeO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃
Wt. per cent (corrected)	19.8	9.3	1.3	4.9	16.2	48.5
Mol. Proportion (x 1000)	491	130	22	31	159	319
Mol. Prop. / Mol. Prop. of SiO ₂	22.30	5.91	1.00	1.41	7.23	14.50
2MgO.SiO ₂	2.00		1.00			
FeO.Cr ₂ O ₃		5.91				5.91
MgO.Fe ₂ O ₃	1.41			1.41		
MgO.Al ₂ O ₃	7.23				7.23	
MgO.Cr ₂ O ₃	8.59					8.59
	19.23	5.91	1.00	1.41	7.23	14.50
MgO (surplus)	3.07					

TABLE XII
THE (A+K)/F-VALUES OF CHROMITE IN UNUSED REFRACTORIES, OF
THE BULK CHROME-MAGNESITE SAMPLE AND OF RAW CHROMITE

	Chromite in used refractory (C43 O ₈)	Transvaal chrome ore	Chrome-magnesite refractory (C43 O ₈)
MgO	19.8	9.44	41.0
FeO	9.3	25.42	n.d.
CaO	n.d.	0.46	1.0
SiO ₂	1.3	1.04	4.1
TiO ₂	n.d.	0.74	n.d.
Fe ₂ O ₃	4.9	0.00	14.4
Al ₂ O ₃	16.2	16.20	10.8
Cr ₂ O ₃	48.5	45.60	28.7
(A+K)/F	7.2	5.40	2.75

n.d. = not determined.

In the chromite from the unused refractory the ratio of $(Al_2O_3 + Cr_2O_3)/Fe_2O_3 = 7.2$ (in order to obtain this value, FeO is converted into Fe_2O_3 according to the formula $Fe_2O_3 = FeO \times 71.8/159.7$). In the unused refractory, though, the ratio is 2.75. As the only source of Fe_2O_3 could have been chromite, this would mean that an amount of approximately 14.8 per cent Fe_2O_3 had been supplied to the ground-mass (including periclase) by chromite. In the case of raw chromite the ratio is 5.40, and the loss of Fe_2O_3 from chromite is 8.8 per cent. This effect is of the greatest importance, as it implies that though the Cr_2O_3 - and Al_2O_3 -contents remain approximately the same, the FeO- and Fe_2O_3 -content of chromite is lowered and the MgO-content increased appreciably when brought in contact with periclase and silicates at high temperatures, resulting in the formation of magnesiochromite.

The diffusion of Fe_2O_3 could have a very important effect when minerals are added to the refractory by the slag. When adding chromite to a refractory, one therefore indirectly adds mainly Fe_2O_3 . As the beneficial effect of Cr_2O_3 (El Shahat and White, 1964, p. 313, and 1966, p. 309) will be small when compared with the detrimental effect of Fe_2O_3 , a reconsideration of the rôle played by chromite in refractories seems necessary.

5.1.2.2. Spinels which have Crystallized from a Melt.- The concentration, composition, and degree to which these spinels exhibit euhedral habits were found to vary according to the types and the concentration of both divalent and trivalent oxides present in the melt. The penetration of other allochthonous ferric oxides has been indicated not to be very deep (Table VIII), but as pointed out chromite contributes noticeably towards an enrichment in mainly Fe_2O_3 and also in Al_2O_3 and Cr_2O_3 . It is accordingly to be expected that in a melt containing Mg^{2+} as well as R_2O_3 , one of the primary phases would be secondary spinel. Judging from its euhedral habit, the secondary spinel crystallizes over a considerable temperature range in an environment of liquid silicates. Eutectic crystallization between MR, C_2S and M_2S (Plate 5) is, however, not a rare occurrence, but this is to be expected as these combinations have relatively high eutectic temperatures. Under these circumstances, MR has been found to be anhedral, implying a rapid crystallization, combined with a slow rate of flow of material to the regions of crystallization.

In accordance with the above, the size and the degree to which the secondary spinel is euhedral, varies according to the rate of cooling

(which is evident) and the composition of the slag. The reason is that the latter will determine the viscosity of the minerals which are metasomatised. In a highly viscous environment, the transfer of material towards the crystallizing nuclei will be slow, resulting in spinels which are small and anhedral.

Spinel that crystallizes from a melt, shows a marked tendency to crystallize on to existing minerals, viz. periclase and chromite (Plate 19) rather than to nucleate and crystallize as discrete grains (Plate 20). This tendency is responsible to a large extent for the direct periclase-periclase bonding by way of a spinel phase (Hayhurst and Laming, 1963, p. 989, and Jackson, Ford and White, 1963, p. 577). It is not quite clear under which conditions spinel crystallizes as discrete grains.

The secondary spinels possess a wide range in composition. The author will, however, make only a few passing comments on this matter.

By studying Plates 19, 20 and 21, the gradual change in composition is striking, i.e. there is definite zoning in that the crystals have either a Fe_2O_3 -poor (Plate 19) or a relatively Fe_2O_3 -rich (Plate 21) core. The question is whether the zoning is a result of normal crystallization, or whether it originated after crystallization of the spinel. During any normal crystallization process the zonal crystals should contain less Fe^{3+} in the cores of the grains than in the rim, as, in any sequence of crystallization, the mineral having the lowest melting point, viz. Fe^{3+} -bearing spinel, is the last to crystallize. This is indeed the case with spinel crystallizing in a relatively Ca-poor environment (Plate 19). In an environment where the liquid contains more lime, reverse zoning prevails. This phenomenon can be ascribed, as already discussed, to the leaching of iron oxide by lime-rich liquids, whereby Fe_2O_3 is extracted from the rim of the crystalline spinel.

Other reactions which take place after the crystallization of spinel are:

1. The creation of small pores in secondary spinel, most probably as a result of coalescence of small holes left behind by atoms that have diffused out of the spinel (Kirkendall effect) (Plate 20).
2. Coherent exsolution of sesquioxides from the secondary spinel as platelets and crystals.

The most important aspect of the spinels discussed in this section,

is that in the pure magnesite refractories, their formation is limited by the depth of intrusion of ferric oxides. The spinels are therefore of metasomatic origin. In chrome-magnesite refractories, they can also be of autochthonous origin, i.e. the source of ferric oxides lies within the brick.

5.1.3. The Effect of the C/S Ratio of the Refractory and of the Slag on Chromite-containing Refractories

5.1.3.1. The Effect of the C/S Ratio of the Refractory on the Refractories containing Chromite.- It has already been mentioned (p. 13, § 2) that according to Pickering and Ford (1964, p. 487) the breaking strength increases at low temperatures upon increasing the C/S ratio, but the relevant curve shows a pendulum-effect at higher temperatures, i.e. it decreases again. No explanation was offered for this phenomenon. The same results were obtained in local laboratories. Samples of chrome-magnesite having different C/S ratios were obtained by impregnating five 1.25 x 1.25 x 22.9 cm samples of Pickford Holland AXP-chrome-magnesite refractories with a solution of $\text{Ca}(\text{NO}_3)_2$. After impregnation, the samples were fired to 700°C, and then after weighing, to 1500°C. The samples were kept for two hours at each temperature. Two specimens of each sample were investigated for their mineralogical composition, viz. a slowly cooled sample and a quenched sample. By quenching, the conditions prevailing in the refractory at 1500°C were frozen and could be studied.

Samples 1A and 1B (Table XIII) represent the original samples, in other words, they were not impregnated with a solution of $\text{Ca}(\text{NO}_3)_2$.

TABLE XIII

THE MINERALOGICAL COMPOSITION OF CHROME-MAGNESITE REFRACTORIES
POSSESSING IDENTICAL OXIDES BUT DIFFERENT C/S RATIOS

Sample (C/S ratio) Mode of cooling	Components	Observations
1A (0.48 Cooled slowly (Plate 22a)	M, chromite, MR (sed) M_2S (ms) CMS (sub)	Exsolution bodies of MR in M, as well as other secondary spinels common. Direct M-M, M-MR-M and M-chromite bonding prominent.

Sample (C/S ratio) Mode of cooling	Components	Observations
1B (0.48) Quenched in water (Plate 22b)	M, chromite, MR, M_2S , CMS	Direct bonding not as well represented as in 1A. Reflectivity of M higher than in 1A, due to sesquioxides still in solid-solution. Small phenocrysts of M_2S surrounded by CMS-crystallites.
2A (0.96) Cooled slowly (Plate 23a)	M, chromite, MR, CMS (ms) M_2S (sub)	Direct bonding and exsolution bodies prominent.
2B (0.96) Quenched in water (Plate 23b)	M, chromite, MR, CMS, M_2S , liquid	Direct bonding not as well developed as in 2A. M grains form small is- lands in a sea of silicates. The li- quid phase is relatively rich in CaO and possibly Fe_2O_3 .
3A (1.3) Cooled slowly	M, chromite, MR, C_3MS_2 (ms) CMS (prom)	Direct bonding well developed. Ex- solved and other secondary spinels prominent.
3B (1.3) Quenched in water (Plate 24b)	M, chromite, MR, C_3MS_2 , glass	Chromite more porous than in the pre- vious samples. Secondary spinels sparsely distributed. A slight in- crease in amount of liquid phase above 2B indicated. Small phenocrysts of C_3MS_2 embedded in a glass which most probably corresponds with CMS in com- position.
4A (1.71) Cooled slowly (Plate 25a)	M, chromite, MR, C_3MS_2 (ms) C_2S (sub)	Texturally very similar to 3A.
4B (1.71) Quenched in air (Plate 25b)	M, chromite, MR, crystallites of C_3MS_2 surrounded by a glass phase corresponding in composition to C_2S	Direct bonding practically non exis- tant. Ferric oxide leaching obvious, leaving rims of chromite phase with lower reflection than their cores. Cryptocrystalline matrix rich in lime and ferric oxides.

the chromite grains (Plate 28).

It is therefore clear that addition of chromite to refractories containing periclase result in the formation of more liquid possessing a low melting point and low viscosity when slags having high C/S ratios are used.

TABLE XIV
THE INFLUENCE OF THE C/S RATIO OF THE
SLAG ON CHROME-MAGNESITE REFRACTORIES

Sample No.	C/S ratio of slag	C/S ratio of refractory	Silicates	Remarks
C40 O ₁ (Plate 27a)	1.18	0.88	M ₂ S+CMS+C ₃ MS ₂	Chromite relatively unattacked.
C41 O ₁ (Plate 27b)	1.91	1.23	C ₃ MS ₂ +CMS	Chromite attacked where C ₃ MS ₂ is present.
C42 O ₁ (Plate 27c)	2.50	1.66	C ₂ S+C ₃ MS ₂	Chromite totally resorbed immediately adjacent to slag.
C43 O ₁ (Plate 27d)	2.91	2.42	C ₂ S+C ₂ F+C ₄ AF	Chromite disappears totally towards the slag content.

5.1.3.3. The Relationship between the C/S Ratio of the Refractory and the Amount of Sesquioxides Present, But Not as Spinel or in Periclase.-

In order to ascertain the relationship, the ground-mass of the hot portions (1.27 cm nearest to the contact zone of the slag) of Mk O refractories used during campaigns 40 - 43 were analysed chemically for Fe₂O₃, Al₂O₃ and Cr₂O₃. Neither periclase nor spinel is attacked in polished sections when boiled in a 10 per cent solution of HNO₃, but the silicates (excepting M₂S) are etched. Accordingly 0.1 gram of each of the samples C40 O₁, C41 O₁, C42 O₁ and C43 O₁ were boiled in a 10 per cent HNO₃-solution of 10 minutes. After filtering off the undissolved residue, each sample was analysed for the sesquioxides (Table XV).

TABLE XV
CHEMICAL ANALYSIS OF OXIDES IN THE GROUND-MASS

Sample No.	C/S ratio	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃ (Wt. per cent)
C40 O ₁	0.84	3.15	0.087	0.090
C41 O ₁	1.49	4.80	0.070	0.143
C42 O ₁	1.66	5.60	0.076	0.141
C43 O ₁	2.43	5.38	0.465	0.748

Analyst: P.J. Botma.

By comparing these analyses with the original sesquioxide contents (Table VIII) of Mk O₁ refractories, the following values are obtained for the ratios of relevant total sesquioxides which are present in the ground-mass (Table XVI).

TABLE XVI
THE AMOUNTS (PER CENT) OF SESQUIOXIDES NOT PRESENT IN SPINEL OR IN PERICLASE I.E. IN THE GROUND-MASS

Sample No.	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃
C40 O ₁	14.5	1.8	0.04
C41 O ₁	29.1	1.6	0.06
C42 O ₁	41.5	1.4	0.07
C43 O ₁	35.6	16.6	2.80

The following facts emerge from the information presented in Table XVI:

1. The amounts of sesquioxides present in the ground-mass increase with corresponding increase in the C/S ratio of the slag (and hence in the adjacent hot fact of the refractory).
2. The sensitivity of the sesquioxides towards changes in the C/S ratio of the slag decreases in the order Fe₂O₃ >> Al₂O₃ >> Cr₂O₃.
3. The influence of Cr₂O₃ will be relatively small when this component is added to a refractory in the form of chromite.
4. At high C/S ratio levels Fe₂O₃ and Al₂O₃ will most probably be present in the form of 2CaO.(Fe³⁺, Al³⁺)₂O₃ whereas at lower C/S ratios (< 2) they can partake in silicate structures.

It should be noted that the chemical composition of the slags used during campaigns 40 - 43 remained constant with respect to their Fe_2O_3 , Al_2O_3 and Cr_2O_3 -contents (Table VI).

5.2. Reactions involving the Silicates

The reactions discussed in the previous section are of considerable importance in the understanding of the behaviour of basic refractories in contact with slags. It is, however, the reactions involving the silicates that constitute the largest single factor for determining the rate of wear of refractories. The intimate relationship between the reactions involving the oxides and those involving the silicates has already been mentioned. The reason is that the C/S ratio of the slag and of the refractory determine the types and mechanisms of mineralogical changes in both the silicate and the non-silicate members. The driving force towards reaction will be the tendency of the refractory to attain chemical and ultimately thermodynamic equilibrium.

5.2.1. Metasomatic Silicates formed by Reaction of Slag and Refractory

Considering the low MgO-content of slags, it is evident that not all the silicates found in refractories are identical to those supplied by the slag. What is implied here, is that not all the primary slag silicates can enter a refractory in an unaltered form. Most metasomatic silicates are therefore formed by a primary reaction between the slag and the refractory. The following comments bear on this issue:

1. Although MgO is not a primary constituent of slags, a certain amount of this component is added to the slag because of wear of refractories.
2. The added amount of MgO is not sufficient to bind the Ca-silicates present in the slag, as Ca-Mg-orthosilicates, and would first bind the Fe_2O_3 present as MF. ✓
3. Depending on the C/S ratio of the slag, Ca-silicates would be present which are either stable or unstable in the presence of MgO. ✓

This can be explained as follows.

5.2.1.1. C/S Ratio of the Slag is < 2. - Different combinations of the following minerals can be expected as primary slag phases: wollastonite, rankinite, iron monticellite, ferrosilicate or any other stable mineral falling in the lime-poor region of the $\text{CaO}-(\text{MgO})-\text{SiO}_2-\text{P}_2\text{O}_5$ -sesquioxides phase diagram. As an example, the mineralogical composition of the slag used during campaign 40 has been calculated from chemical data

(Table XVII). Mineralogical investigation confirmed the presence of the calculated phases in the relevant slag.

TABLE XVIII
CALCULATED MINERALOGICAL COMPOSITION OF THE
SLAG USED DURING CAMPAIGN 40

Components	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Cr ₂ O ₃	P ₂ O ₅
Wt. per cent (corrected)	15.9	30.2	27.4	23.8	1.0	1.0	0.7
Mol. Proportion (x 1000)	395	539	475	149	10	7	5
Mol. Prop. / Mol. Prop. of SiO ₂	0.86	1.18	1.00	0.33	0.02	0.02	0.011
MF	0.33			0.33			
MA	0.02				0.02		
MK	0.02					0.02	
CMS	0.49	0.49	0.49				
C ₃ S ₂		0.54	0.37				
CS		0.15	0.15				

i.e. The mineralogical composition (mol. per cent) is:

MF = 30.2 per cent; MA = 1.3 per cent; MK = 1.7 per cent
 CMS = 35.1 per cent; C₃S₂ = 23.7 per cent; CS = 8.0 per cent

The minerals C₃S₂ and CS will be metastable in the presence of M (of the refractory). In order to obtain equilibrium, the following reactions will take place in the contact area of the slag and the refractory.

1. C₃S₂ - M:
 3C (168 parts by weight) + 2S (120 parts by weight) + M (40.3 parts by weight) → C₃MS₃ (328.3 parts by weight).
2. CS - M:
 C + S + M → CMS.

It is not necessary to go through the whole spectrum of possible reactions, as the general principle has now been described.

By considering the reactions described above, it becomes clear why a slag having a low C/S ratio should exert a high rate of resorption of periclase.

5.2.1.2. C/S Ratio of the slag is > 2. - Different combinations of C₂S and C₃S are primary slag phases. In the presence of Fe₂O₃ the surplus

of lime will preferentially form Ca-ferrites, after the formation of C_2S . Only the lime in excess of Fe_2O_3 will result in C_3S being formed, after the formation of C_2F .

These minerals will be in equilibrium with the refractory in the contact-area between the slag and the refractory. Periclase resorption still takes place, though to a lesser degree, but the mechanism of this reaction is not clear.

5.2.2. Reactions between Metasomatic and Autochthonous Silicates

The reaction between metasomatic and autochthonous silicates are dependent on a multitude of factors, the most important of which are:

1. The make-up of a refractory which includes factors like:
 - a. The oxide composition of the refractory.
 - b. The composition and the quantity of the bonding silicates.
 - c. The processing factors of the brick, viz. the firing temperature, the degree of mixing of the components and the porosity and permeability.
2. The composition of the slag.
3. The operating temperature.
4. The operating atmosphere.

It is obvious that no definite postulation of the silicate (or for that matter any other) reaction can be given, but for the tendency in any system activated by a combination of thermal and concentration effects to move towards a state of lower free energy. Lower free energy is effected in the system by moving in a direction of chemical, mechanical and thermal equilibrium. The question could therefore well be asked: "To what extent is equilibrium obtained within a refractory during its use?".

On this issue only rare examples of obvious inequilibrium were observed in the present study. In those portions of the slag in immediate contact with the refractory, and to a lesser degree in those portions of the refractory in immediate contact with the slag, equilibrium conditions do not always prevail. The reason is most probably that in these regions, the reaction between the refractory and the slag, described above, is still in progress, and to a considerable degree incomplete. It is for example obvious from a study of the phase diagram $MgO - CaO - SiO_2$ (Fig. 1), that the silicates formed under equilibrium conditions

would be assemblages lying on the $M_2S - C_2S$ -join. M_2S would to a large extent be excluded because lime is always present in the slag. One would not expect a break in the series i.e. the assemblages $C_2S + CMS$ or $C_3MS_2 + M_2S$ or $C_2S + C_3MS_2 + CMS$ or $C_2S + CMS + M_2S$ would not take place. In the case of campaign 40, slag having a C/S ratio of 1.18 was used. After reaction with the refractory the primary silicate phases are expected to be $C_3MS_2 + CMS$. The silicates found, however, were C_2MS_2 , C_2S , C_3MS_2 and CMS (Plate 29) which evidently represent a metastable association. Under equilibrium conditions, C_2MS_2 would be found in one of the following associations:

Ternary Peritectica	Temp	Ternary Eutectica	Temp
$C_2MS_2 + CMS + M_2S$	1430°C	$C_2MS_2 + CMS_2 + CS$	1350°C
$C_2MS_2 + \text{pseudo } CS + CS$	1360°C	$C_2MS_2 + CMS_2 + M_2S$	1357°C

The åkermanite (C_2MS_2) is most probably a reaction product between the primary slag mineral rankinite (C_3S_2) and monticellite (CMS), i.e. $C_3S_2 + CMS \longrightarrow C_2MS_2 + C_2S$ (exsolved // long direction of åkermanite). CMS is a reaction product between the primary slag phase wollastonite (CS) and periclase.

In cases where Mg^{2+} -drifting, discussed previously (p. 30), results in the precipitation of Mg -rich minerals like CMS (which have low melting points) in zones where the C/S ratio is relatively high, equilibrium will not be obtained. The reason is that the temperature in this region is too low because of the already discussed temperature gradient. In the example under discussion the phase assemblage is $C_4AF + M_2S + CMS + C_2S$ (Plate 10).

Splendid correlation between the normative mineralogical composition calculated from chemical analyses by the method of Rigby, Richardson and Ball (1947, p. 313-329) and the modal composition obtained microscopically, suggests that equilibrium is obtained in a refractory in use.

Having pointed out the tendency for the phases in a refractory, whilst in use, towards attaining equilibrium, it is not difficult to postulate the reactions that involve the silicates. In order to do this, the reaction between the different slags and the different types of refractory will be considered systematically. The various reactions are grouped into two main categories, viz.

1. Reactions between the different metasomatized silicates and autoch-

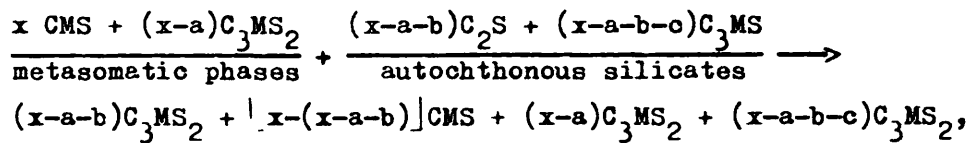
thonous lime-rich silicates (i.e. bonding silicates of magnesite refractories having relatively high C/S ratios).

2. Reactions between the different metasomatised silicates and autochthonous Ca-poor silicates (i.e. bonding silicates of the chromite-containing refractories).

The magnesite refractory Mk B₁ shows a great variation with respect to the composition of its autochthonous silicates, and also a relatively high Fe₂O₃-content, so that it could be placed partly in both categories.

5.2.2.1. Reactions between Metasomatic and Autochthonous Silicates, the Latter having High C/S Ratios.-

5.2.2.1.1. C/S Ratio of Slag = 1.18 (Campaign 40); C/S Ratio of Refractory = 1.95 (Veitsch).- It is evident from the difference in C/S ratio between the slag and the refractory, that the response of the autochthonous silicate to that formed through metasomatism, would be one of considerable reaction involving constitutional changes, viz.



where x , a , b and c are all positive numbers, and $x\text{CMS}$ means x molecules of CMS. It is furthermore evident that the concentration of allochthonous and autochthonous silicate phases will determine the numerical values of x , a , b and c . The values of x and a in particular, depend on the C/S ratio of the slag, eg. as the C/S ratio tends towards unity, C_3MS_2 will gradually disappear, and a tends towards x . If the C/S ratio increases until 50 mol. per cent CMS and 50 mol. per cent C_3MS_2 is formed, then $a \longrightarrow 0$.

In this particular case, $x \gg a$, i.e. $x-a > a$ because of the fact that the C/S ratio of the slag tends towards unity (= 1.18), and because of the low concentration of autochthonous silicates ($\text{C}_2\text{S} \sim 3.4$ per cent, $\text{C}_3\text{MS}_2 \sim 0.4$ per cent), $(x-a) > b$ and $(x-a-b) > c$.

We would thus expect that, at the hot face, $\text{C}_3\text{MS}_2 > \text{CMS}$. This is in fact the case (Fig. 6). Because of the conversion of available CMS into C_3MS_2 , CMS will disappear when C_3MS_2 becomes the sole silicate (Plate 31).

By taking different values for x and a , and also for the autochthonous phases, it is possible to calculate the trends in the concentration of the silicates for any slag yielding CMS and C_3MS_2 as primary reaction

products between the slag and the refractory.

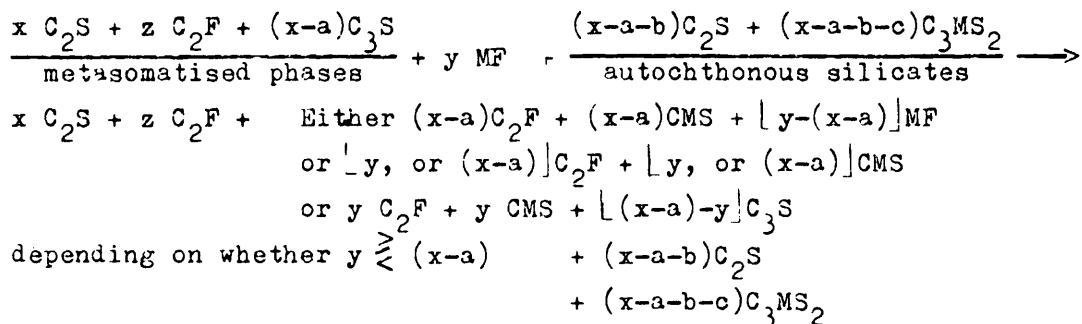
Once they commence, catalysed by C_2S in the refractory, the above reactions will continue until equilibrium is reached, depending of course on the prevailing temperature. The great importance of the concentration and composition of autochthonous silicates now becomes apparent.

The fact that CMS disappears with increasing distance from the hot face, will result in a relatively fast rate of surface-removal of the refractories, especially because of the low melting point and low viscosity of this particular mixture of silicates (see Plate 30).

Allochthonous Fe_2O_3 has no great effect on the reaction mentioned above, because of the fact that it would preferably react with periclase to form spinel.

5.2.2.1.2. C/S Ratio of Slag = 1.91 (Campaign 41); C/S Ratio of Refractory = 1.95. - In the case of the slag used during campaign 41, the metasomatised silicate products are x mols. C_2S and (x-a) mols. C_3MS_2 , in more or less the same ratio as the autochthonous bonding silicates. The effect would thus be one of silicate addition without interreaction. Should the C/S ratio of the slag increase slightly, however, then a \rightarrow x i.e. C_3MS_2 will disappear as a primary product of reaction between slag and refractory.

5.2.2.1.3. C/S Ratio of Slag > 2 (Campaigns 42 and 43); C/S Ratio of Refractory = 1.95. - The stage is now reached where any Mg-rich silicate like C_3MS_2 , or Mg-ferrite, will not be in equilibrium with the metasomatised silicates, and one would expect the following reactions to take place.



In the campaigns run, $y \nless (x-a)$, but as this reaction would occur in dolomite refractories, it is also mentioned. The formed $[y-(x-a)]CMS + [x \text{ or } (x-a-b)]C_2S$ will produce further $C_3MS_2 + C_2S$.

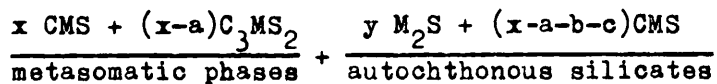
It is therefore clear that when basic slags are used in contact with magnesite refractories having relatively high C/S ratios, there will

always be some surplus of Mg^{2+} -rich silicates, which will not be in equilibrium with the rest of the material in that specific zone (as C_3MS_2 is certainly not in equilibrium with $C_2S + C_2F$). This Mg-rich silicate (C_3MS_2 or CMS) will now penetrate deeper into the refractory as it has a lower melting point, until its movement is stopped by a drop in temperature. This explains why a zone of enrichment in Mg-rich silicate is so consistently found even when slags and refractories with a high C/S ratio are used (Fig. 6) .

In the mineral-association mentioned above, the depth of intrusion of allochthonous Fe_2O_3 is of considerable importance as it will be the main factor which limits the depth to which the metasomatic phases will penetrate into the refractory.

5.2.2.2. Reactions between the Different Metasomatic Silicates and Autochthonous Calcium-poor Silicates.-

5.2.2.2.1. C/S Ratio of Slag = 1.18 (Campaign 40); C/S Ratio of Refractory ~ 0.29 (Mk N and Mk O).- The possible reactions between the metasomatic phases and the autochthonous silicates are the following.



In this, as in all other examples, the concentration of the phases (allochthonous as well as autochthonous) are of considerable importance. Whether or not M_2S will form in the hot-face area, depends on whether $(x-a) \gtrless y$, and, as already shown, on the variations of the value of a. In other words, if

1. $(x-a) > y$: $\longrightarrow x \text{ CMS} + y \text{ CMS} + [(x-a)-y]C_3MS_2 + (x-a-b-c)CMS$
 In this case the minerals present will be CMS as the most prominent silicate and small quantities of C_3MS_2 - as in C40 O₁.
2. $(x-a) = y$: $\longrightarrow x \text{ CMS} + [y \text{ or } (x-a)]CMS + (x-a-b-c)CMS$
 i.e. the sole silicate in the area adjacent to the contact area between the slag and the refractory will be CMS.
3. $(x-a) < y$: $\longrightarrow x \text{ CMS} + (x-a)CMS + [y \text{ or } (x-a)]M_2S + (x-a-b-c)CMS$
 i.e. the silicates present are mostly CMS plus subordinate M_2S .

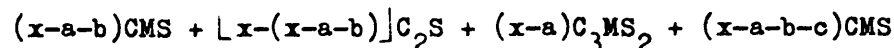
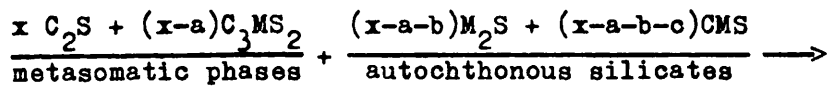
In accordance, once again, with the availability (depth of intrusion) of the metasomatic components, M_2S would be expected to form in ever increasing quantities away from the hot face, and the amount of C_3MS_2 would decrease correspondingly. It could perhaps be added that mixtures of M_2S and CMS have higher viscosities than mixtures of CMS and

C_3MS_2 and that, according to Solacolu's phase diagram, the quaternary eutecticum of the phases $M_2S - CMS - M - MA$ lies at $1380^\circ C$.

It has already been mentioned that in this particular phase-assembly Al_2O_3 and Cr_2O_3 present in chromite will exert little or no influence on the properties of the melt, and the effect of importance here is the structural superiorities of chromite-containing refractories when subjected to "acid slags".

5.2.2.2.2. C/S Ratio of Slag = 1.91 (Campaign 40); C/S Ratio of Refractory ~ 0.29 (Mk N and Mk O). - The author has already discussed (p. 40) the influence exerted by the high C/S-content on chromite-bearing refractories. As the depth of impregnation by Ca-rich silicate is determined by the availability of Fe_2O_3 , which acts as a flux, one can assume that with chromite present as an autochthonous source of Fe_2O_3 , these silicates would be able to penetrate to deeper levels than in the case of pure magnesites, where Fe_2O_3 does not penetrate to great depths.

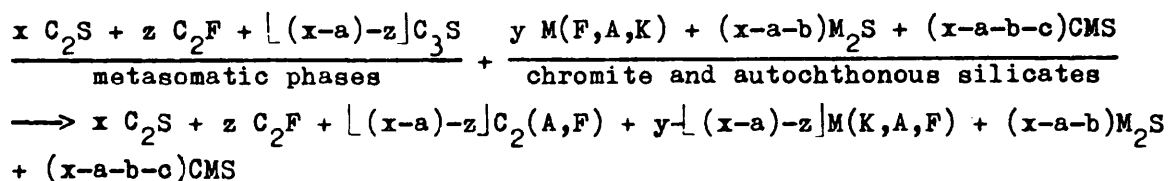
The silicate reactions can be formulated as follows.



Now, depending on whether $(x-a-b) \geq (x-a-b-c)$, either $C_3MS_2 + CMS$ or C_3MS_2 (sole silicate) or $C_2S + C_3MS_2$ will result.

In the latter case the excess of C_2S will react with $(x-a-b)CMS$ to form more C_3MS_2 . If there is still an excess of C_2S over this C_3MS_2 , then the final products would be $C_3MS_2 + C_2S$, as when more basic slags are used.

5.2.2.2.3. C/S Ratio of Slag > 2; C/S Ratio of Refractory ~ 0.29 (Mk N and Mk O). - In cases where chromite-containing refractories are used in contact with slags with a C/S ratio > 2, the silicate reactions become slightly more complicated. The following equation gives a clear picture of these reactions.



As there is a considerable amount of Fe_2O_3 in the slag, and chromite is a primary constituent, there will be no excess of C_3S .

At this stage, however, equilibrium is not yet attained i.e.

further reaction will take place, firstly between $x \text{C}_2\text{S}$ and $(x-a-b)\text{M}_2\text{S}$ to form $(x-a-b)\text{C}_3\text{MS}_2$ and $x-(x-a-b)\text{C}_2\text{S}$.

The remaining C_2S will now react with the remaining CMS to form further C_3MS_2 , so that the final phases will be $\text{C}_2\text{S} + \text{C}_2(\text{A},\text{F}) + \text{C}_3\text{MS}_2$, which is in fact the only stable mineral association that can form when a refractory with a low C/S ratio is in contact with an ultrabasic slag. It is obvious that the C_3MS_2 thus formed will not be in equilibrium with the $\text{C}_2\text{S} - \text{C}_2^{\text{F}} - \text{C}_2(\text{A},\text{F})$ -melt, so that it will migrate deeper into the refractory, where it will once again (and this is important!) react with M_2S to form more CMS. Thus, depending on factors such as the concentrations of allochthonous C_3MS_2 and autochthonous M_2S and CMS, one would expect the following associations (starting off at the contact zone between refractory and slag). $\text{M} + \text{C}_2^{\text{F}} + \text{C}_4\text{AF} + \text{C}_2\text{S} +$ (small quantities if any) chromite (Plates 27d and 28), followed by $\text{C}_2\text{S} + \text{C}_3\text{MS}_2 +$ periclase + chromite (no C_2^{F} and C_4AF), succeeded by $\text{C}_3\text{MS}_2 + \text{CMS} +$ periclase + chromite, and eventually by the original constituents $\text{M}_2\text{S} + \text{CMS} +$ periclase + chromite (Plate 33). This has indeed been found to be the case.

The reactions described above would suggest that a mixture of silicates of low viscosity will form, not at the interface, but in a position within the refractory where the temperature is not particularly low (1500 - 1590°C).

6. SUMMARY

The main points arising from a study of the reactions discussed above can be summarised by means of a series of diagrams drawn from the actual silicate composition as calculated from chemical, and corroborated by microscopic analyses (Fig. 6). In these diagrams the "cold portions" show the silicate composition of the refractories prior to their use. It is clear that Veitsch, Mk N and Mk O refractories have relatively constant C/S ratios in contrast with Mk B₁. The C/S ratio of Veitsch, being so near to 2, would result in the silicate phases being either $\text{C}_2\text{S} + \text{C}_3\text{MS}_2$ or C_2S (sole silicate) or $\text{C}_2\text{S} + \text{C}_3\text{S}$, which in the presence of small amounts of Fe_2O_3 and Al_2O_3 would render the phases $\text{C}_2^{\text{F}} + \text{C}_4\text{AF}$. There is a specific system in the silicate reactions, i.e. when the composition of the refractory and of the slag are known, one should be able to predict the composition of the silicates that will form. The close correlation between the postulated silicate reactions and the

modal silicate composition shown in Fig. 6 proves this.

7. CONCLUSIONS

1. The mineralogical reactions which take place in magnesite- and chromite-containing refractories due to variations in slag composition determine the operating life. In order to obtain the best results from a good refractory, careful control should be exercised over the slag composition and conversely, in order to obtain the best results from the usage of good slags, careful control should be exercised over the composition of the refractory.
2. The formation of liquids inside a refractory is an operational hazard. In order to compensate for this, all attempts should be made to limit the inclusions of harmful constituents in the original refractory which may form liquids having low melting points.
3. The only answer conducive towards improvement in production life, is compensation in the composition of the refractory, relative to a slag which should be rich in lime. The slag should have a high lime content in order to obtain optimum dephosphorization and desulphurization. All those components which are either directly or indirectly unstable or metastable in the presence of liquid ultrabasic slags should therefore be excluded as primary constituents of the refractory.
4. In order to minimize the effect of the autochthonous silicates i.e. in order to prevent the formation of CMS (and to a lesser degree C_3MS_2) the bonding silicates should have a high C/S ratio, preferably > 2 . In practice, however, the C/S ratio should rather be equal to 2, as Al_2O_3 and Fe_2O_3 are invariably present in small quantities.
5. Cr_2O_3 can be expected to improve the refractory properties of magnesite refractories when added as a reagent grade oxide, but not when added as chromite.

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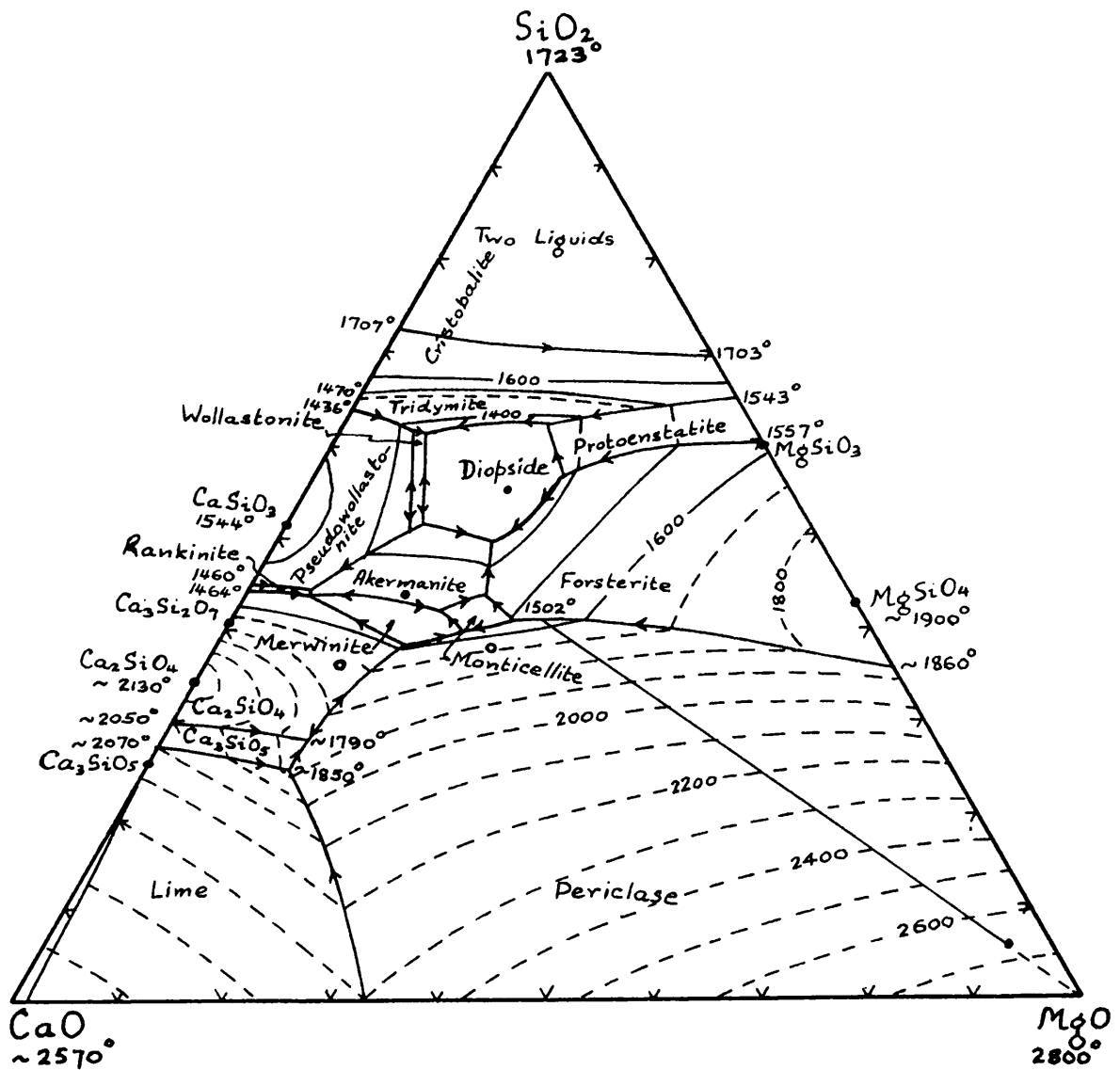


Fig. 1. The system CaO-MgO-SiO_2 ; after E.F. Osborn and Arnulf Muan (1960, Plate 2).

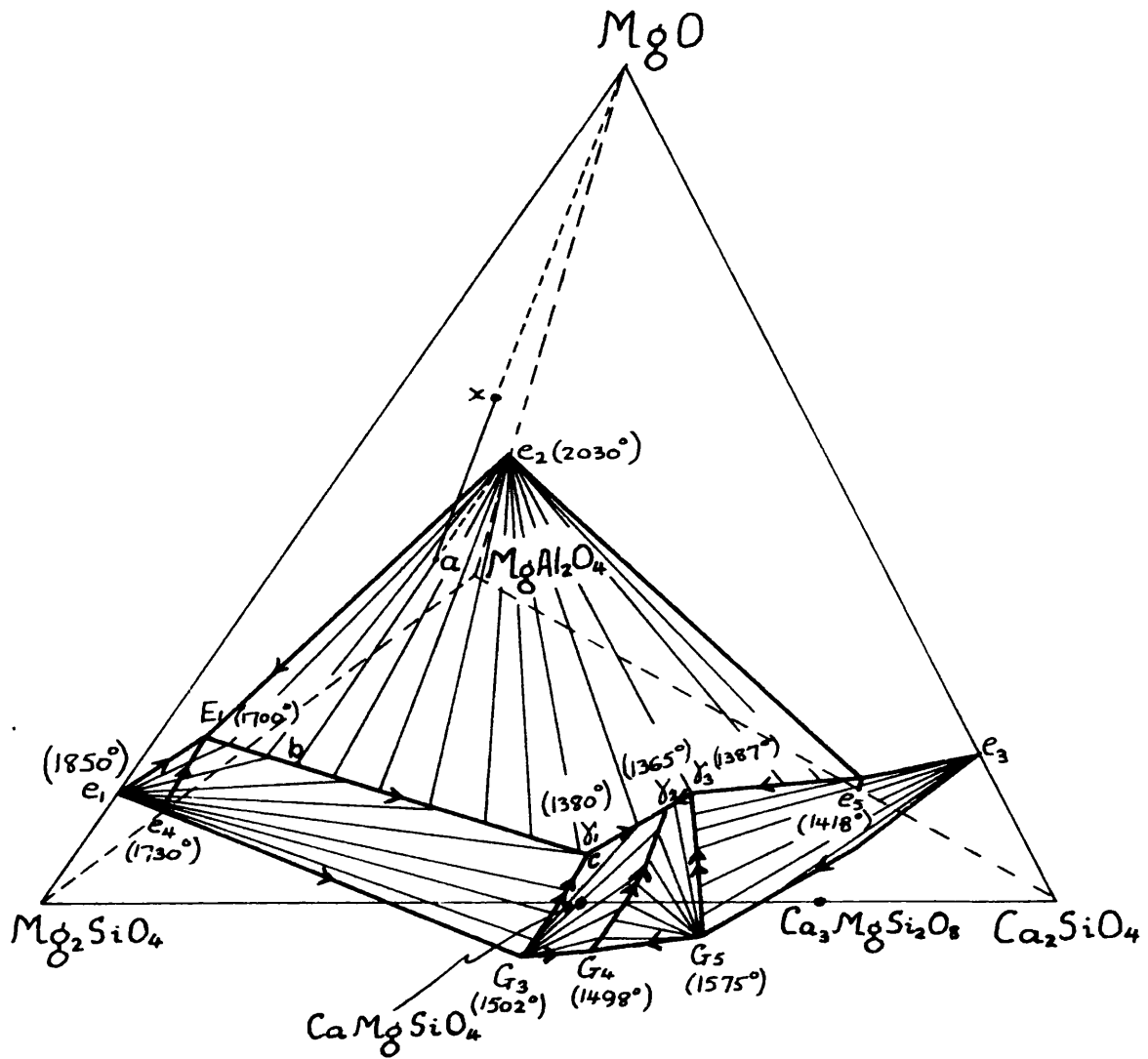


Fig. 2. The phase diagram $\text{MgO-MgAl}_2\text{O}_4\text{-Mg}_2\text{SiO}_4\text{-Ca}_2\text{SiO}_4$; after S. Solacolu (1960, p. 268).

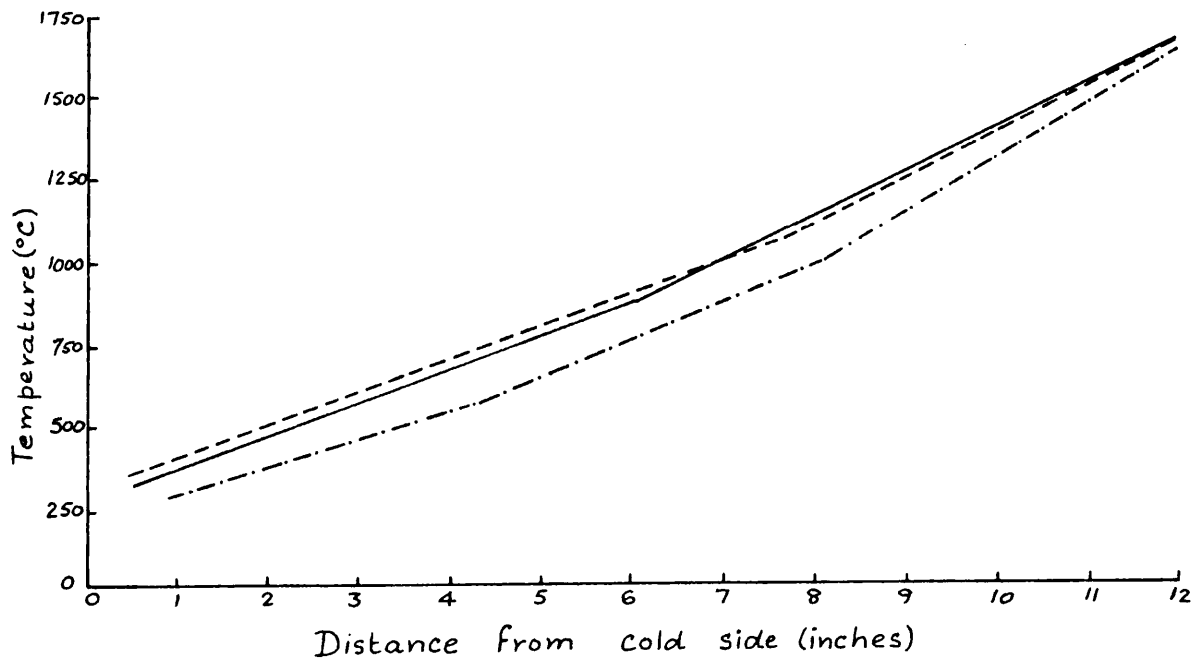


Fig. 3. Approximate thermal gradients in various types of brick after 55 hours in a furnace test (after J. Neely, 1967, p. 581).

- 60 per cent MgO, chemically bonded magnesite-chrome.
- 40 per cent MgO, high-fired chrome-magnesite.
- 60 per cent MgO, high-fired magnesite-chrome.

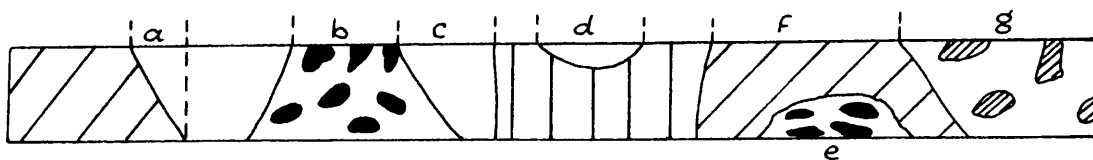


Fig. 5. Edgewise view of a hypothetical thin section of a used refractory (after C. Schouten, 1951, p. 131). Portions a, b, c etc. indicate to which extent inclusions, finely intergrown textures, pits and contamination by opaque components hamper examination by the method of transmitted light microscopy. (For explanation see text.)

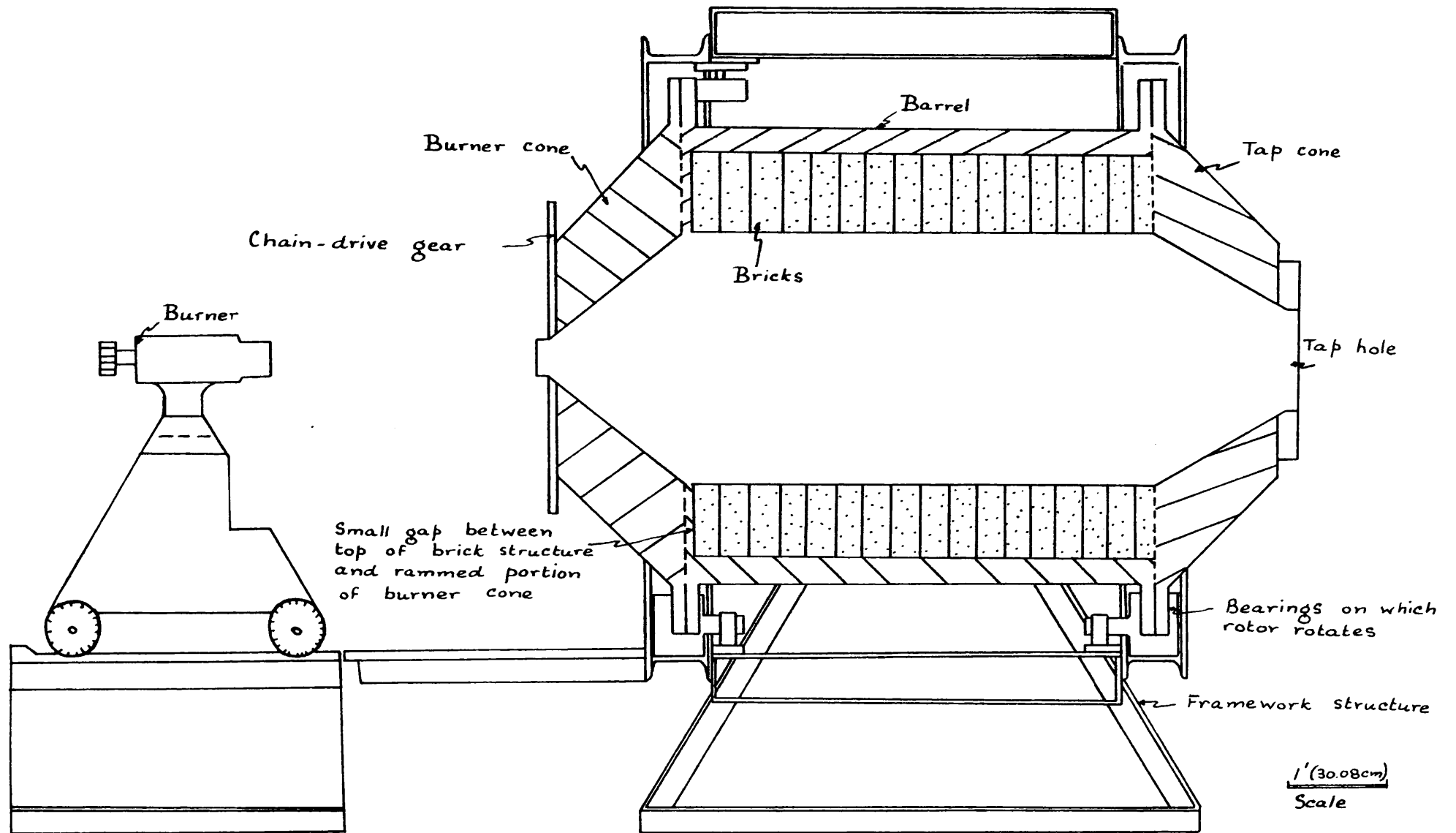
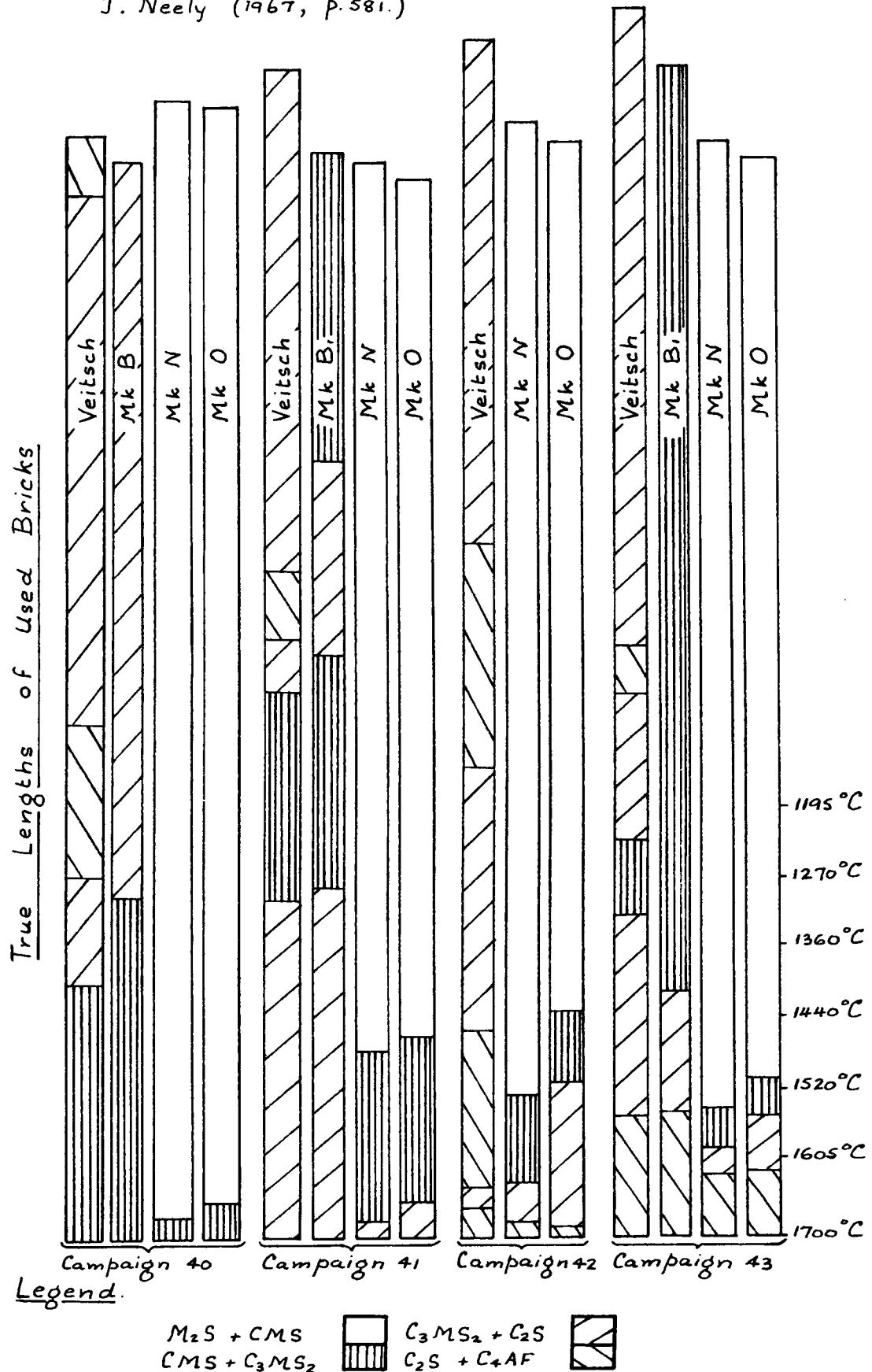


Fig. 4. Profile through experimental rotor

Fig. 6. Distribution of silicates in the refractories used during the experimental work, as calculated from the chemical analyses. The temperature gradient is after J. Neely (1967, p.581.)



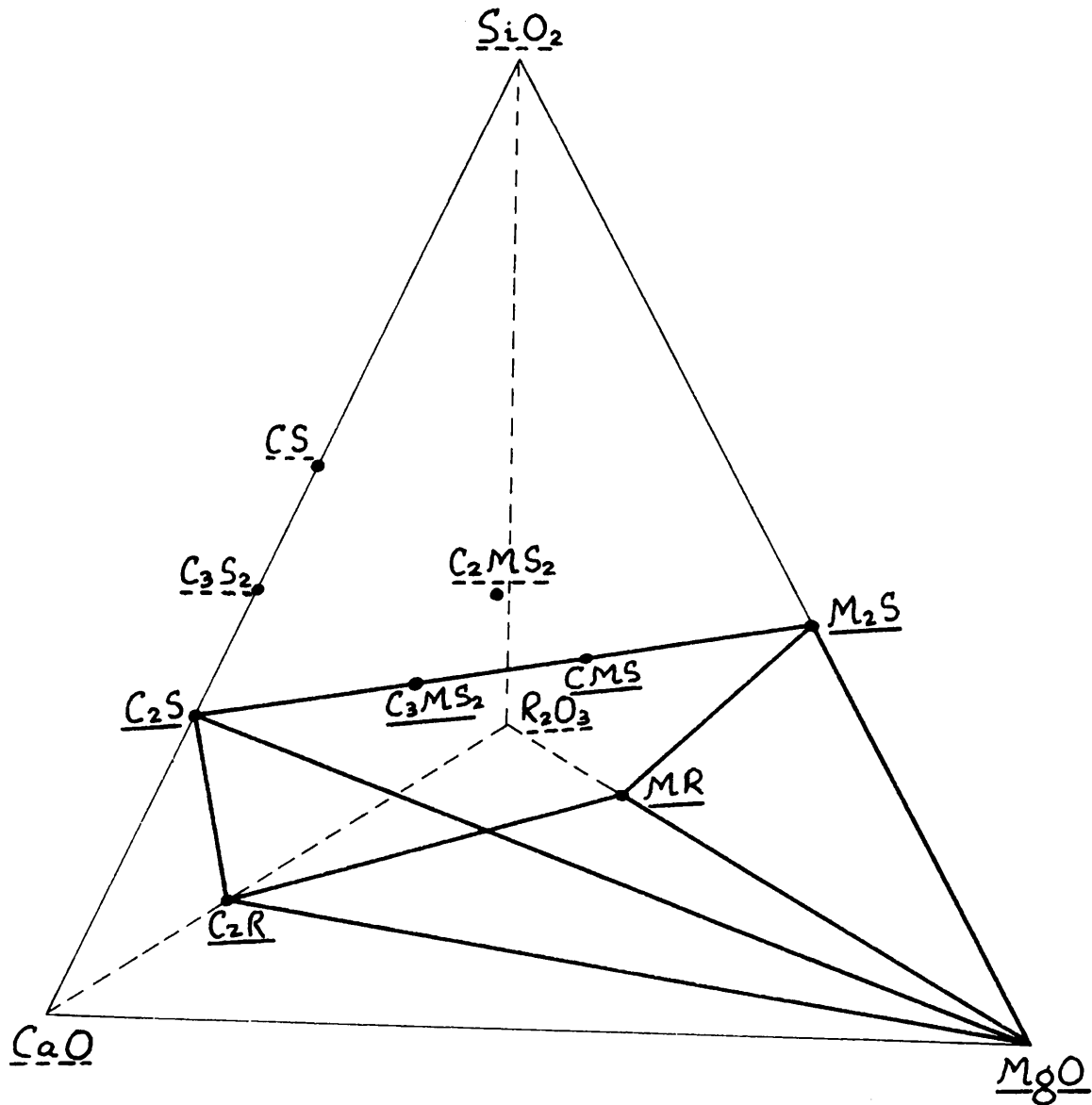


Fig. 7. Bounded by the heavy line is the compositional volume to which the phases occurring in basic refractories are confined. The minerals underlined with broken lines occur under nonequilibrium conditions.

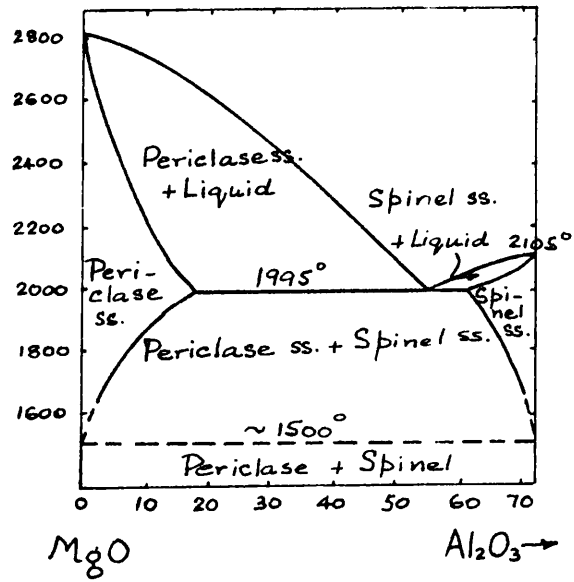


Fig. 8. Part of the system MgO-Al₂O₃ (Alper et al, 1962).

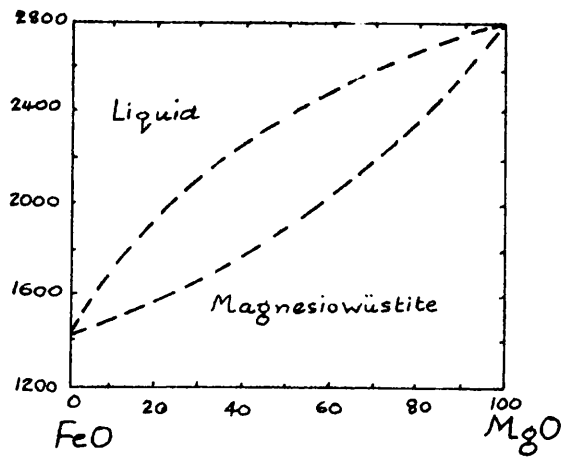


Fig. 9. The system FeO-MgO (Bowen and Schairer, 1935).

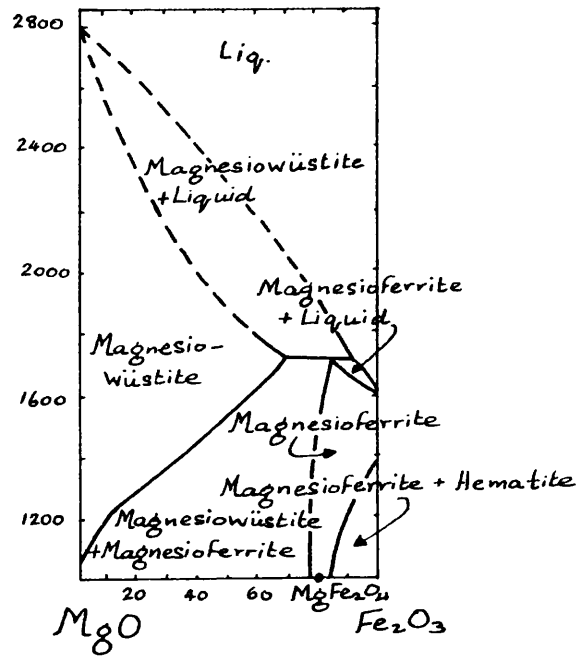


Fig. 10. The system $\text{MgO}-\text{Fe}_2\text{O}_3$ (Philips, Somiya and Muan, 1961).

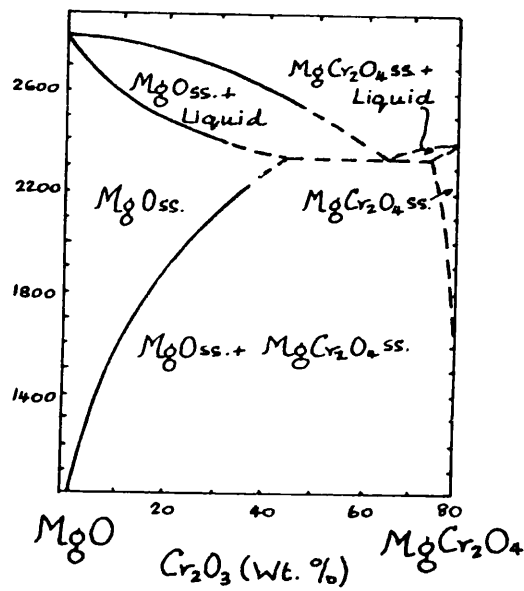


Fig. 11. Part of the system $\text{MgO}-\text{Cr}_2\text{O}_3$ (Alper et al, 1964).

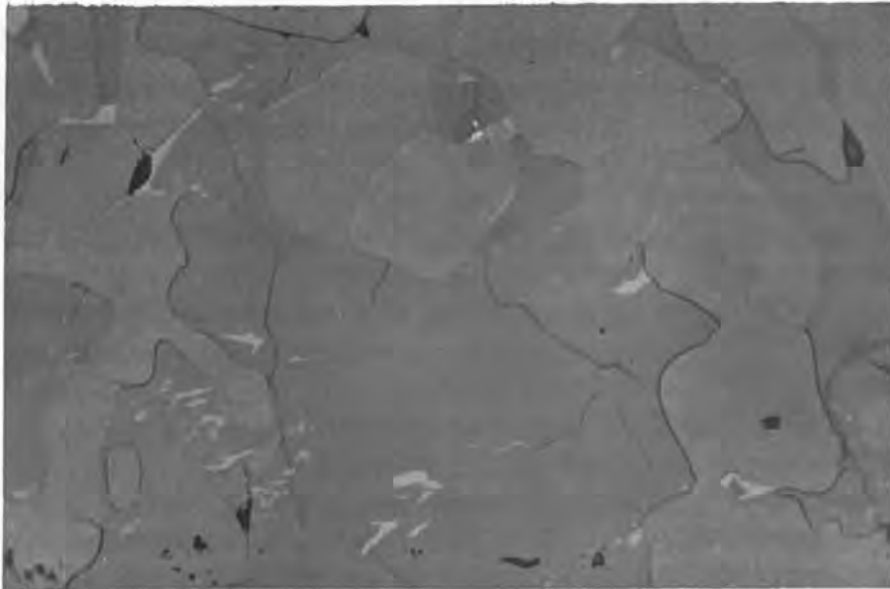


Plate 1. Cracks in β C_2S due to the expansion caused by transformation^F of β C_2S into γ C_2S . The silicates are present 2 cm from the hot face.
Sample: D140 (C42 B₁). (x288)



Plate 2. Merwinite (scratched); larnite (black-etched out) and a variety of spinels. The unetched portion (right) was not exposed to the etchant (5 per cent NH_4Cl) by covering it with petroleum jelly, and shows the nature of the silicates before being etched.
Sample: D132 (C4 B₁-1). (x288)

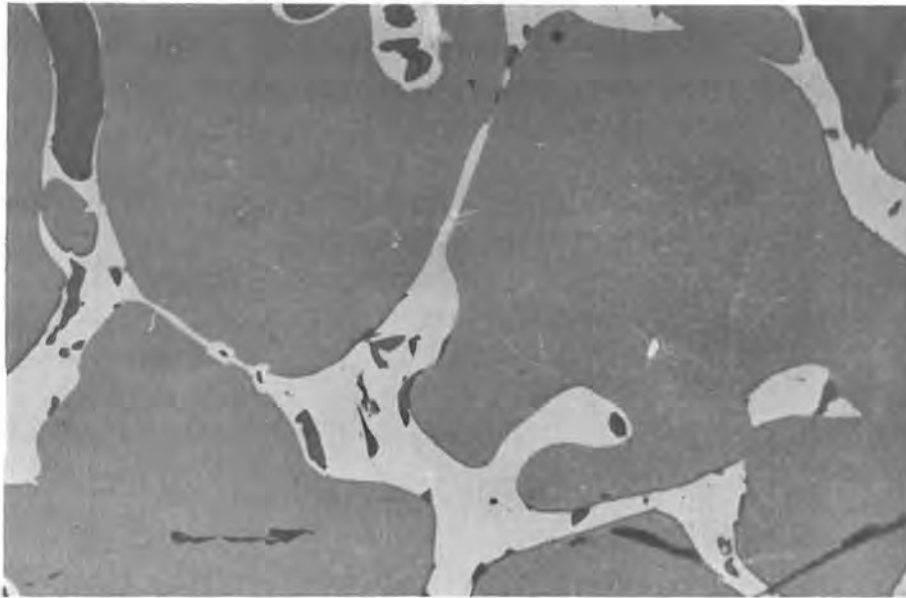


Plate 3. The "blotting-paper" effect of a matrix rich in lime, whereby sesquioxides are extracted from periclase (light-grey). The matrix consists of dicalcium ferrite (white) and larnite (dark-grey, etched).
Sample: D85 (C43 B₁). (x288)

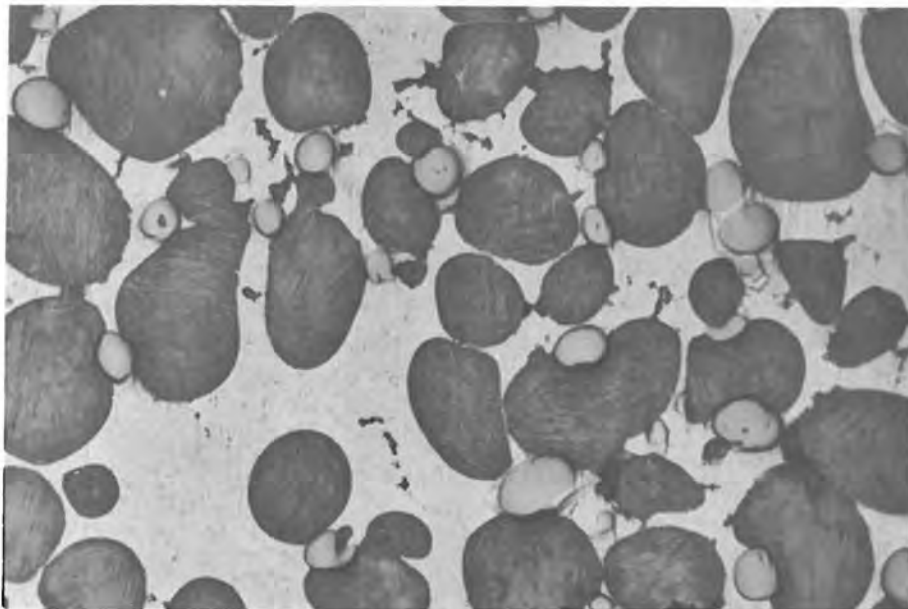


Plate 4. The absence of exsolution of spinel in periclase (light-grey, rounded) as a result of the presence of lime-rich minerals dicalcium ferrite (white matrix) and larnite (dark-grey, rounded).
Sample: Slag C42. (x288)

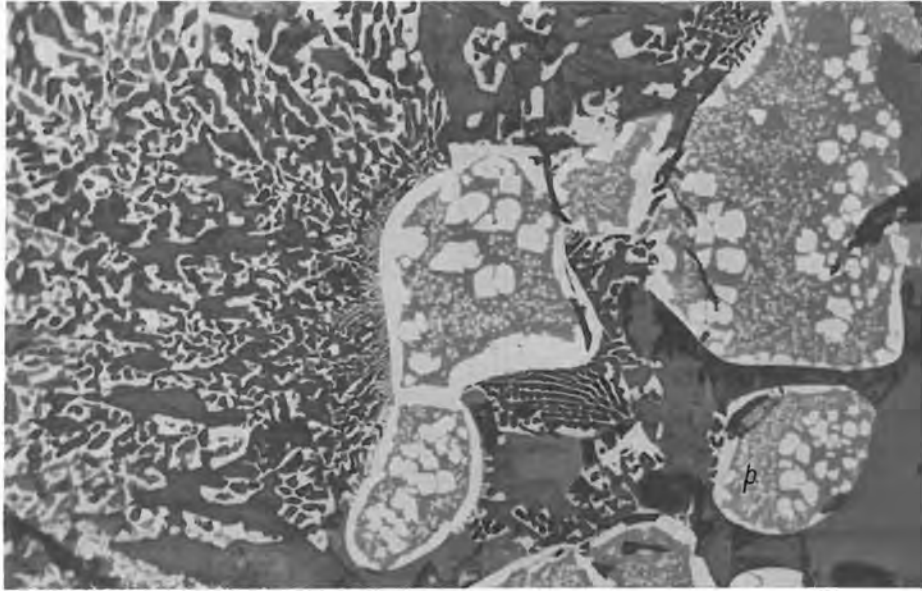


Plate 5. Exsolutions of spinel (white) in periclase (p). Spinel is also eutectically intergrown with larnite (black). The other silicates are merwinite (dark-grey, scratched) and monticellite (light-grey, unetched).
Sample: D29 (C40 B₁-1). (x288)

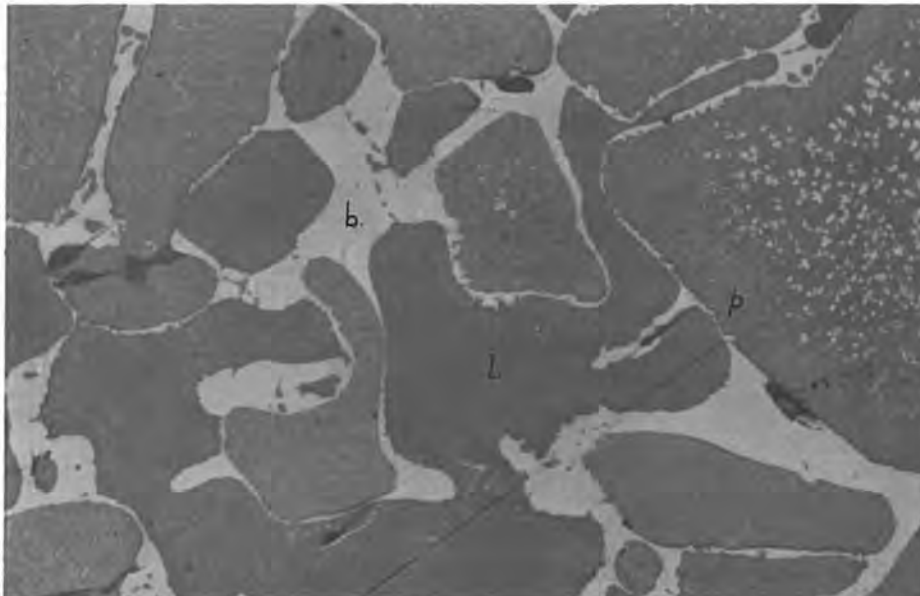


Plate 6. The association between brownmillerite (b), larnite (l), periclase (p) and spinel (white specks in periclase). Unetched.
Sample D100 (C43 O₁). (x288)

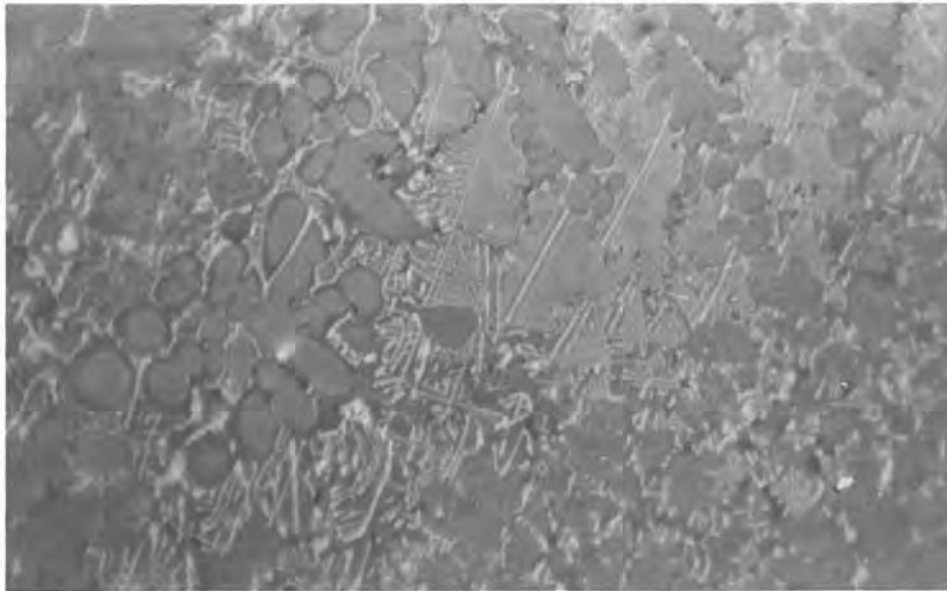


Plate 7. Primary crystallization of C_2F-C_4AF solid solution (grey, rounded), followed by eutectic crystallization of a mixture of spinel (white) and C_4AF .
Sample: Slag C43. (x688 oil)



Plate 8. Solution of periclase in an environment having a low C/S ratio. The silicates are merwinite (dark, etched out) and monticellite (grey, scratched). The formation of chains of periclase can be seen clearly.
Sample: C40 O₁. (x288)

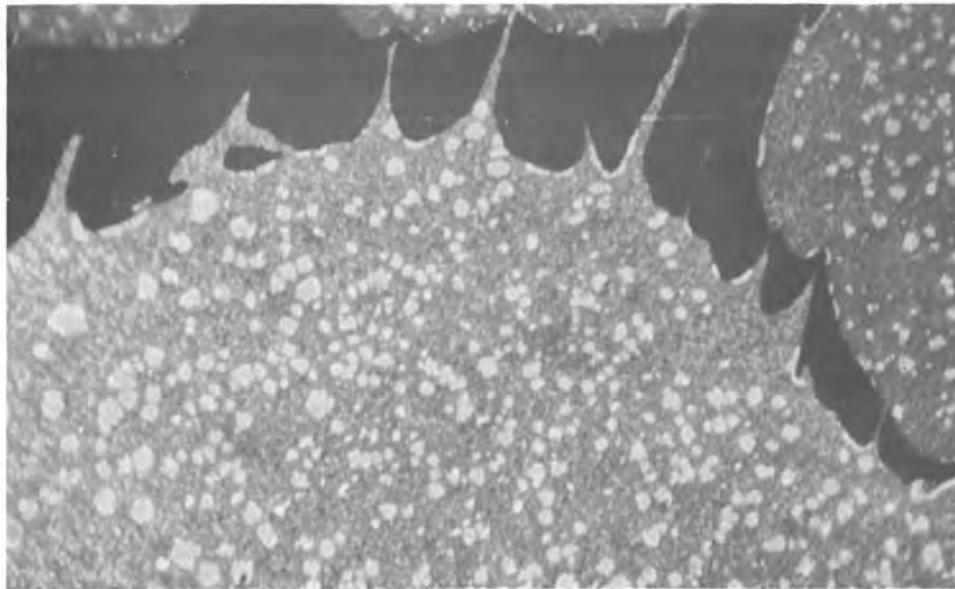


Plate 9. Precipitation of tongues of periclase on to primary periclase grains. It is clear that exsolution of secondary spinel (white) took place after precipitation of periclase. Sample: C62 (C41 V₁). (x688 oil)

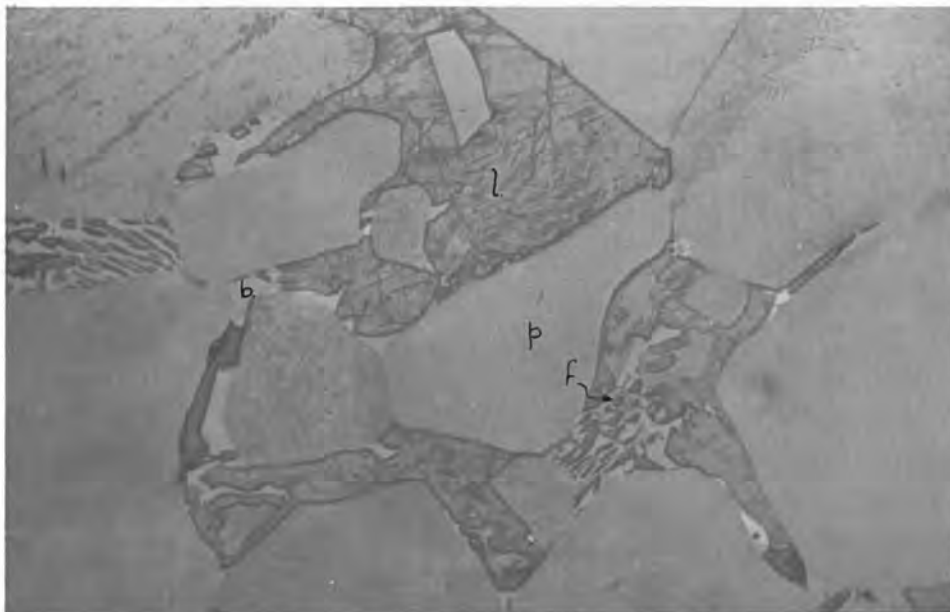


Plate 10. The reappearance of Mg-rich minerals in a refractory having mainly larnite and subordinate merwinite as autochthonous silicates. The minerals present are brownmillerite (b), periclase (p), forsterite (f), larnite (l) and monticellite (m). Sample: D126 (C42 V₂). (x288)

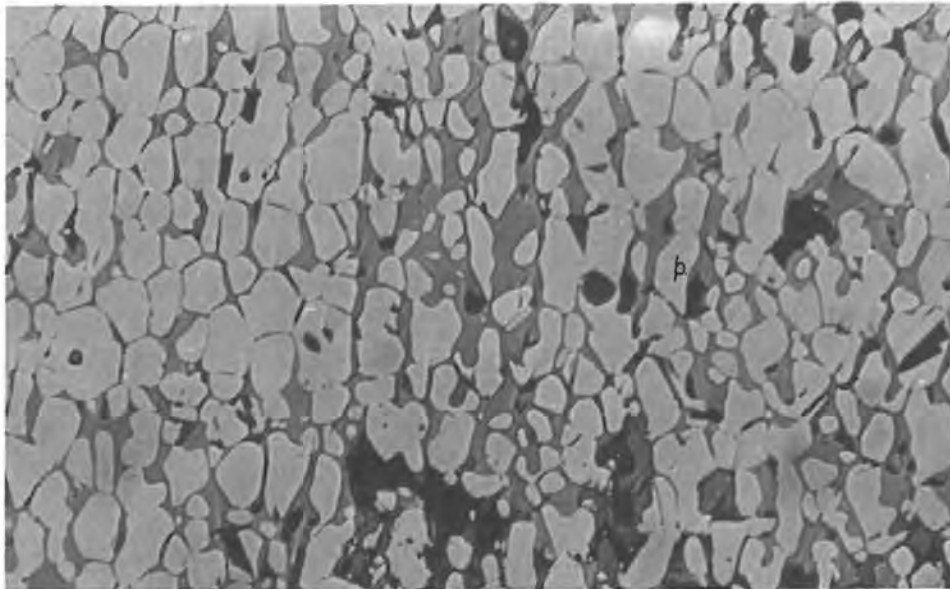


Plate 11. Elongation of periclase grains (p) perpendicular to the hot face. The dark-grey phase is silicates, and the black areas are voids.
Sample: D9 (C40 N₉). (x94)

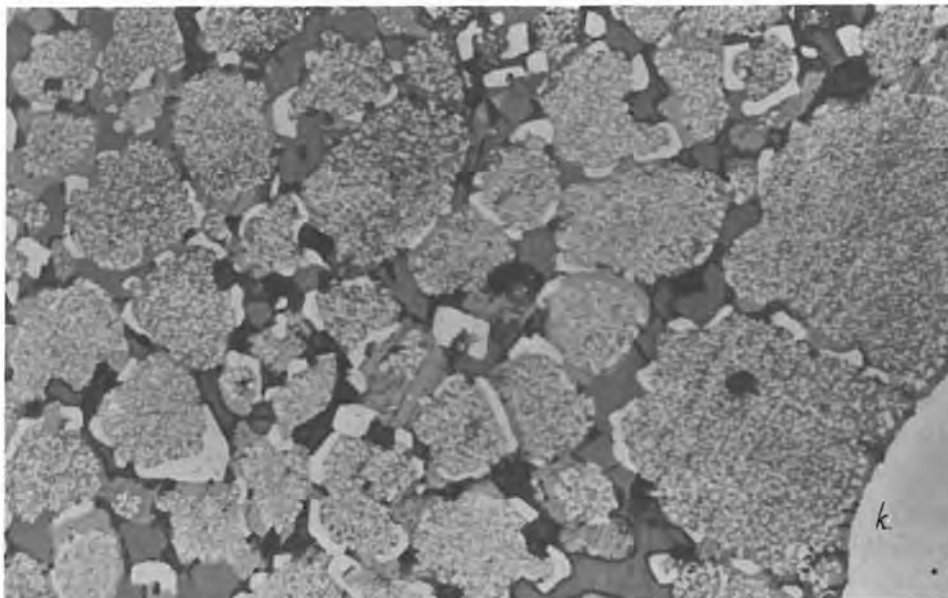


Plate 12. The relative distribution of spinel (white) between the silicate matrix (grey) and the periclase fraction (lighter grey, speckled with secondary spinel). The spinels originate through diffusion of sesquioxides out of chromite (k). The silicates are M₂S (unetched) and CMS (etched).
Sample: C40 O₃. (x288)



Plate 13. Exsolution of spinel (dark, lattice-like) in periclase along the (100)-direction of the latter mineral. The dark colour is due to the large concentration of spinel.
Sample: C40 V₁. (Transmitted light, oil x1290)

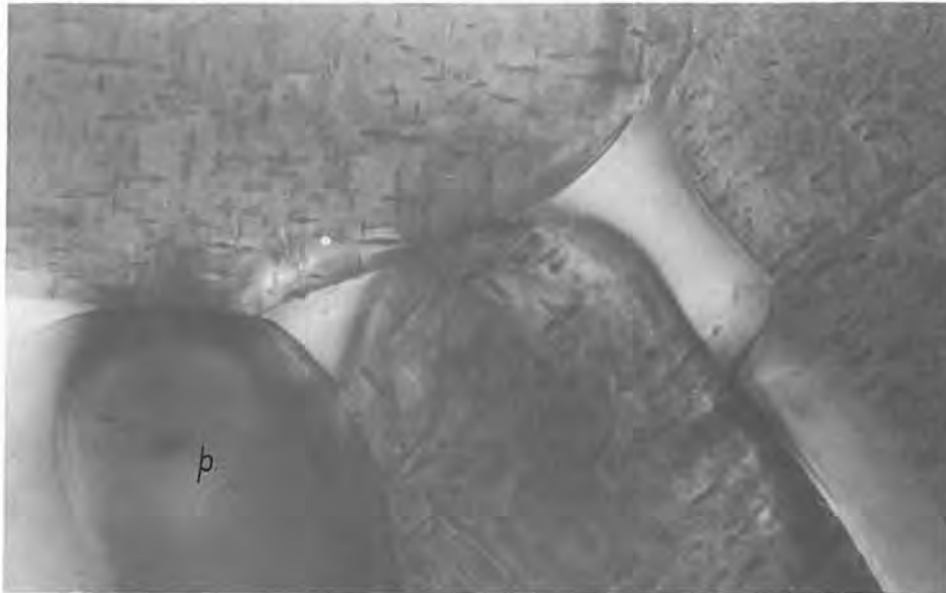


Plate 14. The absence of exsolved spinel (laths) from periclase (p) illustrate the control exerted by the diffusion front of the sesquioxides on the formation of these spinels mentioned above. In the remaining periclase grains the exsolutions of spinel takes place // (100) in periclase.
Sample: C40 B₁. (Transmitted light, oil x1290)



Plate 15. Exsolution of dendritic spinel (white) along the (100)-planes of periclase and also rims of spinel around the borders of the periclase grains.
Sample: C40 V₁. (x288)

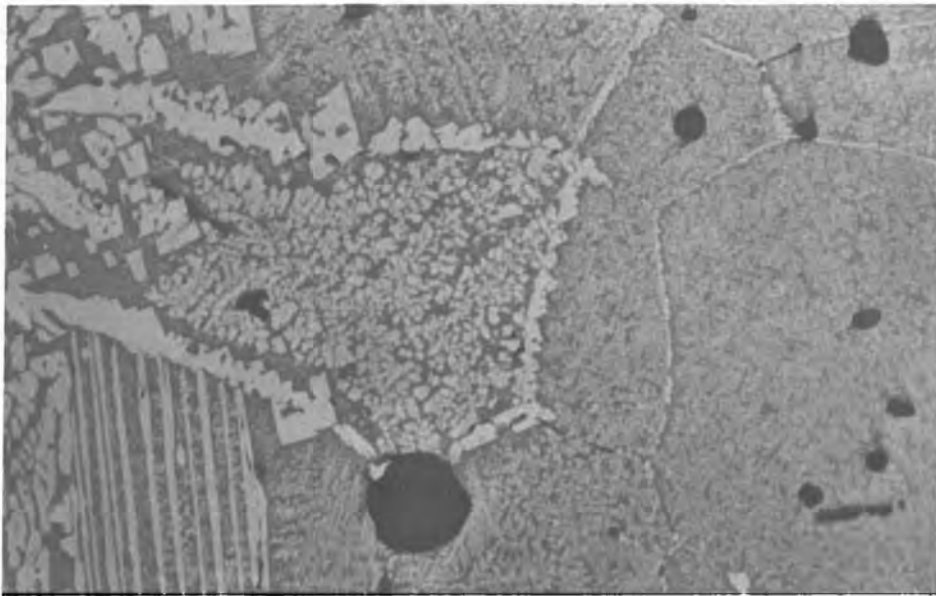


Plate 16. "Transformation" of periclase (grey) into spinel (white).
Sample: C40 B₁-1. (x288)

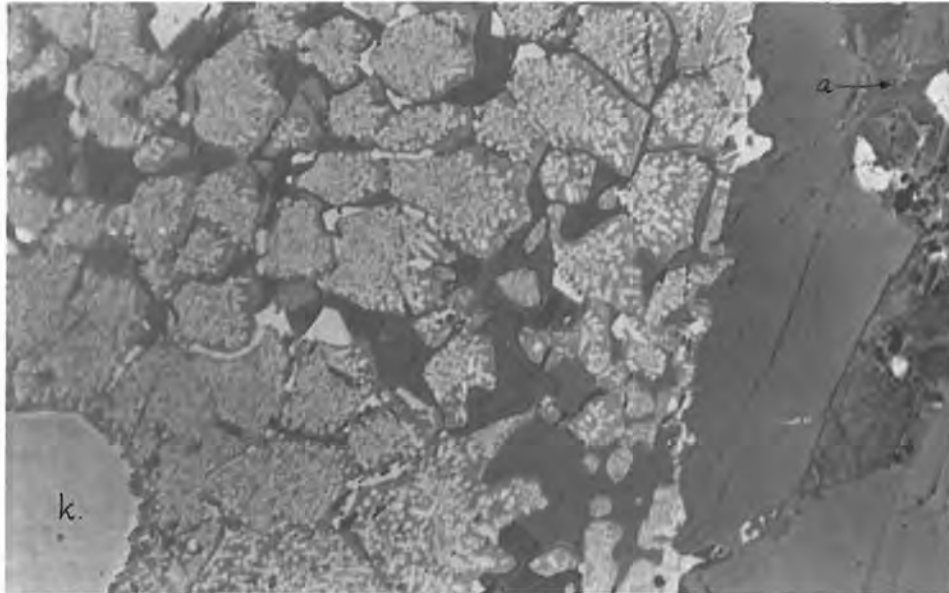


Plate 17. A higher reflecting rim of Fe-rich spinel around the border of chromite (k) in an area immediately adjacent to the contact zone of the refractory and the slag. The silicates are merwinite (etched), Åkermanite (a) and monticellite (unetched).

Sample: D9 (C40 N₁).

(x94)

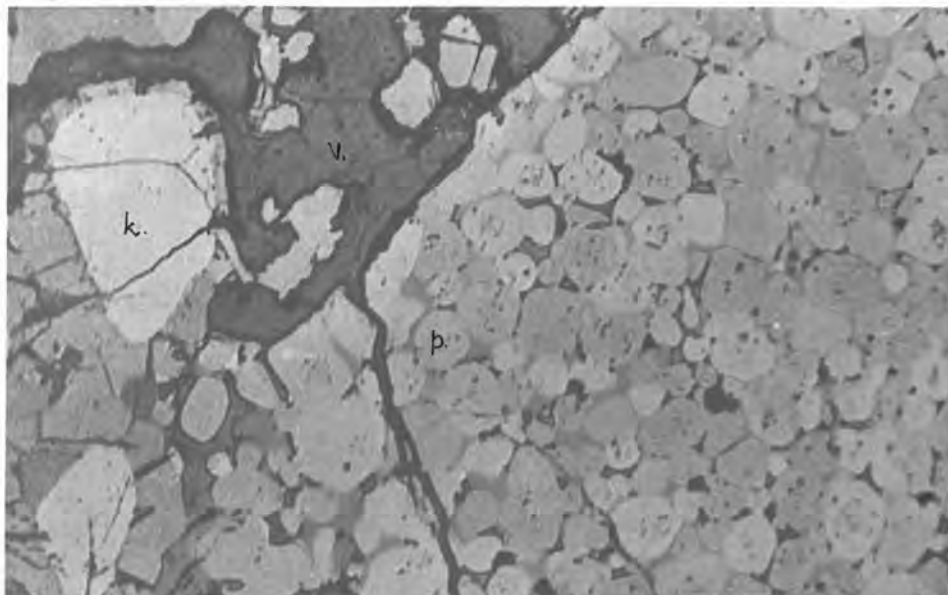


Plate 18. The mode of occurrence of chromite (k) in an unused refractory, polished on an Al₂O₃-impregnated nylon cloth so as to show up the pores (v), forsterite (dark-grey, unetched) and monticellite (darker grey, etched) and periclase (p).

Sample: D18 (C40 N₁₀).

(x94)

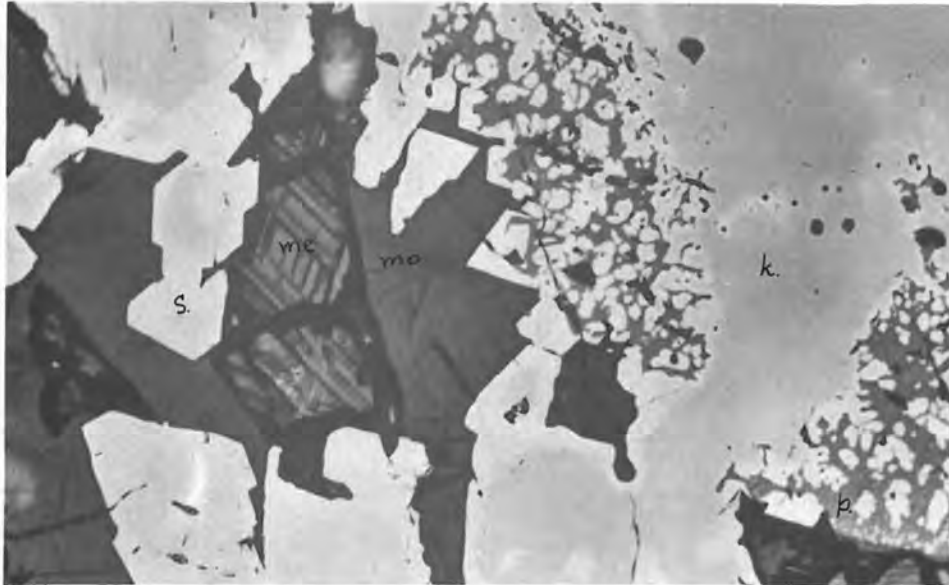


Plate 19. The tendency of secondary spinels (s) to crystallize on to existing phases periclase (p) and chromite (k). The secondary spinel exhibits a variation in composition. The silicates are merwinite (me) and monticellite (mo).
Sample: C40 O₁. (x288)

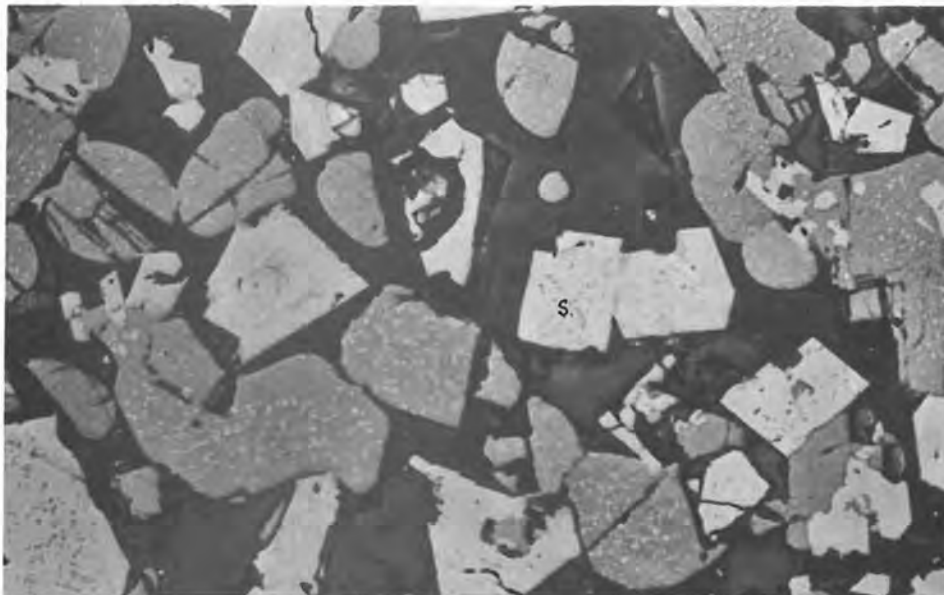


Plate 20. Secondary spinel (s) that has crystallized in the silicate matrix. The silicates are monticellite (stained) and merwinite (etched out).
Sample: C40 O₂. (x288)

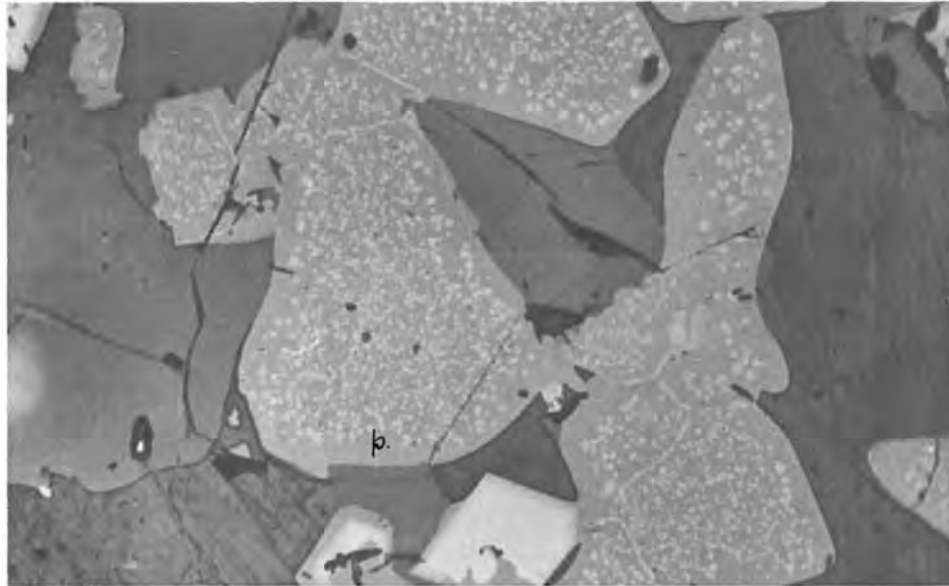


Plate 21. Spinel (white) containing less Fe^{3+} in its rim than in the core. Periclase (p), monticellite (unetched) and merwinite (etched) make up the rest of the plate.
Sample: D37. (x288)

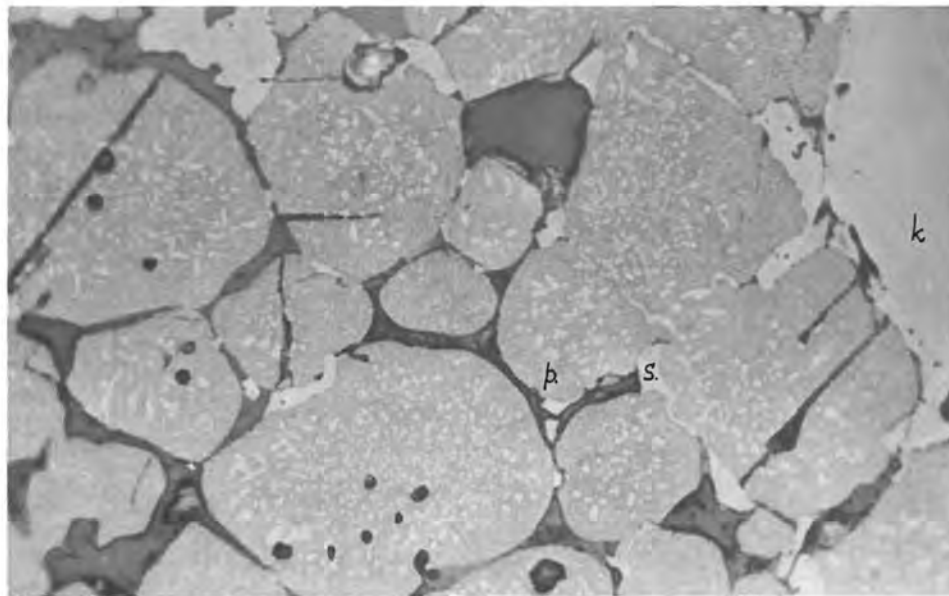


Plate 22a. Exsolved bodies of spinel (white) in periclase (p), as well as other secondary spinels (s). Direct bonding between periclase and periclase, either directly or via secondary spinel is prominent. Chromite (k) is also bonded directly on to periclase. The silicates (M_2S and CMS) cannot be differentiated between on this plate.
Sample: 1A. (x288)

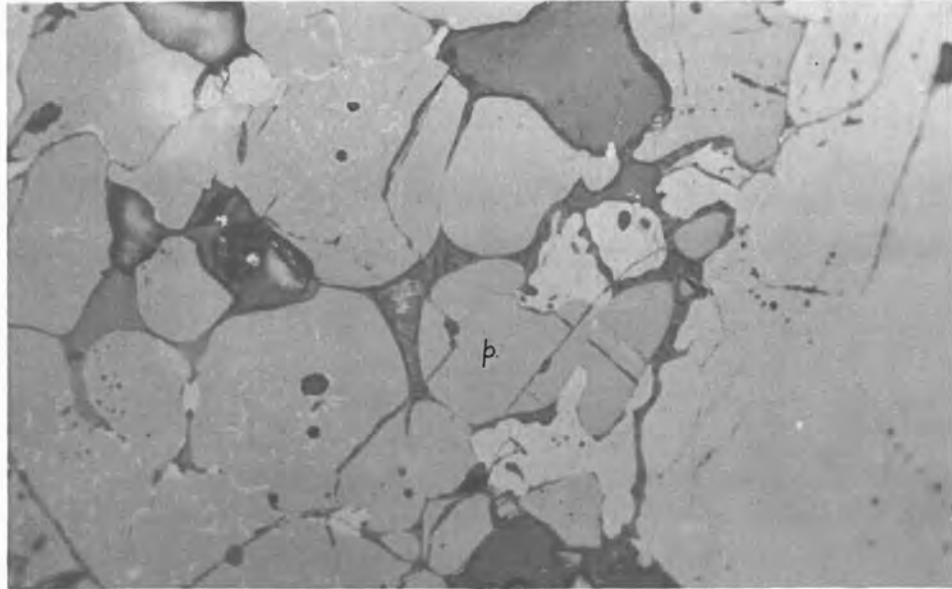


Plate 22b. The reflectivity of periclase (p) is high due to sesquioxides still in solid solution. Direct bonding is not as well developed as in 1A.

Sample: 1B.

(x288)

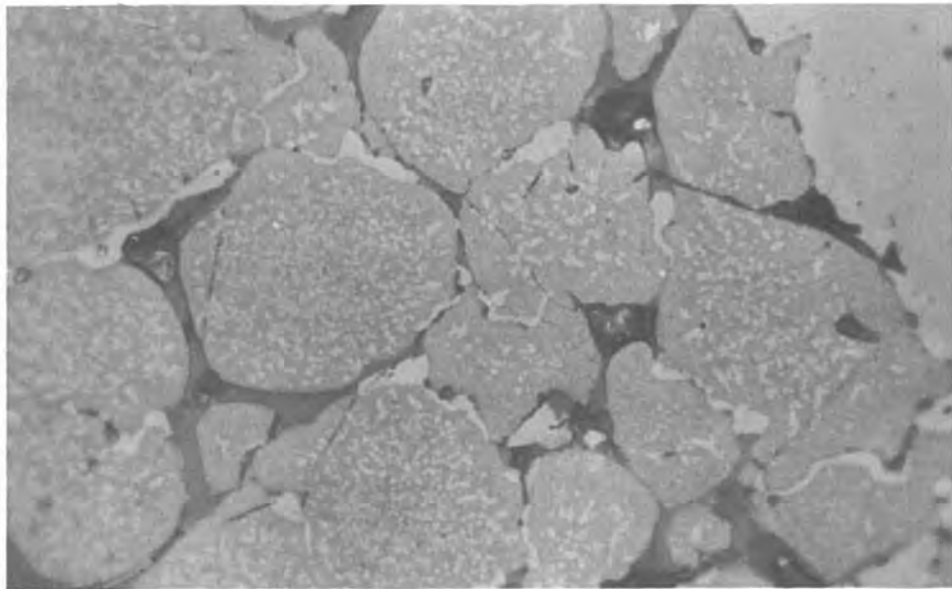


Plate 23a. Direct bonding and exsolution bodies are prominent. The minerals are identical to those described in plate 22a.

Sample: 2A.

(x288)

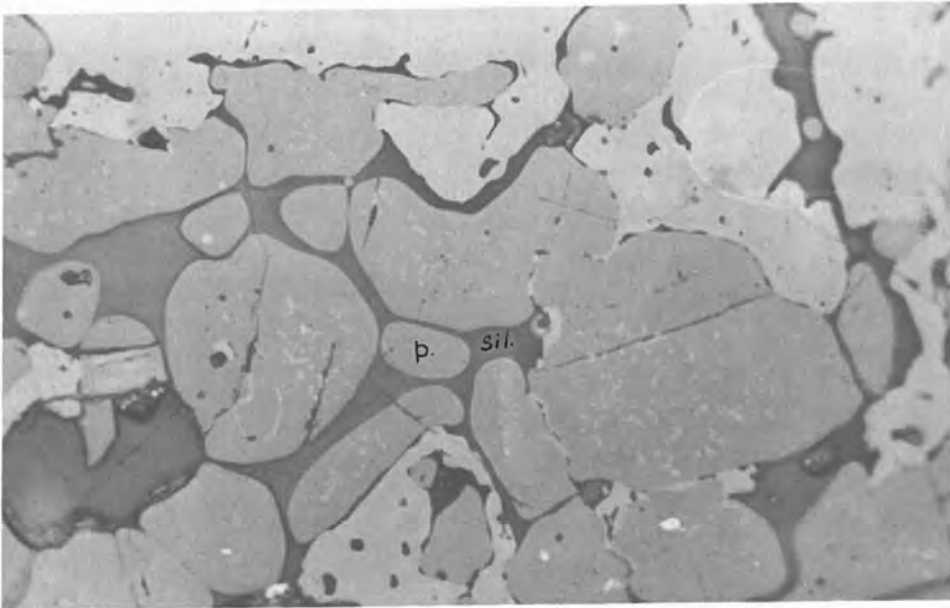


Plate 23b. Direct bonding not as prominent as in 31A. Periclase grains (p) form small islands in a sea of silicates (sil).
Sample: 2B. (x288)

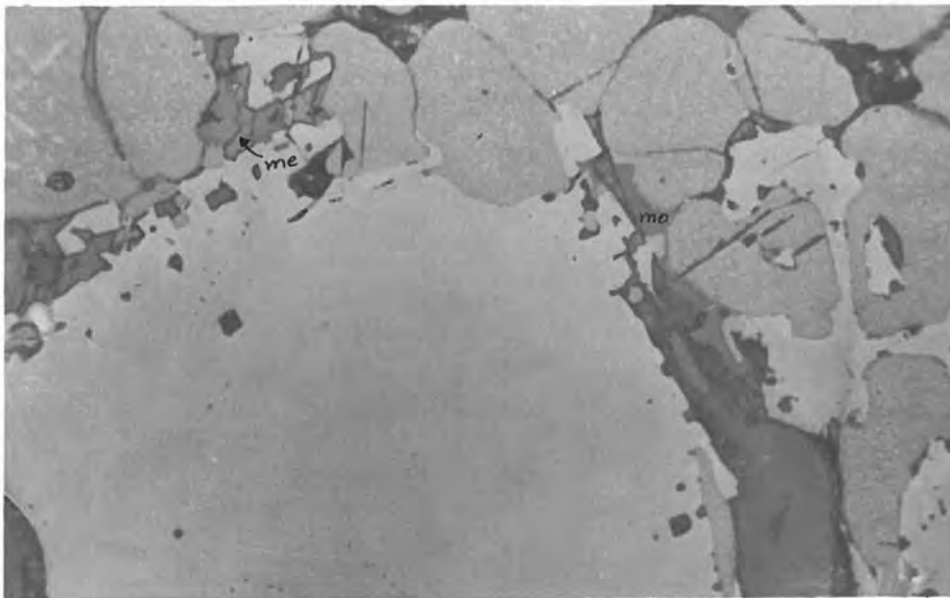


Plate 24a. Direct bonding is well developed. Exsolved and other secondary spinels are prominent. The silicates are C_3MS_2 (me) and CMS (mo).
Sample: 3A. (x288)

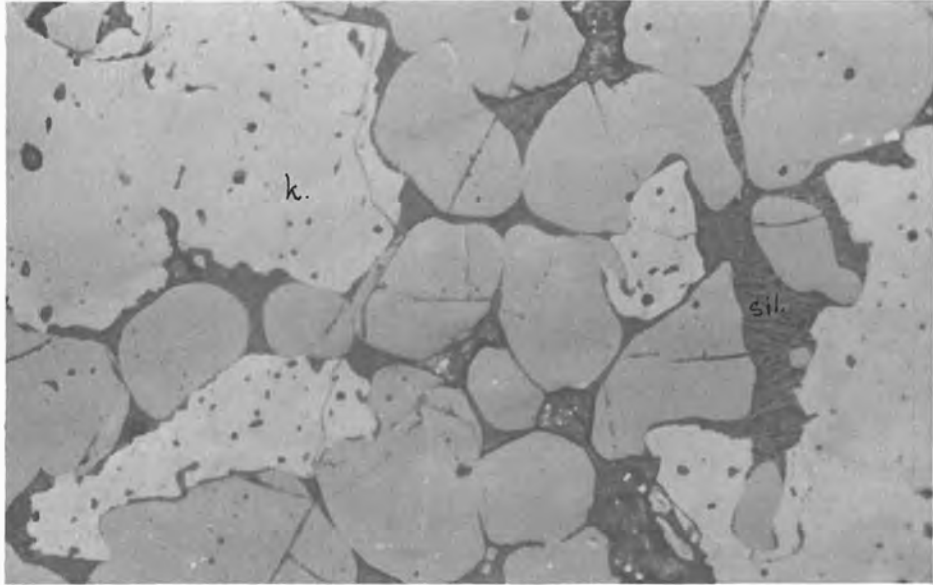


Plate 24b. Chromite (k) is more porous than in previous samples. The slight increase in the amount of liquid phase (sil) above 32a is noticeable.
Sample: 3B. (x288)

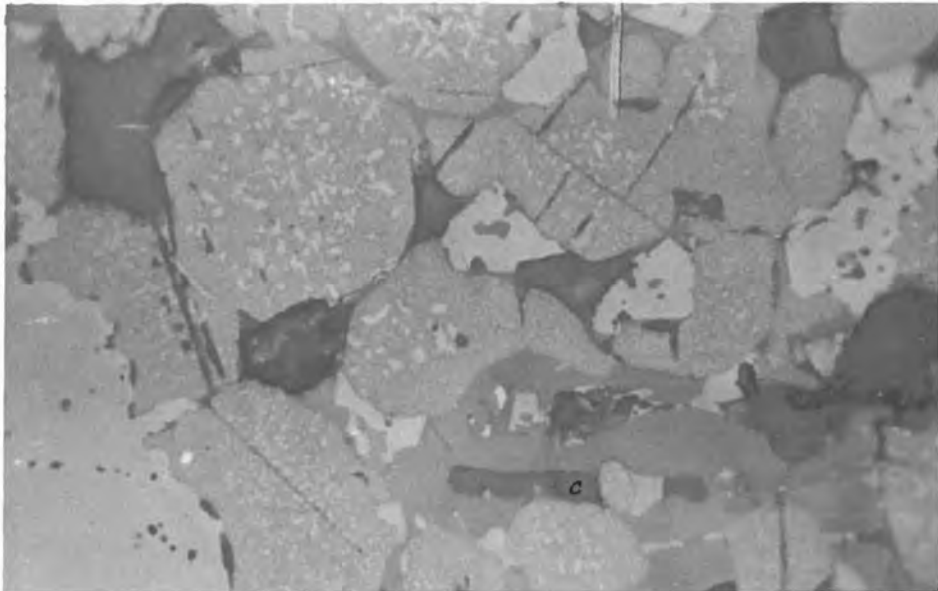


Plate 25a. Texturally very similar to 32a. The minerals are also identical to those found in 32a, except that C_2S (c) replaces CMS.
Sample: 4A. (x288)

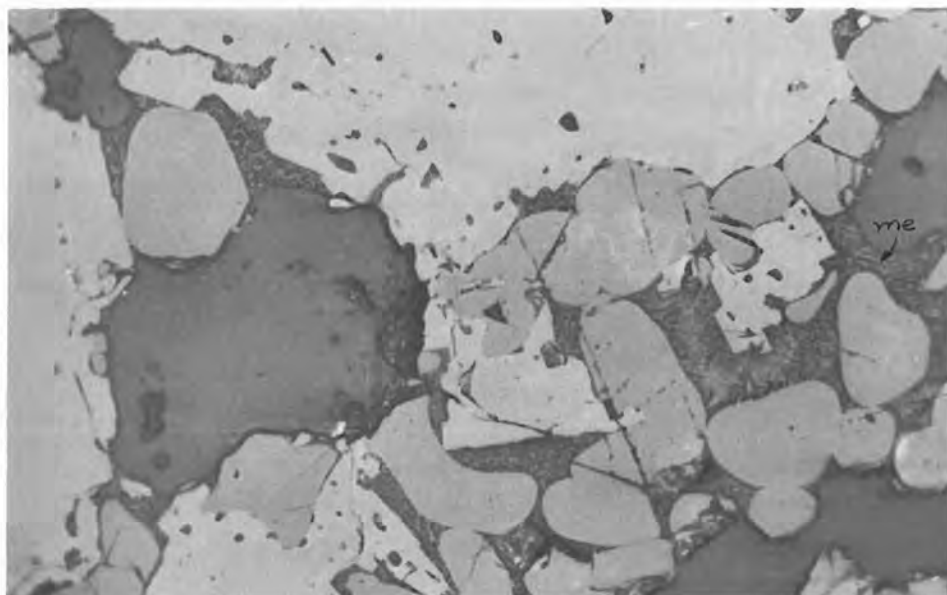


Plate 25b. Direct bonding is practically non-existent. Small laths of C_3MS_2 (me) are surrounded by a glass phase, corresponding in composition to C_2S .
Sample: 4B. (x288)

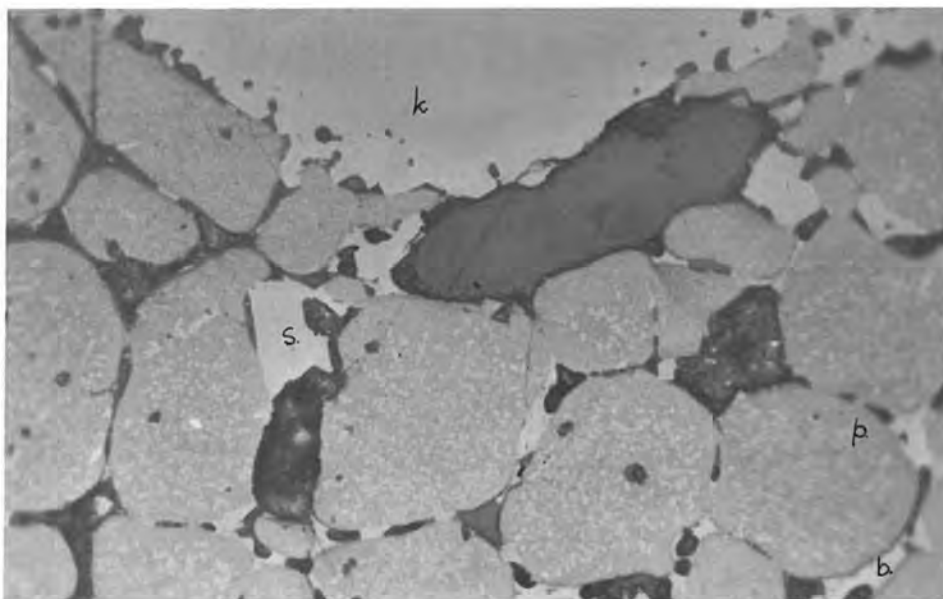


Plate 26a. Direct bonding and relatively large dihedral angles are prominent. The minerals are chromite (k), secondary spinel (s), brownmillerite (b), periclase (p) and larnite (etched out).
Sample: 5A. (x288)

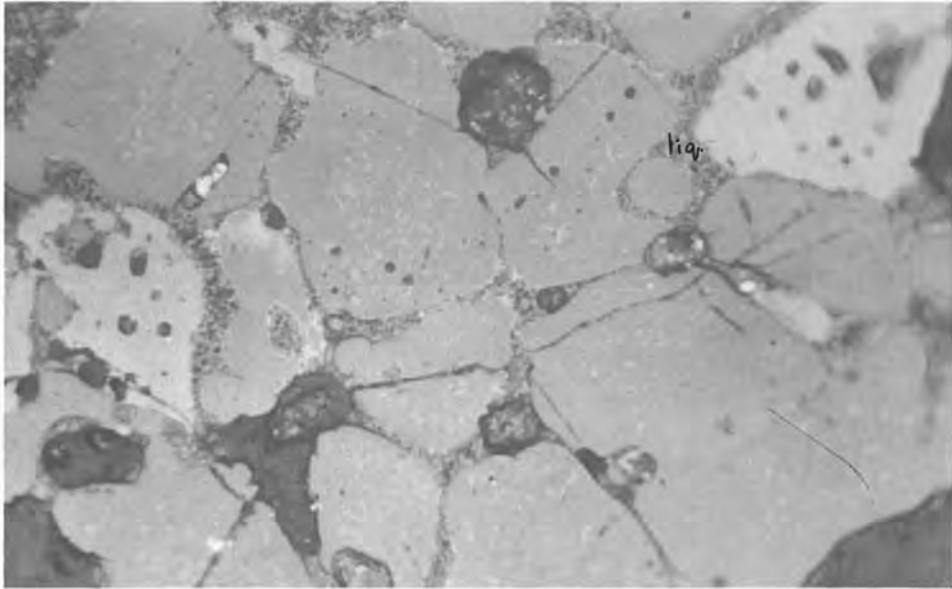


Plate 26b. The vast increase in the amount of liquid phase (liq) leads to the destruction of the direct bond. The liquid phase consists in its solid state of the minerals brownmillerite (white specks) surrounded by a lime-rich glass. Sample: 5B. (x288)

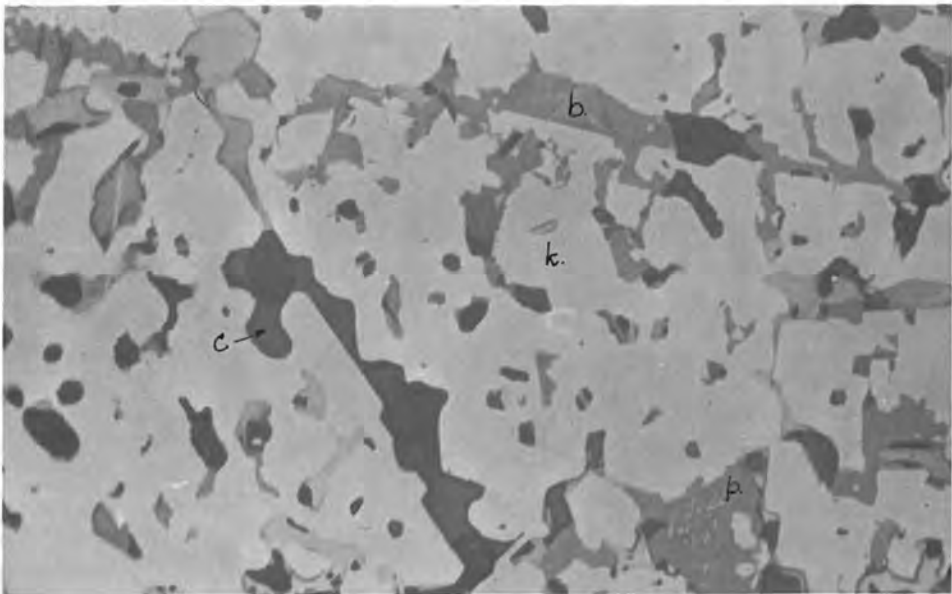


Plate 28. The formation of C_4AF (b) in chromite grains (k). The surface of chromite is porous and filled with larnite (c). Periclase (p) also occurs in the chromite grain. Sample: D101 ($C_43 O_2$). (x288)

Plate 27. The influence of the basicity of the slag on chromite-containing refractories.



- (a) Refractory (C40 O₁), subjected to a slag having a C/S ratio of 1.18. Chromite (k) remains unaltered and periclase (p) shows signs of resorption towards the hot side. The silicates [C₃MS₂, CMS and M₂S (sil)] cannot be distinguished from one another. (x10)



- (b) Refractory (C41 O₁), subjected to a slag having a C/S ratio of 1.91. Chromite (k) shows signs of attack, and periclase (p) remains unaltered. The silicates are C₃MS₂ and CMS.



- (c) Refractory (C42 O₁), subjected to a slag having a C/S ratio of 2.50. Towards the hot face, chromite (k) disappears, and secondary spinel is extracted from periclase (p). The silicates are C₂S and C₃MS₂. (x10)



- (d) Refractory (C40 O₁), subjected to a slag having a C/S ratio of 2.91. Chromite (k) disappears towards hot face (reappears at k). Periclase is free from exsolved spinel. C₄AF (b) and C₂S (c) make up the remainder of the sample. (x10)

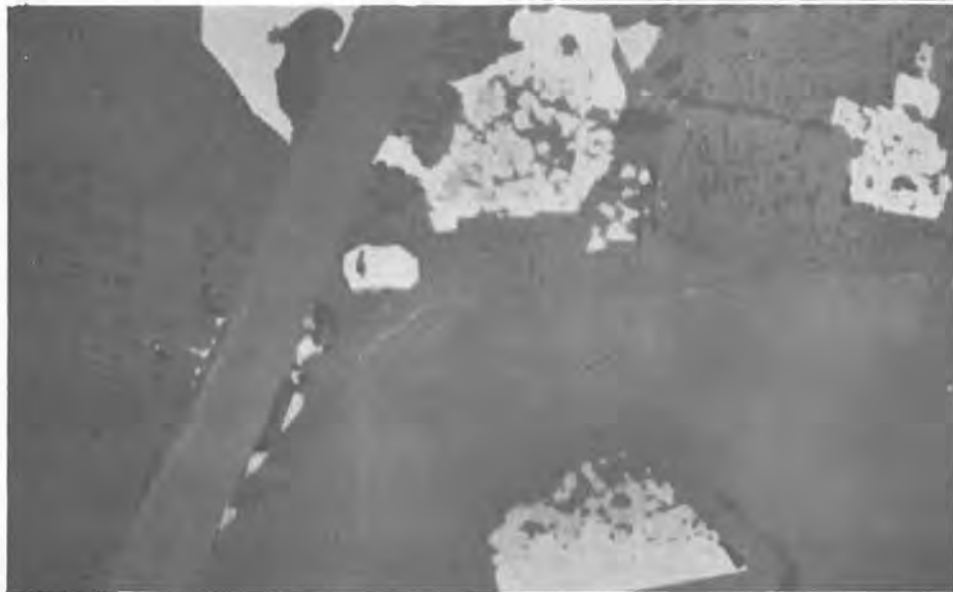


Plate 29. The mode of occurrence of akermanite (mineral having orientated inclusions of larnite - black) in association with monticellite (unetched) and merwinite (lath). The mineral having a high reflectivity is spinel which shows an enrichment in Fe_2O_3 towards its borders.
Sample: C40 O₁ (hot face). (x288)

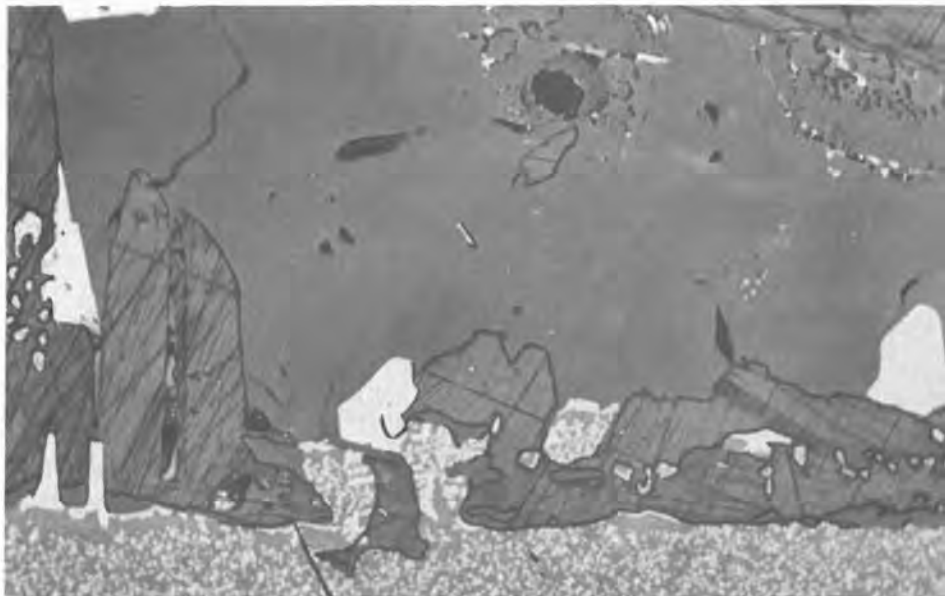


Plate 30. The fast rate of resorption of periclase results in straight border-lines between the slag (above) and the refractory. The mineral associations in the slag are the same as in Plate 29.
Sample: D19 (C40 V₁). (x288)

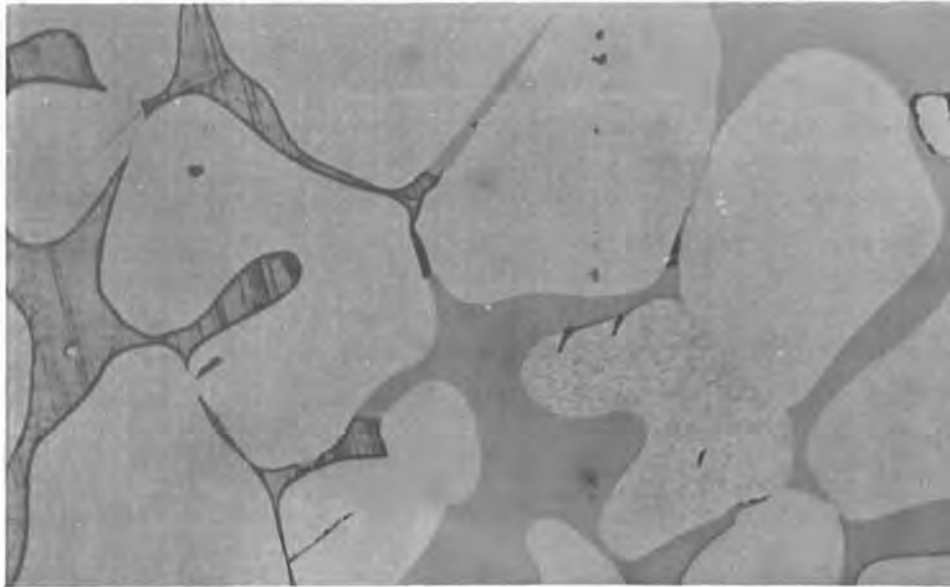


Plate 31. Monticellite (dark-grey, unetched) passing into merwinite (twinning bands etched out) towards the cold side. The rounded grains are periclase.
Sample: C40 V₁. (x288)

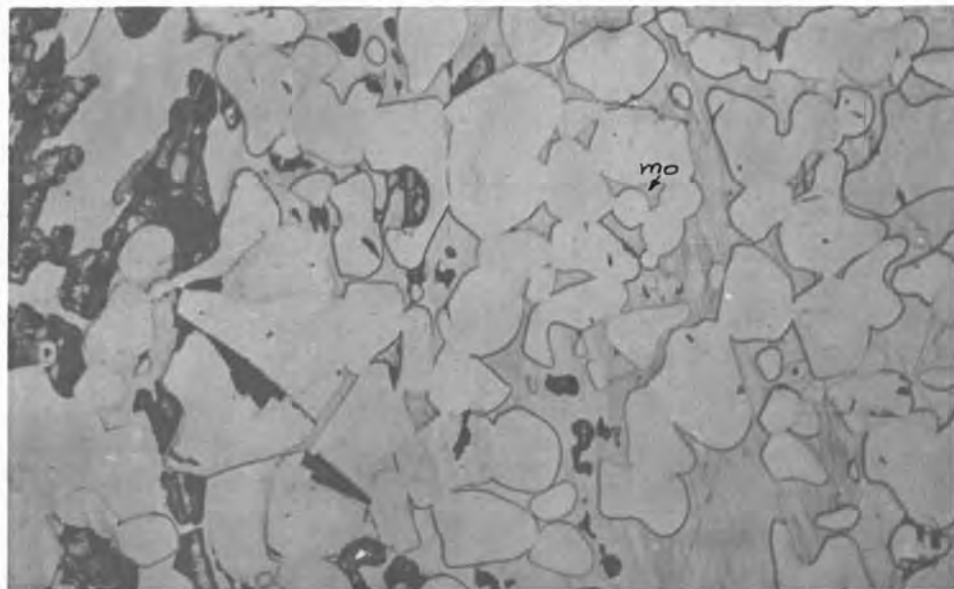


Plate 32. Larnite (etched out, black) which is present from the hot face backwards ends abruptly, and merwinite (scratched) plus traces of monticellite (mo) occur in its place. The mineral with the higher reflectivity is periclase.
Sample: D116 (C43 O₄). (x148)

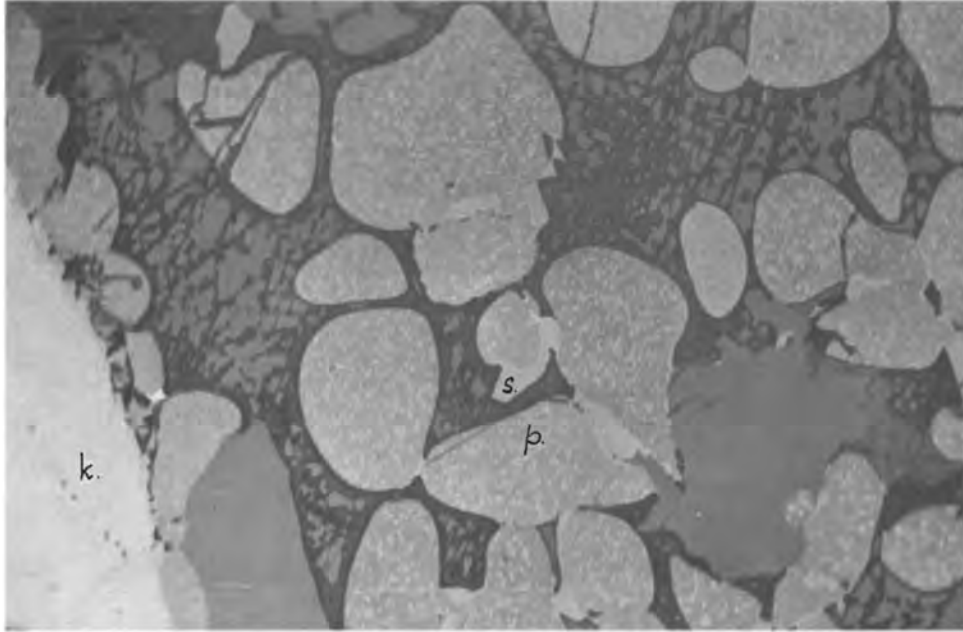


Plate 33. The mode of occurrence of the silicates in an unused magnesite-chrome refractory. The silicates are CMS (stained dark) and M_2S . Chromite (k), secondary spinel (s) and periclase (p) are also shown in the plate.
Sample: D96 (C42 N₉). (x288)