ATTACK OF MAGNESITE REFRACTORIES BY STEELMAKING SLAGS
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by

SUNG-MAN KIM, B.Sc.

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AUTHOR: Sung-Man Kim, B.Sc. (Seoul National University, Korea)

SUPERVISORS: Professors W-K. Lu and P.S. Nicholson

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ABSTRACT

Experimental investigations of the attack of carbon-free and carbon-bearing magnesite refractories by synthetic steel-making slags at 1600°C and relevant theoretical analysis are documented in this thesis.

The attack of carbon-free magnesite brick by steelmaking slags was studied by immersing cylindrical specimens in molten slag contained in a noble metal crucible. The major variable of study was the composition of the slag, i.e., the alumina and magnesia contents and the lime-silica ratio.

The reacted samples are examined macroscopically in terms of elongation, slag climb and penetration. Microscopic examination by petrographic techniques and microprobe analysis further illustrate the macroscopic observations associated with the chemical reactions taking place between the refractories and the penetrating slag.

The role of carbon in extending the lining life of BOF carbon-bearing refractories is the main objective of this research. Test crucibles were reacted with slags. The reacted samples were microscopically studied. The formation and destruction of a dense MgO layer in reacted specimens was studied. Theoretical analysis of the formation of the dense MgO layer was undertaken based on the assumption that the formation of MgO is the result of a gaseous reaction between magnesium vapor and carbon dioxide.

This work has been carried out under conditions relevant to refractory problems involved in a few major steelmaking vessels. The results obtained here have shed light on the kinetics and mechanism of the attack of magnesite refractories by steelmaking slags.
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CHAPTER I
INTRODUCTION

In the metallurgical industry, for kinetic and thermodynamic reasons, many processes are carried out at very high temperatures. Further advantages can be realized by having the reaction products (liquid metal), and the waste oxide melt (slag) in the liquid state, which facilitates their separation as they have limited mutual solubilities. In the case of steelmaking, the process temperature is ~ 1600°C. Steelmaking furnaces and transfer ladles are lined with refractories based on oxides of high melting point and of adequate chemical stability in contact with liquid steels and slags. The economic benefits of longer service life of each refractory lining are many-fold i.e., lower material and labor costs, higher availability and reliability of these vessels. Based on what has happened in the past and the intensity of current activities in the industry, research work on the wear of refractories in steelmaking processes is and will remain a vigorous endeavor.

The refractories normally used in steelmaking shops may be classified into two categories: (1) Acid brick which are alumina-silica based and are used for the lining of transfer ladles, and (2) Basic bricks which are MgO-CaO based and used for lining steelmaking furnaces. Acid bricks can be attacked by both metal and slag phases. On the other hand, basic bricks are very inert.
to liquid steel but vulnerable to slags. This thesis is based on the results obtained in the study of reactions between steel-making slags and MgO-rich basic bricks. The work done by the author on "Corrosion of Aluminosilicate Refractories in Fe-Mn Alloys" is given as an appendix rather than as part of the main body of the thesis. This was decided in order to simplify the presentation of the thesis and not to imply that contributions in the studies of acid bricks are less significant.

MgO-based basic refractories are further divided into (a) pitch-free and (b) pitch-bearing brick; the former are mainly used for lining open hearth and electric arc furnaces, and are the safety lining of the BOF. The latter is used in the BOF (basic oxygen furnace) working lining. Carbon is retained as a result of pyrolysis of the pitch. The success of the BOF in replacing the open hearths as the major steelmaking process owes much to the use of carbon-bearing refractories. The fact that the carbon in BOF brick contributes to the limitation of slag penetration and the extension of lining life is universally accepted but the mechanism by which carbon prevents the slag penetration has not been fully established. In general, magnesite refractories are heterogenous mixtures of polycrystalline magnesium oxide and silicate bonds containing a variable amount of porosity. In addition, carbon-bearing brick contains carbon in the pore network of its structure. In view of the complexity of these oxides, it is expected that the reactions between refractories and slags are complex in nature.

For the purpose of controlling steelmaking reactions such as desulfurization and dephosphorization and improving basic
refractory performance, it is desirable to have lime dissolve into the slag as soon as possible and this is normally done by addition of fluorspar (CaF$_2$). There has recently been a strong demand for substitutes for fluorspar as a flux due to its short supply as well as for environmental considerations. It has been suggested by the AISI, which sponsored this project, that bauxite is a possible candidate as a flux (Al(OH)$_3$Fe(OH)$_3$).

Past studies on the attack of the carbon-bearing magnesite refractories by steelmaking slags have been characterized by a diversity of opinion as to, particularly, the mechanism of decarburization and its influence on the slag resistance of refractories. The purpose of the present work is to investigate the failure mechanism of carbon-bearing brick by steelmaking slags and the effect of Al$_2$O$_3$ additions to calcium silicate slags on the refractory attack. The role of carbon was indeed the main concern. However, carbon-free brick were also studied with the understanding that carbon-bearing bricks with the loss of carbon from the surface regions near the hot face (decarburized zone), would be attacked in the same way as a carbon-free brick. Based on the recommendation of AISI, several types of carbon-free and carbon-bearing commercial BOF bricks were chosen to be tested at 1600°C in contact with synthetic steel-making slags. A mathematical analysis has been carried out to help the interpretation of the experimental results and to design future studies.
CHAPTER II
LITERATURE REVIEW

2.1 INTRODUCTION

All over the world basic oxygen steelmaking is rapidly replacing the open hearth process as the major method for making steel. Among the many advantages of the use of basic oxygen furnace (BOF) is the substantial saving in refractory consumption per ton of steel produced as compared with the open hearth. The adoption of the BOF has been accompanied by an essential change in the type of refractories required for lining the steelmaking furnace. Thus, the chemically-bonded or direct-bonded brick made from periclase and chrome ore, which were used successfully in the open hearth furnace, have been replaced by a variety of pitch-bearing basic refractories.

Historically, pitch-bearing basic refractories have been used in basic Bessemers in some form since the late 1800s. Trials of pitch-free refractories in the basic Bessemer and more recently in the BOF have met with disappointing results. The most modern and successful refractory linings developed for these furnaces are composed of magnesia and carbon; a ceramic composite. It is now apparent that the pyrolysis of the pitch in the brick during heating in service results in the deposition of residual carbon, which significantly improves the performance of the refractory.
In addition to this chapter's purpose of reviewing the literature regarding BOF refractory attack by slag in service and under laboratory conditions, the BOF steelmaking process, brick raw materials and brick properties will be briefly described.

2.2 BASIC OXYGEN FURNACE STEELMAKING AND SLAGMAKING

2.2.1 Basic Oxygen Furnace Steelmaking

In principle, the BOF steelmaking process involves the removal of unwanted chemical elements from a charge of about 70% molten pig iron and 30% scrap by the injection of high-velocity oxygen of commercial purity (minimum 99.5%) through a water-cooled lance onto the surface of the metal bath. Figure 1(1) is a typical example of the modern BOF practice. This figure is not presumed to be an accurate representation of individual BOF heats but is indicative of what is to be expected from an average of many heats. Slag-forming fluxes such as burned lime, fluor spar and mill scale are added in controlled amounts to produce a slag of the desired characteristics.

The supersonic velocity of the oxygen jet causes the formation of an intimate mixture of slag and metal which contributes remarkably to the high speed of the steelmaking operation, requiring only 20 minutes for the blowing of oxygen. It is known that the area of reacting interfaces in BOF steelmaking is extremely large in comparison with that in the open hearth process due to the formation of an emulsion of slag, metal and gas. This effect in combination with the stirring by the oxygen jet and direct contact between oxygen and the melt are 11v considered to be responsible for the high refining
Figure 1: Schematic representation of progress of refining in a BOF. (1)
rate in the BOF.

One of the thermal characteristics of the process is that the carbon in the charge is oxidized only to CO and leaves the vessel largely in this form. It has been reported that the atmosphere in the BOF during the blow in terms of ratios of CO:CO₂ runs around 10:1. This is a disadvantage to the thermal efficiency of the steelmaking process, however, it means lower temperatures in the upper part of the lining and a longer lining life.

During the refining of steel, the reaction takes place mainly at the slag/metal and the gas/metal interfaces. BOF steelmaking relies on slag/metal reactions for phosphorus and sulfur removal while the overall process, including the oxidation of carbon, manganese, and silicon can be accelerated by combining the slag/metal reactions with some degree of direct gas/metal reaction. Slag/metal reactions required for removal of P and S are favorable in a highly basic slag, thus basic refractory linings are required.

2.2.2 Basic Oxygen Furnace Slagmaking

The principal components of slags are SiO₂, CaO, FeₓOᵧ, MnO and CaF₂. Iron oxides come from the charge and mill scale as well as reaction products. SiO₂ and MnO result from the oxidation of Si and Mn in the iron melt to be refined. CaO and CaF₂ are added fluxes.

The general way in which the temperature and composition of the slag evolve during the blow in a BOF is illustrated in Figures 2 and 3. The temperature increases gradually from about 1300°C to 1600 - 1700°C as a result of the heat generated by the refining reactions and the oxide of the
Figure 2: Typical changes in iron-oxide content and temperature with blowing time. (3)

Figure 3: Typical changes in slag composition with blowing time. (3)
bath increases from the unavoidable oxidation of some of the iron. Figure 3 shows that the slag basicity (V-Ratio = CaO/SiO₂) also increases from less than 1:1 at the beginning of the blow to greater than 3:1 after 15 minutes of blowing.

The quenched slag has been the subject of petrographic studies. Treffner⁴ has reported the existence of C₂S (dicalcium silicate), C₃S (tricalcium silicate), C₂F (dicalcium ferrite) and considerable glassy material. The presence of free lime or undissolved CaO may be considered as evidence of the existence of nonequilibrium states in the slag prevailing during the blow. Numerous other slag analyses⁵,⁶,⁷ generally agree on the trend of changes in time but rarely on details of composition. In view of the heterogenous nature of the reactor, and the variety of grades of steel being made and difficulties in sampling, this is certainly not surprising.

Refractories in BOF linings are exposed to a wide range of temperature and slag composition during a blow. It is to be noted that slag is coolest when it is most acidic, and by the time its temperature reaches 1500°C it is fairly reliably basic (i.e., within the C₂S and C₂F field of CaO-SiO₂-FeₓOᵧ diagram). Since it is very unlikely that one could maximize the chemical resistance to both acids and bases in the same material, it would appear well to have BOF brick to be more resistant to a basic slag which exists at the higher temperatures and for longer times.

Recently, van Hoorn et al⁸ reported studies on the aggressiveness of BOF steelmaking slags with respect to MgO refractory in the course of a blow (Figure 4). They defined
Figure 4: The specific aggressiveness as function of time. (8)
"specific aggressiveness" as \( d(MgO/ml)/dt \), where \( MgO \) is the mass of \( MgO \) dissolved and \( ml \) the total mass of slag at time \( t \). In this figure, curves I and II are the determined and equilibrium aggressiveness, respectively. It is seen that the specific aggressiveness is high in the beginning of the blowing period and has small value during the main decarburization period increasing towards the end of the blow. It must be noted that the absolute amount of \( MgO \) dissolved in the later stages is larger than appears in Figure 4 because of the increase in volume of the slag in the final period of blowing.

For the purpose of controlling steelmaking reactions and improving basic refractory performance, it is desirable to have lime dissolved into slag as soon as possible and this is normally done by the addition of fluorspar (\( CaF_2 \)). It is generally considered that fluorspar decreases the viscosity of the slag at lower temperatures, especially for acidic slags, so enhancing mixing. This effect, and that fluorspar in the slag may prevent or reduce the formation of dicalcium silicate rims on the lime particles which would slow down their dissolution are considered to be the beneficial effects of fluorspar additions.

During the past several years, a search for fluxes which might replace fluorspar in BOF steelmaking operations has been under way. The interest in \( CaF_2 \) substitutes has grown because of dwindling spar supplies, high costs and environmentally hazardous by-products such as HF in the gases released to the atmosphere. Among various materials...
and ilmenite which has been suggested as fluorspar substitutes, $\text{Al}_2\text{O}_3$ has been chosen in this work which evaluates its effects on the performance of magnesite refractories (Section 2.7.3).

Among the many factors that influence lining life, the characteristics of the slag are most critical. The incompatibility of slags and refractories must be minimized to achieve maximum economy of steel production, by minimizing the cost and repair time for furnace linings. It has been suggested, however, that improved slagmaking would lead to better quality control of the steel as well as longer lining life.

2.3 REFRACTORIES FOR BASIC OXYGEN FURNACE

This section will briefly describe the various raw materials and processes used in making magnesite refractories and the use of these materials in BOF and/or electric-arc furnace linings.

2.3.1 Classification of BOF Brick

At present, the three general types of brick manufactured for BOF are pitch-bonded, tempered, and burned-impregnated. Any of these three types can be made from the various types of grain (periclase, magnesite or dolomite) or combinations of these grains.

2.3.1.1 Pitch-Bonded and Tempered Magnesite Brick

The carefully sized refractory grains are hot-mixed with a measured quantity of pitch which coats all particles evenly and the mass is warm-compacted into its final shape. This product is called "pitch-bonded" and may be used as is for lining a BOF.
Many different particle-size distributions are used in the manufacture of BOF brick to promote maximum brick density. The relative amount of pitch to be used varies and can exert an important influence on the properties of the brick. The higher pitch contents increase the residual carbon content of the brick, but the handling characteristics of this type of brick are undesirable because of its low strength and tendency to stick to one another. Generally, to obtain the desired combination of brick compactness and residual carbon, the optimum amount of pitch is recommended within the range of 5 to 6% by weight.(3)

It is increasingly widespread practice to heat-treat the pitch-bonded brick between 90 to 650°C for 30 minutes to 48 hours, the shorter times being associated with higher temperatures. Products so treated are called "tempered". Tempering of the pitch-bonded brick has been found to markedly improve the low-temperature hot strength of the brick. This increase in strength eliminates possible failure of the lining during burn-in.

2.3.1.2 Burned Magnesite Brick

The sized refractory grain and fines are cold-mixed, pressed and then fired in the temperature range of 1500 to 1800°C to produce the familiar sintered refractory product, "burned brick". This type of brick is normally used as the safety lining in the BOF brick and electric furnace sidewalls. In normal use, the safety lining refractories last through several campaigns of the pitch-bearing working linings. For this reason, the safety lining is exposed to several tempera-
ture cycles during service. Thus, the safety lining brick must have volume stability under cyclic conditions, which is generally obtained by using brick with low SiO$_2$ and Fe$_2$O$_3$ contents.

The properties of the burned brick may vary widely with composition and firing conditions. For example, the hot strength (modulus of rupture) of a burned periclase brick may vary from 50 to 2000 psi at 1480°C depending on the CaO/SiO$_2$ ratio of the periclase grain in the brick, the level of impurities such as Fe$_2$O$_3$, Al$_2$O$_3$ or B$_2$O$_3$ and the temperature at which the brick was fired. Similarly, the open porosity in the same burned periclase brick may vary between 14 and 22% depending on the raw material and processing variables.

2.3.1.3 Pitch-Impregnated Magnesite Brick

Pitch-impregnated bricks are produced by impregnating hot molten pitch into the open pores of a burned brick using a vacuum-pressure system to accelerate the process. For obvious reasons, the pitch-impregnated brick has found use in the BOF pad, while pitch-bonded and/or tempered brick line part or all of the remainder of the BOF interior. More details concerning the use of various type of bricks will be given in Section 2.6.5 on "Zonal Lining".

2.3.2 Raw Materials of Magnesite Brick

All of the refractory raw materials used lie essentially in the magnesia-lime (MgO-CaO) system which are most resistant to BOF slags and readily available. In this section, MgO will be considered as a principal component of the lining material with lime as either an additives or impurity. The success of
magnesite as a BOF refractory is due to its high melting point (+ 2800°C) and its excellent resistance to iron oxide attack.

2.3.2.1 Magnesite and Periclase

High-MgO grain is made commercially from several sources. It is generally true that the natural mineral magnesite (MgCO₃) and brucite (Mg(OH)₂) are the least pure and of the most variable in composition, while synthetic magnesia, precipitated as Mg(OH)₂ from sea water, is of the highest and most uniform purity. Refractories made by high-temperature calcination from the natural minerals are usually called "magnesite" refractories; these range between 80 and 90% MgO, with higher levels achieved by beneficiation. The aqueous sources yield "periclase" refractories, generally in the range 90 to 98% MgO with a potential for + 99%.

The reactions producing periclase from sea water involve the reacting of slaked lime or dolomite to produce an insoluble Mg(OH)₂ as follows:

\[ \text{Ca(OH)}_2 + \text{MgCl}_2 = \text{Mg(OH)}_2 + \text{CaCl}_2 \]

\[ \text{Ca(OH)}_2 + \text{MgSO}_4 = \text{Mg(OH)}_2 + \text{CaSO}_4 \]

The insoluble Mg(OH)₂ is thickened, dried, and fired between 1700°C and 2200°C to produce periclase. To obtain the various chemical qualities such as the CaO/SiO₂ ratio of the grain products, appropriate additions of iron, silica, and lime are made to the paste before dead-burning. Magnesites are generally characterized by higher iron oxide and alumina contents than periclase. As used in brick form, the lower MgO materials of magnesites are commonly blended to produce products with the sum of MgO and CaO contents above 90%.
Substantial improvements in BOF brick performance have been made by increasing the density of the grain. In large part this has been accomplished by adopting a two-step calcination process. The mineral source material is calcined to active magnesia at temperatures between 900 and 950°C. This firing removes some impurities, converts the major constituents, MgCO₃ or Mg(OH)₂, to MgO, and begins the sintering processes which perfect the lattice structure of the MgO subgrains so beginning densification. This fine powder, after first firing, is compacted at high pressure, usually in briquetting rolls, to yield pellets of high density. These pellets are dead-burned at temperatures in excess of 1800°C. By this second firing, high-purity, high-density large grain is made for refractory brick production. Porosity levels are typically 6 to 8% for magnesite grains.\(^{(9)}\)

2.3.2.2 Pitch\(^{(3)}\)

The properties of the various pitches used as temporary binders and sources of carbon in BOF brick vary widely. The pitches used are produced as by-products in the destructive distillation of bituminous coal. Briefly, the desirable properties of a pitch for use in a BOF brick are:

1. Low viscosity; it flows into the pores of a presintered brick.

2. It yields a bonded brick that is strong enough to be handled when hot (after pressing) and when cold (during storage and installation).

3. It has a minimum volatile content for fuming.

4. It contains a minimum of solid particles to facilitate
its penetration into the brick.

5. It yields the maximum possible amount of carbon in the brick during burn-in or tempering and ultimate use in the BOF lining.

2.4 IMPURITIES IN MAGNESITE

All commercial magnesite grain for BOF brick contain CaO, SiO₂, Fe₂O₃ and Al₂O₃ as major impurities in varying amounts. Apart from Al₂O₃, these are the principal components of steel-making slags. Iron oxide has long been recognized as the compound which depresses the melting point of silicate systems and decreases the interfacial tension between silicates, and MgO. (10, 11) Because of the somewhat controllable nature of Fe₂O₃ contents by beneficiation and the significant effects of CaO and SiO₂ as bonds in magnesite refractories, the MgO-CaO-SiO₂ phase system approximately describes the refractory-grade magnesites and perclase. The phase diagram for this system is shown in Figure 5. The MgO is always in excess and the impurities CaO and SiO₂ freeze on cooling to give crystalline species that coexist in binary equilibrium with the MgO. In order of increasing CaO/SiO₂ mole ratio, these silicates are listed in Table 1.(2)

<table>
<thead>
<tr>
<th>CaO/SiO₂ Ratio</th>
<th>Mineral Name</th>
<th>Nominal Formula</th>
<th>Nominal M.P. °C</th>
<th>Minimum M.P. °C</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Forsterite</td>
<td>2MgO·SiO₂</td>
<td>1900</td>
<td>1860-1430</td>
<td>0.00-0.84</td>
</tr>
<tr>
<td>1</td>
<td>Monticellite</td>
<td>CaO·MgO·SiO₂</td>
<td>1490</td>
<td>1500-1430</td>
<td>0.84-1.00</td>
</tr>
<tr>
<td>1.5</td>
<td>Merwinite</td>
<td>3CaO·MgO·2SiO₂</td>
<td>1575</td>
<td>1575-1435</td>
<td>1.00-1.21</td>
</tr>
<tr>
<td>2</td>
<td>Dicalcium Silicate</td>
<td>2CaO·SiO₂</td>
<td>2130</td>
<td>1800-1575</td>
<td>1.21-2.18</td>
</tr>
<tr>
<td>3</td>
<td>Tricalcium Silicate</td>
<td>3CaO·SiO₂</td>
<td>2140</td>
<td>1850-1790</td>
<td>2.18-2.62</td>
</tr>
</tbody>
</table>
Figure 5: Phase diagram for the system CaO-MgO-SiO₂. (12)
Table 1 illustrates the effect of the CaO/SiO$_2$ ratio in the periclase on the silicates formed and their melting temperatures. Monticellite (CMS) and merwinitite (C$_3$MS$_2$), especially, are capable of wide variations in composition as solid solutions. When small quantities of other impurities are included, e.g., Al$_2$O$_3$, Fe$_2$O$_3$, etc. the minimum melting point ranges given above must be still further depressed. It is readily seen that if the bond phases are not to melt at 1650°C, the mole ratio CaO:SiO$_2$ must be adjusted either well below 0.5 or close to 2. It is undesirable to form C$_3$S (tricalcium silicate) and free lime in the brick because of their susceptibility of hydration. Furthermore, if a ratio below 0.5 is obtained, reactions with CaO-rich slags will produce low-melting compounds by raising the ratio, whereas the lime-rich bond is not subject to this problem. The reverse is true for an acidic slag.\(^{(4, 7)}\)

Consequently, a mole ratio of \approx 2 is preferred in the impurity fraction of the BOF refractory grain; and this ratio becomes the more important to maintain, the higher the content of SiO$_2$. Higher values are actually desirable to allow for the solubility of CaO in MgO at high temperatures\(^{(13, 14)}\) and the presence of impurities such as Al$_2$O$_3$, Cr$_2$O$_3$, and Fe$_2$O$_3$ which combine with CaO in the bond system.\(^{(4, 14, 10, 15)}\)

If Fe$_2$O$_3$ or FeO is present in significant quantity together with MgO, CaO and SiO$_2$ as above, melting at the hot face for BOF temperatures is certain.\(^{(14, 16, 17, 18)}\) At the slag/refractory interface, the bond material in the refractory will form a liquid phase in contact with the slag,
as predicted by the phase diagrams. The resistance to slag attack of the weaker portion of the brick, i.e. the silicate bond, is clearly a matter of kinetics. Efforts such as the adjustments of grain composition and control of the structure of refractories can only diminish the rate of attack, not prevent it.

Current research is bringing similar reasoning to bear on other components of the brick and slag. For example, B$_2$O$_3$ is a characteristic impurity of sea water and brine periclase, and this component depresses still lower the calcium silicate melting points and increases wetting even more severely than Fe$_2$O$_3$. Taylor et al$^{(19)}$ have shown that in part the lower melting can be nullified by increasing the CaO (or C$_2$S) content of the system, whilst other work$^{(17)}$ has been devoted to its elimination from periclase in the course of synthesis.

In contrast with B$_2$O$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$, Cr$_2$O$_3$ raises the minimum melting point of calcium silicate systems$^{(18)}$ and decreases the wetting tendency of the liquid.$^{(10,11)}$ For these and other reasons Cr$_2$O$_3$ is used as an additive in some synthetic BOF periclases. However, such an additive requires an increase of the CaO content if the impurity system is to remain in the C$_2$S field.

Jones and Melford$^{(14)}$ have used the electron probe microanalyzer together with optical microscopy in an extensive study of the partition of elements between major and minor phases in basic refractories. They observed that aluminium and titanium, when present in detectable concentrations, were
located in the bond but not the periclase. High levels of aluminium in the bond or high levels of iron in the periclase are related to a low dihedral angle and hence a low degree of direct bonding. In combination with the findings of these authors, Carniglia et al\(^{(2)}\) have tabulated their laboratory observations thus (Table 2).

**Table 2. Influence of CaO/SiO\(_2\) Ratio on the Phase Distribution of Elements**

<table>
<thead>
<tr>
<th>High CaO/SiO(_2) Ratio</th>
<th>Low CaO/SiO(_2) Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MgO Phase</strong></td>
<td><strong>MgO Phase</strong></td>
</tr>
<tr>
<td>Bond Phase(s)</td>
<td>Bond Phase(s)</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg</td>
</tr>
<tr>
<td>Ca</td>
<td>Ca</td>
</tr>
<tr>
<td>Si</td>
<td>Si</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr</td>
</tr>
<tr>
<td>Al</td>
<td>Al</td>
</tr>
<tr>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

Numerous investigators\(^{(3,4,7,14,17,19,20)}\) have noted the microstructural features of magnesite and periclase grain and fired brick consistent with the foregoing discussion. Carniglia et al\(^{(2)}\) summarized the data (Table 3) in terms of factors which encourage angular MgO grain and "direct" MgO-MgO bonding, with the secondary phases isolated in grain-boundary

**Table 3: Influence of Composition and Microstructure on Bonding**

<table>
<thead>
<tr>
<th>Angular, Direct Bonding</th>
<th>Rounded, Silicate Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large MgO Crystals</td>
<td></td>
</tr>
<tr>
<td>Total Impurity</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td></td>
</tr>
<tr>
<td>SiO(_2)</td>
<td></td>
</tr>
<tr>
<td>FeO(_3)</td>
<td></td>
</tr>
<tr>
<td>CrO(_2)</td>
<td></td>
</tr>
<tr>
<td>AlO(_2)</td>
<td></td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td></td>
</tr>
</tbody>
</table>
pockets; and factors which encourage rounded MgO grain and a "silicate bonding", i.e., a relatively continuous silicate network surrounding the MgO grain. Figure 6(3) illustrates the microstructural features ranging from one extreme to the other. Clearly, not only minimization but also isolation of the silicate bond will impede chemical attack by molten slag.

A knowledge of the impurity chemistry and the microstructure of MgO refractory grain gives considerable insight into the slag resistance of BOF brick made from this grain. It is evident that this same knowledge concerning a fired brick should relate well to the high temperature mechanical properties of the brick, because both slag resistance and high temperature strength depend to some extent on common features.

2.5 CARBON IN BOF MAGNESITE BRICK

2.5.1 Role of Carbon in Brick

The presence of carbon in the matrix of magnesia refractories as a result of pitch impregnation or pitch bonding, greatly increases the slag resistance of BOF refractories. Figure 7(3) shows the chemical composition of two such refractories, and clearly illustrates the significant effect of the residual carbon in the brick in decreasing the depth of penetration of slag. The significant differences in penetration of the brick with and without carbon residue are reflected by the dissimilar behavior in service. Figure 8(3) illustrates an idealized picture of the wear of these two types of brick.

Although all the investigators are in agreement that carbon prevents or modulates slag migration in the brick struc-
Figure 6: Photomicrographs illustrating the structure of three periclase grains. In each case, the large gray crystals are MgO and the silicate location is indicated. A 95 percent MgO grain is shown containing appreciable silicate around the MgO crystals. A 98 percent MgO grain contains less silicate, but the silicate is still located around the crystals. The 97 percent MgO grain with a higher CaO/SiO₂ ratio contains silicate as concentrated areas and not as a film around MgO crystals. Reflected light, X52. (3)

Figure 7: Comparison of chemical compositions of periclase brick used with and without pitch. (3)
ture, they differ as to the particular mechanism of retardation involved. The following are the main mechanisms proposed in the literature to explain the role of carbon in the BOF magnesite brick.

2.5.1.1 Nonwetting of Carbon by Molten Slag

Some authors\(^{(3,4,5,21,22,23,24)}\) suggest that the superior resistance of carbon-bearing refractories in a BOF vessel is due to the nonwetting character of the carbon by the liquid slag. For example, Barthel\(^{(25)}\) showed diagrammatically the effect of the lack of wetting between a silicate liquid and carbon as shown in Figure 9.\(^{(3)}\) This mechanism is widely accepted. Herron et al\(^{(21)}\), after studying laboratory and used BOF refractories, concluded that slag migration into partially filled pores is abruptly checked by certain carbon content indicating a surface phenomenon as the mechanism. They were the first authors to report the development of a dense MgO layer in their laboratory slag-test samples (see Section 2.5.1.3).

2.5.1.2 Gas Evolution

Robinson\(^{(26)}\), on the other hand, did not observe carbon in direct contact with silicates and therefore assumed that wetting could not be a significant factor. He proposed that the reducing atmosphere resulting from oxidation of carbon would alter the wetting characteristics between the liquid slag and the magnesia and/or that the pressure gradient generated by the formation of CO would delay the entry of the liquid slag.
Figure 8: Schematic of wear of indicated brick types. (3)

Figure 9: Illustration of wetting of pores of brick with and without carbon. (3)
2.5.1.3 Dense Layer Formation

Other authors (27, 28, 29, 30) have recently suggested that the formation of a dense magnesia layer just behind the hot face of the BOF brick could explain the retardation of slag penetration. They proposed that the dense magnesia zone is formed by gaseous Mg formation resulting from the carbon reduction of MgO within the brick and the subsequent transportation reoxidation and deposition of MgO near the working face of brick where the atmosphere is more oxidizing.

2.5.2 Carbon Coverage

It is logical that the volume of voids in the brick structure which require protection by residual carbon should be as small as possible. The total volume of pores between grains is minimized by optimizing the size distribution, mixing and compaction of the magnesia grains used to make the brick (3, 20, 31). Inclusion of a milled "fine" fraction (< 100 mesh to submicron) up to 30 volume percent of the brick mix is instrumental in this as well as providing more sinterability for the green brick. Control of the dimensions of voids is important. In a fired brick, those below a limiting size, even if connected, will not fill with pitch.

Any large space between grains will normally be filled with pitch in a bonded brick. When the bonded brick is subjected to burn-in, the volume shrinkage on pitch pyrolysis may cause the resulting carbon to withdraw from the surrounding grain resulting in a dimensional mismatch.

The void dimensions and actual pitch-filled fraction between grains both tend to decrease with increasing brick
density. It has been observed that brick density correlates definitively with slag attack\(^{3,22,23}\) (Fig. 10).\(^{(3)}\) Pitch of lower softening point results in less residual carbon and a higher volume shrinkage on pyrolysis, so yielding a more permeable final structure for equivalent mineral densities. As a result, products having a distribution of fine, evenly distributed carbon are reported to be superior to those having a block-type carbon structure. These factors appear more variable in burned impregnated brick than pitch-bonded products as the latter generally show a fine carbon distribution. This is partly attributed to nucleation on the fine refractory particles and to the carbon additives used in making bonded brick.\(^{(24,32)}\)

2.5.3 **Carbon Structure**

There is some evidence to indicate the carbon present in BOF refractories graphitizes to some degree during service. Figure 11\(^{(3)}\) shows the relative crystallinity of coked-pitch residues and pitch coked at 1650°C for a considerable time has some degree of crystallinity, but is still different from graphite. Examination of used BOF brick indicate that the degree of crystallinity of the pitch residue near the hot face is about the same as observed for pitch coked to 1650°C. As would be expected, the degree of crystallinity decreases rapidly with increased distances behind the brick hot face where temperatures are lower\(^{(4,33)}\).

The microstructure and distribution of the carbon deposit within the pores of the mineral mass are apparently of greater importance, or at least capable of much greater variation, than
Figure 10: Relative slag erosion versus density of periclase brick made with indicated pitches. (3)

Figure 11: Effect of heat treatment of pitch on crystallinity of carbon residue. (3)

Figure 12: Typical wear pattern of BOF lining. (38)
the degree of crystallinity of the carbon.\textsuperscript{(2,24)}

2.5.4 Decarburization

The destruction of brick might occur before the elimination of carbon from the refractories through washing or eroding of large particles. In general, the wear of BOF refractories follows the decarburization by oxidation. Relevant information on the subject is also given in Section 2.6.4.

2.5.4.1 Decarburization by Furnace Atmosphere

It is apparent that an oxidizing atmosphere containing $O_2$ and $CO_2$ in the BOF would burn the carbon in the brick if it is exposed. In the cone of the BOF slag coverage of the lining is usually incomplete and, therefore, gaseous oxidation is the dominating mechanism of decarburization.\textsuperscript{(2,21,34)} In the lifetime of the lining, conditions favoring gaseous oxidation can occur during initial burn-in, holding time, turndown for sampling and tapping and charging. However, from practical experience the slag coating on the lining gives some protection from oxidation by the furnace atmosphere to the carbon inside the brick. Poor slag coverage in the trunnion areas and the removal of the slag coating by impact in the charge pad leads to the high wear rates in this area.\textsuperscript{(21,23)}

2.5.4.2 Decarburization by the Slag Components

It is the general opinion of many authors that, in the barrel section where the lining is covered by metal and slag, little direct oxidation of carbon by gases occurs during a heat. The primary oxidizing agent here is considered to be the $FeO$ in the slag. It has been reported that immediately behind the hot face, metallic iron is usually found accompany-
ing carbon depletion.\(^{(2,3,4,7,23,24,35)}\) This reaction was generally accepted as the mechanism of decarburization of BOF brick until recently. It has also been noted that iron oxide as an impurity present in the raw materials of the refractories results in carbon loss. The appearance of Fe metal during service in the brick interior far deeper than the reach of penetrating slag and even in the absence of slag\(^{(4,24)}\) has been noted. For example, Herron and Runk\(^{(24)}\), having considered the lack of direct contact between iron oxide and carbon, as well as the gradual increase in carbon, proposed that the reduction of iron oxide occurs by a gas phase reaction, as shown below, rather than by a direct solid-phase reaction.

\[
\text{FeO} + \text{CO} \rightarrow \text{CO}_2 + \text{Fe} \quad \text{CO}_2 + \text{C} \rightarrow 2\text{CO}
\]

in slag \quad \text{in brick}

2.5.4.3 Decarburization by MgO and SiO\(_2\).

Recent studies have identified three more potential oxidizers of the carbon, inherent in the refractory material \((27,28,29)\), i.e. MgO, SiO\(_2\) and possibly Al\(_2\)O\(_3\).

Herron and Runk\(^{(24)}\) reported in 1969 that the structure of magnesite specimens heated above 1370°C had a less continuous carbon phase and the periclase structure had an etched appearance. Pickering and Batchelor\(^{(27)}\) experimentally observed weight and strength losses for BOF brick held for two hours between 1500 and 1600°C. It has been suggested that the reduction of MgO and the oxidation of carbon produced extensive microstructural changes. When oxidizing conditions
were maintained by a flowing oxidizing gas, a dense impervious layer of MgO formed at 1600°C between the external surface and the remaining carbon and large external MgO protrusions were observed to occur at 1750°C. They concluded that the two principal components in BOF refractories, carbon and magnesia, under steelmaking conditions at 1600°C, are thermodynamically incompatible and kinetically their interreaction is significant. They also noted that at that time, this mechanism of self-destruction had not yet been observed in the field but it could become a serious wear mechanism if operating temperatures were raised or pressures lowered. They also reported that carbon can reduce MgO selectively from mixed silicates in the calcia-magnesia-silica (CaO-MgO-SiO₂) system, i.e., MgO can be reduced from a calcium-magnesium silicate without altering the CaO:SiO₂ ratio.

From the laboratory data and theoretical analysis, Leonard and Herron(28) reached a similar conclusion but in addition noted that the reduction reaction appears to be limited by diffusion across the dense layer. They observed that the MgO layer dissolves quickly in low CaO:SiO₂ slags unsaturated with MgO but is quite impervious to slags of high CaO:SiO₂ ratios. They further observed a region of low CaO:SiO₂ material adjacent to the dense layer on the carbon side, regardless of the original CaO:SiO₂ ratio of the brick. Therefore, they concluded that this material results from the enrichment of SiO₂ in this region as a result of the oxidation of SiO which is another reduction product, this time from the brick SiO₂. Brezny and Landy(29) theorized from thermodynamic considerations and ex-
perimental results that $\text{SiO}_2$ and possibly $\text{Al}_2\text{O}_3$, in addition to $\text{MgO}$ and $\text{Fe}_2\text{O}_3$ will react at BOF temperatures with carbon to produce their respective suboxides $\text{SiO}$ and $\text{AlO}$. Their proposed mechanism for dense layer formation is essentially an expansion of that of previous authors. They also reported monticellite ($\text{CMS}$) and merwinitie ($\text{C}_3\text{MS}_2$) formed from $\text{MgO}$ and $\text{C}_2\text{S}$ with the $\text{SiO}_2$ product of the gaseous reaction.

Carniglia\(^{(36)}\) investigated the kinetics of the $\text{MgO-C}$ reaction based on a diffusion-limited model wherein the rate of escape of $\text{CO}$ and $\text{Mg}(\text{g})$ from the interior is rate controlling. He concluded that the reaction in the BOF is restricted to a very narrow zone at the carbon boundary behind the hot face and is less rapid than might otherwise be predicted from laboratory results on isothermally-heated small specimens. He concluded further that oxidizing agents such as $\text{Fe}_2\text{O}_3$, $\text{CO}_2$, and $\text{O}_2$ cause the most of carbon recession and transport of silica via $\text{SiO}$ is not important at $1650^\circ\text{C}$.

Recently, however, Howe et al\(^{(30)}\) reported evidence for a dense $\text{MgO}$ layer in pitch-bonded magnesite refractories after service in the BOF in which calcined dolomite was used as part of the steelmaking fluxes. They also commented that because the dense magnesia layer is dissolved by the slag, calcined or magnesia additions to the slag should in principle reduce the corrosion rate. It should be pointed out that this is the only report in the literature of the dense $\text{MgO}$ layer in a specimen taken from a BOF. Baker et al\(^{(37)}\) reported the failure of carbon to retard slag penetration into refractories in an argon oxygen decarburization (AOD) vessel lined with carbon-
bearing MgO brick. They further noted that deeper penetration of slag behind the hot face into the carbon-bearing matrix of the brick led to rapid dissolution of MgO in the slag and poor refractory performance in the AOD process. They ascribed this to the lack of formation of a dense zone of the type seen in BOF brick due to the extremely lower oxygen potential prevailing in AOD slags.

2.6 THE FAILURE OF MAGNESITE BRICK

A typical example of the wear pattern of a BOF lining is shown in Figure 12. Kappmeyer and Hubble discussed the properties of BOF refractories in terms of four principal failure mechanisms, viz.:

1. Spalling during burn-in
2. Abrasion from scrap impact
3. Sheet spalling
4. Slag attack

2.6.1 Spalling During Burn-in

A new lining of pitch-bonded and pitch-impregnated brick is brought into service by first heating it up with burning coke in oxygen. The critical factor involved is the pattern of strength change during heating due to the softening of the pitch. Brick with pitch contents above a critical level showed virtually no strength for a short time at temperatures between 100 and 425°C. This loss in strength resulted as the pitch softened and lubricated the refractory grains. It would appear that for each brick type and particular particle-size distribution, there exists a critical pitch content above
which the brick may have very low hot strengths during burn-in. Tempered brick have a strength corresponding to that of much lower pitch contents because of the redistribution of pitch during tempering. With tempered brick made with controlled additions of pitch, spalling during heat-up is not usually a problem as it is with bonded brick.

2.6.2 Abrasion from Scrap Impact

Abrasion can occur in certain areas in the BOF due to the impact of charging scrap and the washing of the slag and melt. For these reasons, the hot strength of BOF refractories is of major importance. For burned pitch-impregnated brick, strength measurements can be related to the CaO:SiO$_2$ ratio and the levels of Fe$_2$O$_3$, Al$_2$O$_3$ and B$_2$O$_3$ present in the fired brick. Factors controlling the hot strength in burned magnesite brick were presented in Section 2.4.

2.6.3 Sheet Spalling

This is a relatively rare and little understood form of failure in BOF linings that may occur after 20 - 200 heats. A 1 - 4 inch layer breaks away from the working face. This, however, is a universal problem with carbon free linings such as those in electric-arc and open-hearth furnaces. The presence of carbon in a BOF brick has generally limited the alteration of the brick and eliminated structural spalling as a wear mechanism. Kappmeyer and Hubble$^3$ suggest that it may be due to insufficient pitch content in brickmaking, excessively coarse grading, or too high a heating rate during tempering.
2.6.4 Slag Attack

The resistance of BOF refractories to slag attack is most difficult to characterize or measure. At present, slag resistance may be indicated by a variety of slag tests as well as measurements of related properties such as bulk composition, carbon content, and brick density. Pitch-free magnesite refractories are not used as working linings in the BOF but are used in electric-arc furnaces and open hearths. It is reasonable, however, to consider that the slag attack of carbon-bearing refractories after the depletion of carbon will follow the same mechanism as for carbon-free refractories.

2.6.4.1 Attack of Carbon-Bearing Magnesite Brick

Samples of used brick from service all show a characteristic pattern. (23) The hot face is coated with a slag layer behind which there is a thin white section of about 1/4 inch where the carbon has been depleted. Behind this is a relatively unaltered brick, varying only in the degree of decarburization of the pitch fraction. The remaining carbon seems to limit the penetration of slag deep into the body of the brick, a characteristic of open hearth and electric furnace refractories which are carbon-free.

It was established by Kappmeyer and Hubble (3) that burned brick containing pitch exhibit several times the resistance to attack of burned brick without pitch and are also less subject to spalling. Perhaps the most important data, however, are those given in Figure 13 (3) which confirm the effect of residual carbon content on the slag erosion of a tempered periclase and magnesite brick.
Figure 13: Relation of residual carbon content and relative slag erosion for indicated tempered-periclase and magnesite brick. (3)

Figure 14: Typical zonal lining of BOF. (38)
From a laboratory test with slags of varying CaO/SiO₂ ratio, Landy(40) reported that the difference in performance between tempered brick and pitch-impregnated brick changes significantly with varying slag composition. His results showed that both brick types are eroded more by the lower CaO/SiO₂ slags than by the higher CaO/SiO₂ slags. Moreover, the tempered brick is superior to the burned impregnated version at the lower CaO/SiO₂ ratios, but becomes inferior at higher CaO/SiO₂ ratios. He presented an explanation in terms of the relative contents of carbon in the two bricks, the rate of decarburization and the rate of erosion. In the more erosive, lower CaO/SiO₂ slags, the rate of decarburization apparently controls the rate of erosion so the brick with higher carbon content (tempered brick) has less overall penetration and erosion. In the higher CaO/SiO₂, the rate of erosion is slower than the rate of decarburization and an extensive slagged decarburized zone forms which is resistant to erosion during the test.

Slag attack is not strictly chemically corrosive in nature. It is also closely associated with the erosive action of moving liquids relative to and solids which expose fresh refractory surface to the slag.(3) Thus, the hot strength or degree of sintering of the hot face must also have a definite bearing on the resistance of a brick to slag attack. Herron et al(21) studied the mechanism of MgO removal by means of a laboratory slag test and compared these results with those of BOF refractories. They concluded that the bulk of the MgO is removed by solution in the slag, with erosion playing a
minor role.

2.6.4.2 Attack of Carbon-Free Magnesite Brick

In 1969, Gilpin\(^{17}\) remarked in his Frank Scott Russel Memorial Lecture that, other factors being equal, high hot strength is the key to long lining life in those environments where erosion, in addition to corrosion, is an important factor, and quoted, as evidence to his statement a paragraph from Chesters' Steelplant Refractories (1945 Edition):

"Observation of a large number of such sections show that, particularly with Austrian magnesite, the grains break down into a series of rounded crystals which float out undissolved into the slag. At times complete grains float away. Such breakdown affords further illustration of the fact that the bond exerts a controlling influence on the properties of a magnesite brick."

Many authors\(^{41,42}\) used refractories recovered from electric arc furnace walls to determine the mechanism of deterioration. They reached the similar conclusion that slag penetration of the subgrain boundaries within the magnesite grains caused breakdown of the fines into individual periclase crystals and partial breakdown of the coarse grains. As the groundmass would be fluid during operation, erosion takes place by the washing away of undissolved periclase. As to the mechanism of fragmentation of the MgO grains, Kriek et al\(^{43}\) suggested, after studying used magnesite brick from a production unit as well as from an experimental rotor vessel, that the FeO and MnO of the slag go into solid solution with the MgO in the brick as a result of which the larger grains expand
and break up into smaller fragments which dissolve further into the slag.

Little work has been done on the attack by Al₂O₃-containing steelmaking slags on magnesite refractories, since Al₂O₃ is rarely utilized as a flux on a commercial scale. Miyatake and Yagi(44) observed that increasing the Al₂O₃ content up to 50% in a lime-silica synthetic slag of CaO/SiO₂ = 3.0 caused increased creep of magnesite crucibles at 1550°C and a combined addition of Al₂O₃ and Fe₂O₃ to the same silicate resulted in the lowest refactoriness in terms of Seger cone number in the range of compositions tested. They ascribed the former effect to the formation of low-melting aluminates such as tricalcium aluminate (C₃A), anorthite (CAS₂), and gehlenite (C₂AS) and the latter result to the formation of the low-melting compound brownmillerite (C₄AF).

As with other applications, high purity and density are desirable together with reasonable spalling resistance. In fact, the brick density can override the influence of most other factors such as composition or residual carbon content so that changes in other variables can give false results unless carefully interpreted. This is because slag attack on a brick must be preceded by slag penetration.

2.6.5 The Zonal Lining in a BOF

The conditions that refractories must withstand during the process of making steel were well summarized by Kappmeyer and Hubble(3):

"During scrap and hot metal charging, the charge side or pad of the furnace is subjected to abrasion and erosion."
During the oxygen blow, the entire furnace is subjected to erosion and corrosion by a molten slag/metal emulsion with variable composition and temperature. The bottom of the furnace is partly protected by the depth of the bath. The cone of the furnace is subjected to some metal and slag contact and to the movement of high-velocity gases bearing solid particles. In the early stage of blowing, the lining may also be subjected briefly to impingement of the high-velocity oxygen stream ricocheting off the steel scrap. After a period of blowing, the furnace is turned down to the charging side to allow metal and/or slag sampling and temperature measurements. During this period, the hot slag contacts a portion of the lining in the turndown slag area. During cooling or hold periods in the vertical position, the slag contacts the area immediately above the bath level. On tapping, the slag contacts still another area of the furnace on the tapping side."

They also mentioned:

"These variable conditions throughout the furnace mean that different parts of the lining do not wear evenly. For this reason, it is common to use different type and/or thicknesses of brick in the same BOF lining so that the total wear of each zone will be similar, and efficient use will be made of all the brick. Thus, all areas of the lining are expended at nearly the same time."

As an example, Figure 14 shows a zonal lining using several kinds of brick and considerable variation in lining
thickness. The bulk of the lining in this case consists of tempered brick (either magnesite or dolomite) with an impregnated brick in the charge-pad area to resist the impact of scrap. These lining designs have been developed primarily on the basis of observations of the severity of lining wear at various locations in furnaces in a given shop (Figure 12). Refractory consumption has been reported in the range of 5 - 10 lb/ton of steel produced, or on the average between 0.03 and 0.06 inches recession per heat.\textsuperscript{(2)}

In the vessel barrel, the trunnion areas in particular, are the major wear zone. This area contributes most to lining failure and is lined with a variety of brick in different steelmaking shops. Acidic slags probably remain in this area for a longer period of time. Vessels are mounted on trunnions to be tiltable about their axes for charging, blowing, sampling or tapping. Probably a major reason for the increased attack is the stresses developed at the trunnions on rotation of the vessel. In rotation, the sidewalls become arched with major stresses concentrated in the trunnion areas.\textsuperscript{(3)}

2.7 THE EFFECTS OF STEELMAKING PRACTICE ON LINING PERFORMANCE

It is not possible at the present time to predict a BOF lining life solely based on refractory properties. There are a number of additional variables which are known to have definite effects on lining life. This statement can be supported by the relation noted between lining life and shop experience in Figure 15.\textsuperscript{(3)} In all cases, the lining lives obtained have shown marked improvements with time. Although changes in brick
Figure 15: Lining number versus lining life. (3)

Figure 16: Frequency curves of turndown temperature on BOF campaigns. (23)

Figure 17: Effect of Si and Ti contents of iron on lining life. (3)
type and design have naturally been a part of the evolutionary process associated with these improvements, the importance of steelmaking operational factors has recently been recognized.\(^{(9,45)}\)

2.7.1 The Operational Control of Steelmaking

The purpose of a process control is usually to ensure a product of acceptable quality, high productivity and low cost. Among many factors involved, the end-point control is the most critical in a BOF operation. Recently, a dynamic control system incorporating a substance has been reported successful for end-point control, in particular, both for carbon content and temperature.\(^{(46,47)}\)

2.7.1.1 The Iron Oxide Content of Slag

It is a well-established fact that hot fluid slags high in FeO are detrimental to the lining. Oxygen lance practice and design thus become a factor in refractory destruction since they largely control the iron content of the slag. MacNamara\(^{(48)}\) reported that replacement of a one-hole lance by a three-hole lance resulted in reduced FeO content in the tap slag, lower hot metal silicon content and increased oxygen blowing rate, in addition to significantly improved lining life. The eroding potential of small droplets of metal and slag driven at high velocity from the oxygen jet has also been proposed as a factor in refractory wear.\(^{(49)}\)

2.7.1.2 End-Point Control

It is apparent that at the end of the blow, when the temperature is exceedingly high, the highly fluid slag promotes wear of the refractories. It was also found that a good correlation exists between lining life and low turndown temperatures.
As shown in Figure 16(23), the good service pattern was developed when a majority of the turndown temperatures were in a favorable range, whereas the lining suffered from a majority of variable turndown temperatures, many on the low side. These low turndown temperatures required a reblow which significantly increased the iron oxide content of the slag and the holding time. Reblow is also required when the carbon content at turndown deviates on the high side of the acceptable carbon content. This situation has resulted in, for example, a development of dynamic control. End-point control is claimed to be the most important single factor affecting the performance of refractories in the BOF. (45)

2.7.2 Hot Metal Composition

The composition of hot metal is known to affect the lining life, as illustrated in Figure 17. (3) For example, higher silicon or titanium contents in the hot metal have been found to adversely affect lining life.

2.7.2.1 Hot Metal Silicon Content

Reduced silicon content but remaining above the minimum value required for a given practice usually improves both blast furnace production and BOF lining life. (48) The oxidation of silicon serves as an igniter for subsequent decarburization of the metal in the BOF as the bath is relatively cold when the blow starts. In view of refractory performance, therefore, the silicon content must be as low as possible as long as silicon serves this purpose. However, the heat generated by silicon oxidation is partly used to melt the scrap charge. The required compromise may be resolved by requirements of
individual BOF shops with respect to production and costs of steelmaking as well as ironmaking. The optimum condition for overall practice, of course, does not necessarily result in the longest possible lining life.

2.7.2.2 The Minimization of Carried-Over Slag

Blast furnace operators generally do their best to prevent slag, which contains about 40% SiO$_2$ and 10% Al$_2$O$_3$ and runner brick materials picked up by flowing slag and metal, from entering the torpedo cars and eventual pouring into the BOF. The carried-over slag contributes both to the acidity and amount of the BOF slag both of which are detrimental to the BOF lining.

As an ever-increasing demand for quality steel requires, particularly a low sulfur content, external desulfurization is often carried out. For instance, soda ash is used as a desulfurizer in the ladle. This makes the slag highly fluid so that it readily penetrates the BOF refractories when not eliminated. For this and similar reasons, it is recommended that the slag to be thoroughly removed from the ladle before charging the basic oxygen furnace.

2.7.3 Fluorspar Substitutes

As mentioned earlier, the search for effective substitutes for fluorspar in BOF steelmaking has been underway for a number of years. Several laboratory, pilot-scale and full-scale tests of candidate materials have been attempted.\cite{50,51,52,53,54,55,56} Based on these authors' findings, Clum\cite{57} summarized that three groups based on (1) colemanite, (2) ilmenite (FeO•TiO$_2$), and (3) iron/manganese-lime mixtures give evidence of good performance but none of the substitute fluxes tested matched that of
CaF₂. He added that blast furnace and BOF slag mixtures have characteristics which should promote lime dissolution in BOF slagmaking.

2.7.3.1 Al₂O₃-Based Materials

Bauxite (impure Al₂O₃) has a fluxing action somewhat similar to that of fluorspar.⁵⁸ Successful use of so-called "high-iron bauxite" to replace fluorspar in open hearth steelmaking has been reported from Australia and from trials in the U.S.A. Wartime experience⁵⁹ showed that alumina dross and ilmenite were fair substitutes for fluorspar. Recent trials⁶⁰ using bauxite as a flux at a replacement ratio of bauxite/fluorspar = ~ 2 indicated that the desulfurizing capacity of such slag was equivalent to that of CaF₂ slag in terms of V-ratio of the slag and the partition of sulfur between the slag and metal phases but the dephosphorizing power of the bauxite slag was inferior to that of a CaF₂ slag. No refractory performance data have been reported.

Derge⁶¹, however, pointed out that Al₂O₃, TiO₂ and B₂O₃ are more or less acidic and therefore react with the basic refractories as well as with CaO. Their use cannot therefore be expected to improve refractory life.

2.7.3.2 MgO-Based Materials

Recently, it has become a widespread practice to add dolomitic lime or calcined dolomite as a flux in BOF steelmaking. Magnesia acts as a mild flux in steelmaking up to a point beyond which it thickens the slags.⁹⁶² Magnesia in the range of 5 to 7% will lower the fusion temperature of BOF slags and probably decrease the viscosity and speed up the
slagmaking rate. Limes\(^9\) speculates that it may be possible that \(C_2S\) does not form on the surface of the dolomitic lime when contacted by silica.

**Obinata\(^{63}\)** reported a record-breaking service life of BOF lining of 5035 heats at Nippon Steel's Kimitsu Works with MgO-supersaturated slag using soft-burned dolomitic lime. On the other hand, the typical BOF lining life in North America is about 1000 heats with the use of high silicon hot metal. He also reported that dolomitic lime has been completely substituted for fluorspar and that desulfurizing capacity of such a slag is equivalent to that of a CaF\(_2\) slag but the deposphorizing power is slightly inferior.

It is well known that if the MgO is supplied in the form of dolomitic lime, then the slag should be at least partly pacified vis à vis MgO and therefore, have less tendency to dissolve MgO from the lining. Tadsen\(^{61}\) reported that for slags nearly saturated with magnesia, the viscosity and melting temperature increased very rapidly with increased MgO. As the slag is chilled when it comes in contact with the cooler refractory wall, a heavier and more refractory-coating will form on the brick, in the case of MgO-rich slags, thus protecting the brick in the early stages of the next heat.

There are, however, reported instances of higher magnesia-containing slags having a detrimental effect on the metallurgical aspects of the steelmaking process, notably phosphorus and sulfur removal\(^{62,63}\) and a lack of rimming action.\(^{62}\) Snyder\(^{62}\) inferred that the high-MgO slags do not appear to have the oxidizing power of the lower-MgO slags for the same
wt % FeO level. Thus, the oxygen level in the steel seems to be depressed by increasing the amount of MgO in the slag. Authors have suggested that further studies under closely controlled conditions are needed before positive conclusions can be made regarding the various effects of the addition of MgO as a flux in slagmaking in the BOF.
CHAPTER III
EXPERIMENTAL

3.1 INTRODUCTION

The most common tests for refractory slag attack in the laboratory are the immersion and crucible methods. The immersion method involves a small refractory rod in contact with large quantities of corrosive slag contained in a crucible. The crucible method involves relatively large quantities of refractory in contact with small amounts of slag. In the crucible method, the slag in powder form is placed in the refractory specimen, i.e., the crucible cut from a brick. The materials are heated together to the desired temperature. In this method, accordingly, the time zero of the reaction cannot be well defined.

Both immersion and crucible methods were used whenever feasible in this work. The immersion method was exclusively used for testing slag attack of pitch-free burned magnesite brick specimens of a cylindrical shape. The crucible method was used for both pitch-free and pitch-bearing magnesite brick.

The majority of experiments were performed in a molybdenum wire-wound resistance furnace. A few experiments were conducted in a Globar furnace without a controlled atmosphere.

Cylindrical pitch-free brick specimens were visually inspected before and after immersion and their weight and dimen-
sion changes noted whenever possible. Petrographic thin sections were cut from all the reacted specimens and studied. Electron microprobe analysis was also used on these thin sections. X-ray diffraction was used to determine the phases present in the reacted brick samples but the low sensitivity restricted its utilization.

In designing the experimental set-up, attention was paid to the charging or discharging of the slag-containing crucible into or out of the furnace at temperatures as high as possible. This was necessitated in the immersion method as the crucible must be emptied whilst the slag is still fluid to avoid its breakage during the solidification of the slag. In this method it is also desirable to shorten the duration of the heating and cooling cycles so to improve the estimate of the total reaction time.

3.2 **FURNACE ASSEMBLY**

3.2.1 **Molybdenum Wire-Wound Furnace**

The furnace design is shown in Figure 18. The furnace has a double-walled outer jacket to permit water cooling. The top plate is fitted with 6", single ply stainless steel bellows to allow expansion and contraction of the refractory furnace tube. A gas entrance is located on the top plate for the introduction of the protective furnace gas, a 95:5 mixture of dried nitrogen and hydrogen. The gas outlet is located on the bottom plate.

3.2.2 **Reaction Tube Assembly**

The furnace tube is 998PT3 alumina tube (McDanel Refractory
1. Stainless steel rod
2. Gas inlet
3. Sealing cap
4. Stainless steel bellows
5. Furnace gas inlet
6. Water-cooling jacket
7. Specimen holder
8. Furnace shell
9. Refractory specimen
10. Molten slag
11. Crucible
12. Crucible support
13. Alumina tubes
14. Molybdenum wire winding

15. Alumina bubbles
16. Firebrick
17. Graphite block
18. Stainless steel rod
19. Sealing cap
20. Gas outlet
21. Thermocouple

Figure 18: Schematic diagram of furnace.
Porcelain Co.) with dimensions 25" long x 3-1/4" O.D. x 3" I.D. and is wound with 120' of 0.050" molybdenum wire over a 14" length. The molybdenum resistance wire is wound on the tube by means of a lathe, using 10 turns per inch for 2 inches, 9 turns per inch for 3 inches and 10 turns per inch for 4 inches, 9 turns per inch for 3 inches, and 10 turns per inch for 2 inches. In this manner a constant temperature zone is produced.

The working tube is 998PT212 alumina tube with dimensions 30" long x 2-3/4 O.D. x 2-1/2" I.D. and is fitted top and bottom with gas-tight water-cooled brass caps. The top cap is equipped with a sight hole, a 5/8" diameter stoppered hole for charging and discharging the refractory test specimens and a gas inlet for introduction of argon or air as required.

The bottom cap is similarly fitted with a centrally located 1/2" swagelock fitting through which the crucible support assembly is moved into or out of the furnace hot zone. The bottom cap also contains a gas outlet.

3.2.3 Crucible Support Assembly

In this work, the crucible support assembly played a key role. The assembly consists of a 1/2" diameter stainless steel rod with an end threaded into a short cylindrical graphite block. Close to the periphery of the other flat-end of the graphite block, a 1/8" wide by 1" deep groove is cut, into which a 9-1/2" long x 1-3/4" O.D. x 1-1/2" I.D. alumina tube is pressed. The slag-containing crucible is seated on the alumina tube. The other end of the stainless steel rod is attached to a pulley system allowing insertion and removal of the crucible from the furnace hot zone. The crucible, whether
a Pt-Rh crucible for the immersion method or a test brick crucible for the crucible method, could be placed directly into the hot zone at 1600°C without breaking the alumina reaction tube.

3.2.4 Refractory Specimen-Holder

The refractory specimen-holder assembly consisted of a 5/16" diameter stainless rod threaded into a graphite specimen-holder. This was used only for the immersion method. The assembly could be raised or lowered at desired rate through the stoppered hole in the top brass cap.

3.2.5 Temperature Control

Power to the furnace was supplied by a proportional power controller (Barber Coleman Series 621) driven by a null balance milli-voltmeter controller (Barber Coleman Series 520) and the control thermocouple (Figure 18). The thermocouple was placed inside a thin recrystallized alumina sheath located at the side of the furnace shell and extending into the hot zone of the furnace. The temperature profile of the furnace was determined with a vertically travelling thermocouple with a steady flow of argon through the reaction tube. The temperature profile obtained at 1600°C is shown in Figure 19. The temperature variation in the hot zone was 2°C over 1-inch and 5°C over 2 inches. The estimated error in temperature measurements was ±5°C.

3.2.6 Furnace Atmosphere

The furnace atmosphere was controlled by argon (or air), deoxidized over copper turnings at 725°C prior to admission to the furnace working tube. The flow rate of deoxidized argon was kept constant during the experiment at 500cc stp/min.
Figure 19: Temperature profile of furnace at 1600°C.
3.2.7 Globar Furnace

Preliminary work was carried out in this furnace. It was used to prefuse synthetic slags. Some experiments using both immersion and crucible techniques were carried out in a flowing argon atmosphere. Close control of the atmosphere in this furnace was impossible and its use was abandoned.

3.3 MATERIALS

3.3.1 Refractory Materials

The refractories used in this work were burned magnesite (OXIBAK H), burned pitch-impregnated magnesite brick (OXILINE B) and pitch-bonded tempered magnesite brick (OXILINE KL) supplied by Harbison-Walker Refractories of Pittsburgh, Pa., U.S.A. These are products of general BOF use. Pitch-impregnated brick was made by pitch-impregnation of burned magnesite brick. The chemical composition of the third type of brick (pitch-bonded tempered brick) is approximately that of the other two on a calcined basis. Chemical analyses and physical data supplied by the manufacturer for these bricks are given in Table 4.

Cylindrical rods of nominal size 4-1/2" long by 3/4" diameter were core drilled from pitch-free burned magnesite brick while crucibles of 2" O.D. x 1" I.D. x 2-1/2" depth were cut from the three types of brick.

Pitch-impregnated and pitch-bonded magnesite brick was tested by the crucible technique. This type of brick always required coking before an experimental run to avoid evaporation of volatile material in the pitch during the experiment. Crucibles cut from pitch-bearing brick were placed in cylindrical
Table 4: Chemical Analysis and Physical Data of Refractory Bricks

<table>
<thead>
<tr>
<th>Physical Data</th>
<th>Burned Brick</th>
<th>Burned Pitch-Impregnated Brick</th>
<th>Pitch-Bonded Tempered Brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density, Grams/cm³</td>
<td>2.96</td>
<td>3.14</td>
<td>3.12</td>
</tr>
<tr>
<td>Apparent Porosity, %</td>
<td>16.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cold Crushing Strength, kg/cm²</td>
<td>388</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Modulus of Rupture, kg/cm² – at 21°C</td>
<td>155</td>
<td>247</td>
<td>120</td>
</tr>
<tr>
<td>- at 1480°C</td>
<td>85</td>
<td>84*</td>
<td>-</td>
</tr>
<tr>
<td>Preheat Test, % Linear Change – at 1725°C</td>
<td>-0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Load Test 25 psi (1.76 kg/cm²) Withstands Load to:</td>
<td>3200°F (1760°C)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Retained Carbon After Coking to 2000°F (1093°C)</td>
<td>-</td>
<td>2.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Loss After Ignition at 2000°F (1093°C)</td>
<td>-</td>
<td>5.4</td>
<td>6.0</td>
</tr>
<tr>
<td>Apparent Porosity After Ignition to 2000°F (1093°C)</td>
<td>-</td>
<td>15.8</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Chemical Analyses

<table>
<thead>
<tr>
<th></th>
<th>Burned Brick</th>
<th>Burned Pitch-Impregnated Brick</th>
<th>Pitch-Bonded Tempered Brick</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica (SiO₂)</td>
<td>1.3</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Iron Oxide (Fe₂O₃)</td>
<td>0.9</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Lime (CaO)</td>
<td>2.4</td>
<td>2.4</td>
<td>2.3</td>
</tr>
<tr>
<td>Magnesia (MgO)</td>
<td>94.7</td>
<td>94.7</td>
<td>96.4</td>
</tr>
</tbody>
</table>

* Tests on carbon-free samples.
graphite containers 6" long x 3-1/2" O.D. x 2-1/4" I.D. and heated up to 1600°C in the Globar furnace. The weight change before and after coking was recorded.

3.3.2 Slag Preparation

3.3.2.1 Slag Composition

Slags of various compositions were made from reagent-grade chemicals and wustite. A "master slag", representative of an early BOF slag was designed on the recommendation of the American Iron and Steel Institute (AISI) Refractory Panel. It had the following composition: CaO - 46%, SiO₂ - 30%, FeO - 17%, and MnO - 7%. The "master slag" is used as a reference composition throughout this work. The compositions of all slags used in the present work are listed in Table 5.

3.3.2.2 Wustite

Chemicals for synthetic slagmaking such as CaO, SiO₂, MnO, Al₂O₃, and Fe₂O₃ are commercially available. FeO is not. The wustite used in this work was prepared by ferric oxide reduction in an iron crucible. Reagent-grade ferric oxide was melted inductively in a heavy iron crucible in air. Wustite was formed according to the reaction

\[ \text{Fe}_2\text{O}_3 + \text{Fe} = 3\cdot \text{FeO} \]

and was quenched by pouring the melt into a steel trough. Wustite product was confirmed by x-ray diffraction.

3.3.2.3 Prefusion of Slag

When the mixtures of oxide powders were melted in a refractory crucible, the melt obtained was not necessarily of the desired homogeneity. Prefusion of the slag was therefore necessary. The excessive volume of the powder mixture compared
<table>
<thead>
<tr>
<th>Table 5: Composition of Slags.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>Slag A</td>
</tr>
<tr>
<td>Slag B</td>
</tr>
<tr>
<td>Slag C</td>
</tr>
<tr>
<td>Slag D</td>
</tr>
<tr>
<td>Slag E</td>
</tr>
<tr>
<td>Slag F</td>
</tr>
<tr>
<td>Slag G</td>
</tr>
<tr>
<td>Slag H</td>
</tr>
<tr>
<td>Slag I</td>
</tr>
<tr>
<td>Slag J</td>
</tr>
<tr>
<td>Slag M</td>
</tr>
<tr>
<td>Slag N</td>
</tr>
<tr>
<td>Slag P</td>
</tr>
<tr>
<td>Slag Q</td>
</tr>
<tr>
<td>Slag R</td>
</tr>
<tr>
<td>Slag T</td>
</tr>
<tr>
<td>Slag U</td>
</tr>
<tr>
<td>Slag V</td>
</tr>
</tbody>
</table>
with that of the fused slag was another reason for prefusion.

Two hundred grams of a powder mixture was placed in a Pt-Rh crucible and introduced into the molybdenum furnace at 1600°C by a pulley arrangement. The furnace reaction tube was flushed with argon for 30 minutes before the insertion. After 30 minutes, the crucible was quickly withdrawn and emptied into a steel trough to quench the slag. It was noted that the master slag, slag V (CaO:SiO₂ = 2:1; 5% MgO), and MgO-containing slags (J, K and L) crumbled on quenching.

3.3.3 80% Platinum - 20% Rhodium Crucible

Platinum alloyed with rhodium in the ratio of 4:1 was used as the crucible material. These crucibles were 3" deep x 2" O.D. x 0.030" wall thickness. Previous investigators (64) reported rapid and extensive grain growth in pure platinum crucibles in contact with silicate slags at 1410°C and premature failure of the crucibles. This failure was attributed to the coarse metal grains (about 1/16" in diameter) falling from the base of the crucible.

3.4 EXPERIMENTAL PROCEDURE

3.4.1 Immersion Test

Cylindrical specimens of the pitch-free magnesite brick at a temperature close to 1600°C were dipped into the molten slag contained in a noble metal crucible for predetermined times in desired atmospheres. The procedure is as follows:

1. The diameter of the refractory specimen was measured in intervals of 1/4" over a distance of 3" using a micrometer. The weight of the dry specimens was
recorded. The volume measurement of the specimens was made in a volumetric cylinder with mercury. The specimen was press-fitted into the graphite holder threaded into the stainless steel rod.

2. Approximately 200 grams of well mixed powder chemicals was placed in the crucible. The crucible was then placed in the furnace at 1600°C. Previously, the reaction tube had been flushed with argon for 30 minutes.

3. The specimen holder assembly was slowly lowered at a rate of 1" per 5 minutes until the specimen was directly above the molten slag in the crucible. The assembly was maintained in this position 5 minutes to allow the test piece to come to the slag temperature. The lowering the specimen to the slag surface took ~ 30 minutes.

4. The assembly was then lowered so that the specimen was immersed in the slag melt. The clearance between the refractory rod and the bottom of the crucible was approximately 1/4".

5. After the desired length of time had elapsed, the refractory specimen was raised out of the molten slag and lifted at 1" per 5 minutes. Figure 20 is a sketch of the specimen temperature heating and cooling schedule.

6. As soon as the refractory specimen was removed from the furnace, the crucible of molten slag was withdrawn from the hot zone and emptied into a heavy steel trough. The remaining slag on the inside of the crucible was removed with warm hydrochloric acid. Failure to empty
Figure 20: Specimen temperature and heating and cooling schedule.
the crucible of fluid slag caused crucible breakage.

3.4.2 Refractory Crucible Test in a Graphite Container

Approximately 50 grams of powdered prefused slag were placed in a crucible cut from burned pitch-impregnated and pitch-bonded tempered magnesite brick. The crucible was then placed in a graphite container with a smooth fitting lid. The graphite container assembly was positioned on the Globar furnace chamber at 1600°C in flowing argon. The container assembly which was at room temperature chilled the furnace by ~ 600°C and the regaining at 1600°C took ~ 5 hours. Test specimens were maintained at 1600°C for 30 minutes, then removed from the furnace and air-cooled with a water spray. This set of experiments was carried out as a trial to avoid probable oxidation of the brick carbon by the air atmosphere during the experimental runs.

3.4.3 Refractory Crucible Test in Air Atmosphere

This experimental design was intended to see how oxidizing atmospheres affect formation of the decarburized zone and/or the dense MgO layer in pitch-bearing magnesite brick. Fifty grams of prefused slag was placed in coked crucibles of pitch-impregnated magnesite brick. The crucible was placed on the alumina tube of the crucible support assembly and brought into the 1600°C hot zone of the molybdenum furnace. The crucible was held at this position for 2 hours in an air atmosphere supplied from utility compressed air at a rate of 1000 cc stp/min. Before introduction into the reaction tube, the air was filtered and preheated through a quartz tube at 725°C. Upon removal from the furnace, the crucible was placed in a graphite
container and cooled to room temperature.

3.4.4 Examination of Reacted Specimens

3.4.4.1 Macroscopic Observations

Cylindrical carbon-free brick specimens were visually inspected before and after immersion and the weight and dimensional changes recorded. The diameter of the refractory specimens was measured at 1/4" intervals over 3" using a micrometer. The volume of the specimen was determined in a volumetric cylinder with mercury.

After 30 seconds immersion in the slags at 1600°C, the weight and length of the reacted specimens increased. The weight gain was due to absorption of slag by brick specimens during immersion. Length gain was due to the creep deformation of weakened specimens during withdrawal. The total weight gain divided by the initial volume of the portion of specimen under the slag-line was listed as the "pénétration". The portion of specimen under the slag-line during immersion was calculated by comparing the original total length and that to the top to the initial slag-line obtained by measurement. The measured change in total length of the specimen divided by the original length of the portion under the slag-line was listed as the "elongation". Low magnification photographs were found to be useful for realistic presentation of the slag attack on carbon-free and carbon-bearing magnesite brick specimens.

3.4.4.2 Microscopic Observations

Thin sections were cut from all the reacted specimens and as-received brick samples and studied with the petrographic microscope. The great advantage of the thin
that it reveals the constituent phases in their original location. Under the microscope, the periclase, silicate and carbon phases and pores can be differentiated. The periclase appears dark under crossed nicols since it is an isotropic mineral, whereas the silicates appear bright under crossed nicols due to their high birefringence. Carbon is opaque.

The pattern of slag penetration into the brick specimen is appreciated by observing the brown iron oxide coloration. However, due to the variation of thickness of the thin sections, the intensity of coloration alone could not be used to quantitatively indicate iron oxide concentrations. Thin sections of the samples which had survived 5 minutes immersion were cut from those portions of the specimen rods which had been submerged in the slag. With brick specimens that disintegrated in the 5 minutes reaction, petrographic sections were made from the remaining portions of the rods, i.e. from the portion above the slag-line.

3.4.4.3 Electron Probe Analysis

Composition gradient profiles of thin sections of brick specimens were traced with an electron microprobe (ACTON CAMECA MS-64) equipped with an automatic stage drive. The transversing speed was 0.62 mm/min. and data were recorded on a 2-pen strip chart recorder. Actual percentages are not given because the data are not calibrated against proper standards and hence the results obtained are qualitative. The use of thin sections on the electron microprobe has unavoidably resulted in fallible Si pick-up from the glass slide at the voids in the refractory thin section. This can be readily
detected, however, by checking the corresponding intensity of Mg. This technique has been found powerful in the detection of slag penetration into the brick, particularly in the region of the brick/slag interface of the carbon-bearing brick test samples.
CHAPTER IV
EXPERIMENTAL RESULTS

4.1 INTRODUCTION

Due to the nature of the experiments carried out in the present work, some results which cannot be quantified easily, are presented in the form of photographs. It is considered that pictorial presentation in these cases is certainly the best way in recording the results objectively and completely.

In the order of presentation, tests on carbon-free specimens in immersion experiments will precede that on BOF/brick using the crucible method. In each case the results of macroscopic observations will be followed by that of microscopic examinations.

4.2 IMMERSION TESTS OF CARBON-FREE BRICK

The composition of various slags used in these experiments are listed in Table 5. For each slag, the time of immersion of the specimens at 1600°C was 30 seconds and 5 minutes, except for the master slag which time was up to 100 minutes. The reaction time of 5 minutes was found to be useful in showing the various extents and modes of attack on the same kind of brick by different slags at the same temperature, as shown in Figure 22. The experiments involving a 30 second reaction time were designed to assess the variation in slag penetration by differ-
ent slags as shown in the partially sectioned specimens of Figure 23. The height of slag climb with reference to the initial slag line and the elongation of the specimens can be seen in these photographs. These observations are also summarized in Table 6, Figure 26 and 27 in quantified form. The details of the immersion experiment results are as follows.

**Master Slag:**

Figure 21 shows a series of 5 brick specimens which were immersed in the master slag in the Globar furnace with flowing argon, for reaction times ranging from 20 to 100 minutes in intervals of 20 minutes. They appear similar except for the extent of dissolution at the 3-phase contact line slag-refractory-atmosphere.

Close visual examination of the reacted specimen surfaces shows that large grains with dark slagged skin stand out to give a knobbly surface. Large grains seem to withstand slag attack more effectively than the matrix around them.

**Al$_2$O$_3$-Containing Slags:**

The appearance of specimens after 5 minutes immersion in Al$_2$O$_3$-containing slags is shown in Figure 22. No specimen survived 5 minutes in slags containing 10% or more Al$_2$O$_3$. The ability of Al$_2$O$_3$-containing slags to climb above the slag-line is clearly shown. Some specimens weakened to the extent of breaking off, even at locations above the slag-line. This clearly illustrates the detrimental effect of Al$_2$O$_3$ in calcium silicate slags on magnesite brick.

**MgO-Containing Slags:**

Brick specimens survived the 5 minute reaction time in
**Table 6: Specimen elongation, slag climb and penetration**

<table>
<thead>
<tr>
<th></th>
<th>Elongation (%)</th>
<th>Climb (cm)</th>
<th>Penetration (g/m cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag A (Master Slag): 46% CaO, 30% SiO₂, 17% FeO, 7% MnO</td>
<td>1.7</td>
<td>1.84</td>
<td>0.45</td>
</tr>
<tr>
<td>Slag B: 95% Slag A + 5% Al₂O₃</td>
<td>2.2</td>
<td>2.72</td>
<td>0.51</td>
</tr>
<tr>
<td>Slag C: 90% Slag A + 10% Al₂O₃</td>
<td>4.6</td>
<td>5.00</td>
<td>0.61</td>
</tr>
<tr>
<td>Slag D: 85% Slag A + 15% Al₂O₃</td>
<td>6.3</td>
<td>4.25</td>
<td>0.66</td>
</tr>
<tr>
<td>Slag E: 85% Slag A + 10% Al₂O₃ + 5% MgO</td>
<td>3.2</td>
<td>3.17</td>
<td>0.49</td>
</tr>
<tr>
<td>Slag F: 77% Slag A + 15% Al₂O₃ + 8% MgO</td>
<td>-</td>
<td>2.17</td>
<td>0.46</td>
</tr>
<tr>
<td>Slag G: 77% Slag A + 10% Al₂O₃ + 15% MgO</td>
<td>1.4</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>Slag H: 70% Slag A + 15% Al₂O₃ + 15% MgO</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Slag J: 95% Slag A + 5% MgO</td>
<td>0.37</td>
<td>1.79</td>
<td>0.44</td>
</tr>
<tr>
<td>Slag K: 92% Slag A + 8% MgO</td>
<td>0.34</td>
<td>1.73</td>
<td>0.38</td>
</tr>
<tr>
<td>Slag L: 87% Slag A + 13% MgO</td>
<td>0.80</td>
<td>1.54</td>
<td>0.45</td>
</tr>
<tr>
<td>Slag N: 38% CaO, 38% SiO₂, 17% FeO, 7% MnO</td>
<td>9.82</td>
<td>2.23</td>
<td>0.55</td>
</tr>
<tr>
<td>Slag P: 46% CaO, 30% SiO₂, 17% Fe₂O₃, 7% MnO</td>
<td>1.98</td>
<td>4.39</td>
<td>0.47</td>
</tr>
<tr>
<td>Slag Q: 90% Slag P + 10% Al₂O₃</td>
<td>1.53</td>
<td>3.85</td>
<td>0.38</td>
</tr>
<tr>
<td>Slag R: 77% Slag P + 15% Al₂O₃ + 8% MgO</td>
<td>1.03</td>
<td>1.62</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Slag A (Master Slag)*: 46% CaO, 30% SiO₂, 17% FeO, 7% MnO

Slag C*: 90% Slag A + 10% Al₂O₃

Slag F*: 77% Slag A + 15% Al₂O₃ + 8% MgO
MgO-containing slags, J (5% MgO), K (8% MgO) and L (13% MgO) in the absence of Al₂O₃. From Figures 22 and 23, it can be seen that MgO in the slag moderates the detrimental effect of Al₂O₃. For the case of 30 seconds immersion, the depth of slag penetration in this series was less than that of the master slag (Figure 23).

With a relatively low MgO content (up to 8%) in the Al₂O₃-containing slags, the effect of the MgO addition was not pronounced (Figure 22). This is illustrated by the disintegration of the brick specimens and the climbing of slag above the slag-line. However, slag G (10% Al₂O₃-13% MgO) and H (15% Al₂O₃-15% MgO) caused granular separation from the surface resulting in reduced specimen diameter and a rough surface (Figures 22 and 24). The climbing tendency of slag above the slag-line was substantially reduced. Beyond a certain MgO level in Al-Ca silicate slag, the MgO addition was beneficial for the resistance of samples to slag attack.

Oxidation State of Slags:

Slags P, Q, and R were made, by substituting FeO in slags A (master slag), C (10% Al₂O₃), and F (15% Al₂O₃-8% MgO), respectively by Fe₂O₃, as shown in Table 5. In terms of the slag resistance of the refractory specimens, these two series showed the same order of corrosivity: brick specimens reacted with slags A and P survived the 5 minute tests whilst specimens reacted with slags C, F, Q and R, disintegrated (Figure 22).

It is interesting to note, however, the marked difference in the height of climb of
slags, the climb of slags Q and R (containing Fe$_2$O$_3$) were less than C and F (containing FeO). The effect of Al$_2$O$_3$ is evident.

**Basicity of Slag**:

The influence of slag basicity on the refractory attack was investigated. To compare with the master slag, the CaO/SiO$_2$ ratio was adjusted to be 2:1 (slag M) and 1:1 (slag N), respectively. The FeO and MnO were kept constant at 17% and 7%.

The result of immersion tests of refractory specimens in slag N was remarkable (Figure 22). The specimen broke during the 5 minute reaction time, in striking contrast to the 100 minutes immersion results in the master slag (CaO/SiO$_2$ = 1.5) (Figure 21). The shape of the broken end of this specimen (Figure 22) is uniquely pointed. The climb of slag above the slag-line was comparable to that of the master slag. On the other hand, slag M (CaO/SiO$_2$ = 2) did not melt at 1600°C under the same experimental conditions. The immersion test could not be carried out with this slag composition.

**Effect of CaF$_2$ in Slag**:

Slag I, consisting of 85% master slag and 15% CaF$_2$, was designed to determine the influence of CaF$_2$ on refractory attack vis-à-vis other fluxes. The immersion test was unsuccessful due to slag climb out of the noble metal crucible, as reported in the literature. (65)

The crucible test with slag I was conducted and the depth of penetration into the wall of a carbon-free magnesite brick crucible was comparable with slag B (5% Al$_2$O$_3$) and E (10% Al$_2$O$_3$ - 5% MgO).
4.2.1 Effect of Temperature

To evaluate the effect of temperature on the resistance of a refractory specimen to slag attack, experiments were performed at 1550°C under the same experimental conditions.

At 1550°C, brick specimens survived a 5 minute immersion in slags A (master slag), C (10% Al₂O₃) and F (15% Al₂O₃ -8% MgO) (Figure 25). In contrast, specimens disintegrated after a 5 minute immersion in slags C and F at 1600°C. The climb of each slag was substantially reduced at the lower temperature.

4.2.2 Slag Penetration and Climb

After a 30 second immersion in the slags at 1600°C, the weight and length of reacted specimens increased. The weight gain was due to absorption of slag by the specimens during immersion. The total weight gain divided by the initial volume of the portion of specimen under the slag-line was listed as the "penetration" in Table 6 and is plotted in Figure 27.

The length gain of the specimens is believed to result from the deformation of weakened specimens in response to gravity during withdrawal. The temperature-time relationship in this period was shown in Figure 20. The portion of specimen under the slag-line during immersion can be calculated by comparing the original total length with that of the top to initial slag-line obtained by measurement (Figure 23). The measured total length change of the specimen divided by the original length of the portion under the slag-line is listed as "elongation" in Table 6 and graphically represented in Figure 26.

As shown in Figure 22, the specimens broke at below or above the initial slag-line in the high Al₂O₃ slags and the
low Al₂O₃/MgO ratio, slags E (10% Al₂O₃ - 5% MgO) and F (15% 
Al₂O₃ - 8% MgO). The climb of slag above the slag-line of the 
brick specimens was measured and is listed in Table 6 and 
graphically represented in Figure 26. The height of the slag 
climb above the slag-line increased with Al₂O₃ content and 
decreased with increasing ratio of MgO to Al₂O₃ in the slag. 
Climb of slag appears highest in the Al₂O₃-rich cases and low-
est in the MgO-rich cases. Low Al₂O₃/MgO ratio slags (E and F) 
fell between these extremes. Slag N (CaO/SiO₂ = 1) climbed the 
least.

4.2.3 An Index of Hot Strength and the Failure of Specimens

During withdrawal of the specimen following immersion, it 
was under a tensile stress due to its own weight and that of 
the penetrated slag. As shown in Figure 20, the temperature 
of specimens decreased gradually on lifting from the hot zone 
(Standard Procedure - Section 3.4.1). It is conceivable that 
during the period when the temperature was high enough to pro-
mote fluxing of the bonding phase, by the penetrated slag, a 
highly viscous "mushy" liquid was formed. Unbroken or loosely-
bonded specimens may be the result of the viscosity of the 
silicate liquid being high enough to hold the periclase grains 
together. Consequently, elongation may be an index of the 
relative hot strength or creep resistance under the attack of 
various slags. The temperature-time relationships in all the 
experiments were carefully controlled to be identical.

Slag penetration over nearly the entire cross-section 

was in the of to o
the two specimens reacted with high MgO/Al₂O₃ ratios (G and H) slags were in striking contrast to the others. Partial penetration of the slag into the brick specimens led to peripheral disintegration or granular separation with an intact central portion (Figure 24).

Furthermore, large MgO grains disrupted from specimens were found in the slags (particularly D, E and F) maintained at 1600°C for 30 minutes (Figure 28). It is believed that these are evidence that the attack of magnesite brick in contact with highly fluid slags is by disruption of the periclase grains out of the brick rather than the dissolution of magnesia.

4.3 MICROSCOPIC EXAMINATION OF CARBON-FREE SPECIMENS

The experimental results described so far are based on macroscopic observations. These will be further elucidated by microscopic observations.

For comparison, a thin section micrograph of an as-received brick is also included (Figure 29).

Under the microscope, the periclase, silicate, carbon phases and pores can be differentiated. The periclase appears dark under crossed nicols since it is an isotropic mineral, whereas the silicates appear bright due to their high birefringence. Carbon is opaque. The pattern of slag penetration into the brick specimen is traced by the brown iron-oxide coloration. However, due to the variation of thickness of the thin sections, the intensity of coloration alone cannot be used to quantitatively indicate the iron concentration. The slag can penetrate the specimens from the external surface via open
channels and connected pores. From these secondary sources within the specimen, the spread of slag to the rest of the specimen through the matrix takes place relatively slowly.

It should be pointed out that thin sections of samples which had survived the 5 minute immersions (Figure 22) were cut from those portions of the specimen rods which had been submerged in the slag. With brick specimens that disintegrated in the 5 minute reaction, petrographic sections were made from the remaining portions of the rods, i.e., from the portion above the slag-line.

**Magnesite Brick As-Received**

In commercial magnesite brick the coarse grains of periclase are polycrystalline and the subgrain boundaries are veins of silicate phase (Figure 29). The silicate of the matrix in this magnesite refractory is essentially C₂S (dicalcium silicate). Pores are also seen (Figure 29).

**Specimens Reacted with Master and MgO-Containing Slags**

With the master slag, even after 100 minutes of reaction, the coarse grains of periclase were unattacked by the slag. The external surfaces of these grains were stained yellow due to MW (magnesiowustite) formation. Following 5 minutes' immersion in the master slag, highly localized black areas were noted while the rest were slightly colored (Figure 30). Retained iron oxide is typically found at grain boundaries, boundary cracks and in the matrix. MgO-containing slags show a similar morphology (Figure 31), but the spreading of the iron oxide is more uniform and the crystallization better developed
Specimens Reacted with Al₂O₃-Containing Slags

With increasing Al₂O₃ in the slag, both penetration and refractory disruption increased (Figure 32). The elongation and break-off phenomena seemed to be accompanied by the creation of void space by localized creep and separation of the matrix. Opacity as a result of iron oxide coloration is lower than for the master and MgO-containing slag series. The slag has been widely spread out. The high degree of reaction and dissolution of the matrix has created large voids in some areas. Dendrites are observed, which could be Ca-Al-silicate type compounds such as C₂AS (gehlenite) or melilite (C₂AS-C₂MS₂ solid solution) (Figure 33).

Specimens Reacted with Al₂O₃/MgO-Containing Slags

Similar high degrees of reaction in many areas of the matrix were observed with slag F which contains intermediate levels of Al₂O₃ and MgO (Figure 34). Typically, large areas are crystallized with common extinction indicating a higher degree of crystallization as compared with the Al₂O₃-containing slags.

In contrast, it is interesting to note that for samples reacted with the two slags of high MgO content (slags G and H) (Figures 24 and 35), the slag penetration is restricted to a shallow periphery. The overall degree of reaction is substantially reduced. Many small areas show Ca-Al-silicate compounds (Figure 36). No large areas of extinction are noted, indicating that the slag was partially solidified.

Specimens Reacted with Fe₂O₃-Containing Slags

The microstructural characteristics of specimens reacted
with Fe$_2$O$_3$-containing slags are similar to those of FeO-containing slags vis à vis the additions of Al$_2$O$_3$ and Al$_2$O$_3$/MgO. However, extensive spreading of the slag is observed with relatively little reaction, particularly with the periclase grains (Figure 37). Periclase grains are stained but not corroded, reflecting the formation of MF (magnesioferrite).

The specimen (Figure 38) which was reacted with Fe$_2$O$_3$-slag Q (10% Al$_2$O$_3$) shows a similar degree of spreading of slag through the specimen, i.e., complete penetration. Again, a high degree of reaction with the matrix is noted but is less than that for the FeO slag C (10% Al$_2$O$_3$). Dendritic crystallization is evident (Figure 39). The specimen (Figure 40) reacted with Fe$_2$O$_3$-slag R (15% Al$_2$O$_3$-8% MgO) shows a moderate degree of matrix reaction and little reaction with the periclase, resulting in reduced disruption.

**Specimens Reacted with Slag N (CaO/SiO$_2$ = 1)**

In parallel with the Al$_2$O$_3$-rich slags, the extreme case is the specimen reacted with slag N (CaO/SiO$_2$ = 1) (Figure 41). This section shows the highest degree of matrix dissolution and periclase corrosion (Figure 42). Fines in the matrix have disappeared completely in some areas. Well-crystallized monticellite (CMS) is evident from the lower birefringence and the composition of the slag (Figure 42). This may have formed by complete dissolution and recrystallization. There are many voids but less disruption than for the high-Al$_2$O$_3$ slags.

**Specimen Fragments Recovered from Slag**

The large fragments of the broken specimens which fell into and remained in the slag during the experiments were re-
covered for making thin sections. The fragments (slag D, 15% 
Al₂O₃) (Figure 28) appear similar to those portions of the sam-
ples remaining in the specimen holder, except for less disrup-
tion of the bonding matrix or across the periclase grains.

Slag and reaction products in the matrix of MgO grains
are fully crystallized. There is no indication of any further
reaction with the periclase grains, though these broken pieces
had been in the slag for an extra 30 minutes at 1600°C.

**Slag-Penetrated Zone, in Carbon-Free Brick**

Figure 43 shows some interesting features in the micro-
structure of the specimen reacted with slag H (15% Al₂O₃-15% MgO)
for 30 seconds by the immersion test. The portion which was sub-
merged in the slag shows a brown slag-penetrated outer layer of
non-uniform thickness. There is no sharp boundary between the
colored layer and the uncolored core. Nevertheless, the dense
core was absent in the portion which was above the slag-line
and did not contact the slag.

Under the microscope, the texture in the dense but uncol-
ored core was observed to be very different from that of as-
received brick samples which are similar to the upper portion
in Figure 43. The amount of silicate phase, which has filled
up the pores, has greatly increased in the core region. The
silicate phase in the core is connected to the brown slag pene-
trated layer (Figure 43(b)). It seems that part of silicate
slag has penetrated the specimen extensively without the iron
and manganese oxides. However, the microstructure of the coarse
MgO grains in the dense core remained the same.
men, tested by the standard experimental procedure except for a very rapid removal from immersion to room temperature, showed that the core was only partially densified and penetrated by the silicate (Figure 44(a)). A brick specimen which underwent the same experimental procedure except for 5 minutes, shows complete penetration of the silicate across the section (Figure 44(b)). The thickness of the brown coloration at the periphery of the specimen is the same for the three cases.

4.4 ELECTRON MICROPROBE ANALYSIS OF CARBON-FREE SPECIMENS

Figure 45(a) shows graphically the concentration profile of the constituent elements in an unreacted pitch-free magnesite brick. From these profiles, it is clear that Mg, Fe and Mn go together whilst Ca, Si and Al go together in the magnesite brick, i.e., Fe and Mn in the MgO grains and Ca, Si, and Al in the matrix of the brick.

Figure 45(b) shows the transversal concentration gradients in a brick specimen reacted with slag H (15% Al$_2$O$_3$-15% MgO) on a cross-section cut through the center of the cylindrical specimen. As in the case of the unreacted brick specimen, Mg, Mn and Fe go together but Fe and Mn have steep concentration gradients downward from the specimen surface towards the center. This is consistent with the variation of a color. Ca, Si and Al have almost the same peak concentration between the center and the surface in the matrix of the specimen, i.e., show no concentration gradient throughout the cross-section. This is consistent with the evidence under crossed nicols (Figure 43(b)).

The of the other s showed almost the same
peak concentration following the reaction with the master slag, with or without the $\text{Al}_2\text{O}_3$ addition. The boundary of the densified region above the slag-line, however, was located higher than the boundary of coloration.

4.5 SUMMARY OF IMMERSION TESTS WITH CARBON-FREE BRICK SPECIMENS

$\text{Al}_2\text{O}_3$ in a calcium silicate slag is detrimental to magnesite refractories as a result of weakening the silicate bond. This is believed due mainly to formation of Ca-Al-silicate compounds which are low-melting and highly fluid at 1600°C. Beyond a certain MgO level in a Ca-Al-silicate slag, the MgO addition was beneficial and the resistance of refractory samples to slag attack increased. In terms of slag resistance, the oxidation state of the slag played no obvious role. The basicity of slag in terms of $\text{CaO}/\text{SiO}_2$ ratio is the most critical factor in terms of the corrosiveness of the slag, i.e., a low basicity slag attacked not only the silicate bond but also the periclase grains. The temperature is also a significant factor in the slag resistance of refractory specimens, i.e., with decreasing temperature, the slag resistance of the refractories increases.

4.6 CRUCIBLE TESTS OF CARBON-BEARING REFRACTORIES

The crucible method was exclusively used in the studies of carbon-bearing refractories. Crucibles (2-1/2" deep x 2" O.D. x 1" I.D.) were cut from pitch-impregnated and pitch-bonded tempered brick. The immersion technique was not used to avoid probable damage to the platinum-rhodium crucible, by the iron resulting from the reduction of iron oxide in the slag by carbon.
Some authors proposed that an oxidizing furnace atmosphere may be responsible for the formation of the decarburized zone in these refractories observed universally in BOF practice. Others report the existence of a dense MgO layer within the decarburized zone in oxidizing atmospheres such as air and CO₂ but not in neutral or reducing atmospheres such as He, Ar, N₂ or CO in their laboratory tests with BOF slag. Therefore, in this work both atmospheres will be utilized in an attempt to resolve the controversy.

Several authors have observed dense layer formation in brick, in contact with slag in the laboratory, and for one case in industrial practice. Others (3,4,34,25,21) have suggested that the slag component oxides, particularly, iron oxide may oxidize the carbon in the brick. Since iron oxide has a far higher oxygen potential than any of the other constituents in the slag, both iron oxide-containing and iron oxide-free slags were used in this work.

4.6.1 Tests with Oxidizing Slags in Flowing Air Atmosphere

Flowing air is considered sufficient to maintain the oxygen potential of the slag. This series of experiments showed the formation of a dense MgO layer within the decarburized zone in the brick for various slag compositions.

Figure 46 shows cross-sections cut through the center of crucibles (made from the brick of the brand name OXILINE B) after 2 hours in a molybdenum furnace at 1600°C. In this figure specimens are arranged from left to right as follows: the crucible has reacted with (1) no slag, (2) slag C (10% Al₂O₃), (3) slag F (15% Al₂O₃ ~8% MgO), (4) slag N (CaO/SiO₂ = 1), and
(5) slag V \((\text{CaO}/\text{SiO}_2 = 2)\). Due to the higher melting point of slag V, \(1650^\circ\text{C}\) was the temperature used.

As illustrated in this figure, the region near the outer surface of the crucibles in direct contact with the flowing air atmosphere has suffered decarburization. With various slags, a distinctive white zone exists due to the absence of carbon between the slag phase and the bulk of crucible wall. Under closer examination, these white zones are located between the slag-penetrated region and the unreacted interior of the refractories. These are generally referred to as the "decarburized zone" in the literature.

Crucibles reacted with the master slag and slag V show the characteristic feature of disintegration, unlike the fracture and cracking due to a thermal shock. This might be due to "dusting" of the slags in coating. Dusting is believed due to the formation of \(\text{C}_2\text{S}\). Attack by this type of slag (master slag and V) appears the least serious of the slags used in this series of experiments.

The crucibles reacted with slags C \((10\% \text{Al}_2\text{O}_3)\), F \((15\% \text{Al}_2\text{O}_3 - 8\% \text{MgO})\), and N \((\text{CaO}/\text{SiO}_2 = 1)\) show severe attack. The solidified slags in the crucible are very porous possibly due to gas generation. Slag overflow down the surface of the crucible is also visible. Surfaces covered by oxidizing slags have less carbon removal than for direct contact with air (Figure 46). For the slags used presently, the relative standings vis à vis attack of carbon-bearing refractories are the same as the carbon-free brick.
4.6.2 Tests with Iron Oxide-Free Slags in Air Atmosphere

The same experimental procedures were followed using different slag compositions. Replacement of FeO in the A, C, and F slags of the master slag series with CaO and SiO₂ resulted in slags S, T and U. This new series of slags have the CaO/SiO₂ ratio = 1.5 as before. Slag S did not melt at 1600°C.

Figure 47 shows the crucibles following reaction with slag T (50.7% CaO, 33.0% SiO₂, 6.3% MnO and 10.0% Al₂O₃) and U (48.3% CaO, 28.3% SiO₂, 5.4% MnO, 15.0% Al₂O₃, and 8.0% MgO). Most remarkable is the absence of the "decarburized zone" as defined in the last section and the honeycomb porosity in the solidified slag. No overflowing of slag has occurred and the carbon seems unaffected. In the carbon-bearing region adjacent to the slag/brick interface, a densified layer, in a sense of filling up pores by slag is found, of ~2mm thickness. Microprobe analysis will confirm that the densified layer is the result of slag penetration. Such a layer is better defined and more consistent in thickness with crucibles reacted with slag T (Figure 47 (KT120A)) than with slag U (Figure 47 (KU120A)).

4.6.3 Tests in Reducing Atmosphere

A highly reducing atmosphere was obtained by placing the crucible specimen inside a closed graphite container to avoid oxidation of the brick carbon and slag by the air atmosphere during the experimental runs.

Results obtained for these experimental conditions are shown in Figure 48 and no significant refractory wear is evident. The influence of the variation of slag composition is not obvi-
indicates the slag to be in direct contact with carbon in the brick. Small dispersed iron droplets were observed in the solidified slag ([15% Al₂O₃-15% MgO] (Figure 48 (KH30R)) and a single iron sphere was found on the bottom of the crucible for slag D ([15% Al₂O₃] (Figure 48 (KD30R))). The master slag became a powdery mixture containing extremely fine iron droplets.

The amount of slag in each experiment was limited, hence, there was no way to maintain the levels of iron and manganese oxides in the slag during the course of experimentation. The color of the solidified slag after the experiments was the light green characteristic of manganese oxide-containing slags.

An altered layer was observed (more dense and glassy), to form in the carbon-bearing region adjacent to the hot face (Figure 48). This layer was 2 to 8 mm thick. Without slag, this layer was unobserved (Figure 48 (K30R)). The observation of this layer above the slag-line for the partially slag-filled crucible is the result of the initial packing of the slag powder. The thickness of this layer with slag D ([15% Al₂O₃] (Figure 48 (KD30R)) and slag H ([15% Al₂O₃-15% MgO]) (Figure 48 (KH30R)) is generally thicker than for the master slag (Figure 48 (KA30R)). The altered layers formed with slags of this series are generally thicker and more recognizable than those formed with the iron oxide-free slags of the previous section.

On the other hand, pitch-impregnated brick crucibles decarburized in air were tested with the master slag and slag D ([15% Al₂O₃]) under the same reducing conditions. Slag penetration into the brick crucibles was substantially reduced compared
tainer protection. Iron droplets were also found in this case. The significant influence of reducing atmospheres may have been to simply change the slag by eliminating the major portion of iron and manganese oxides therefrom. It is interesting to note that the cross-section of those carbon-free crucibles which were not penetrated by slag underwent a drastic color change from dull yellow to light gray. As a spot-check, the white gray crucibles were heated in the air and the color returned to the original. This reversible color change is due to the change in oxidation state of the iron oxide in the brick.

4.7 MICROSCOPIC OBSERVATIONS OF CARBON-BEARING SPECIMENS

Figure 49 shows a typical thin section micrograph of a pitch-impregnated brick coked in a graphite container at 1600°C for 30 minutes. Carbon is observed between the coarse MgO grains and fines but not within them. The bulk carbon content may be uniform throughout. This clearly demonstrates that channels through which the slag could penetrate into the brick would be abundantly available on carbon burnout. Some isolated pores not penetrated by pitch are also noticed.

4.7.1 Empty Crucible Reacted with Flowing Air Atmosphere

Figure 50 shows a thin section micrograph of a pitch-impregnated brick specimen which has been maintained at 1600°C in a flowing air atmosphere for 2 hours. The thickness of the decarburized layer in this specimen is 1 to 3 mm. When the same experiment was repeated at temperatures slightly below 1000°C, no carbon was left in reacted specimens of same dimen-
rate of decarburization by flowing air for the 2 hours is much lower at 1600°C than observed at lower temperatures. The explanation of this phenomenon will be given later.

The region near the outer surface of the crucible which has been depleted in carbon appears similar to the unaltered carbon-bearing interior (Figure 49). There is a transient region with a gradient of carbon concentration (Figure 50). At the fringe of the outside carbon-bearing region MgO grains are observed to be connected. The MgO grains have bridged one to another in a row, similar to the necks observed in sintered ceramic particles (Figure 50). The diameter of the neck is ~0.2 to 0.4 mm. In the matrix of the transient region just behind the continuous MgO layer, (which is referred to as the "dense layer" or "dense MgO layer" in the literature), carbon and MgO particles exist. The fines have become extremely diffusive or etched and the porosity seems to have increased considerably. Extensive cleavage cracks or grain-growth have developed in the decarburized zone (Figure 52(c)).

4.7.2 Crucibles Reacted with Iron Oxide-Containing Slags

Figure 51 shows micrographs of thin sections of carbon-bearing crucibles reacted in an air atmosphere for two hours with slags N (CaO/SiO₂ = 1) and C (CaO/SiO₂ = 1.5; 10% Al₂O₃) at 1600°C and slag V (CaO/SiO₂ = 2) at 1650°C. The slag corrosion of the crucible makes it difficult to identify or define the exact location of the slag/brick interface.

In the slag phase close to the refractory surface, many round voids are observed (Figure 51(a)), i.e., gas bubbles trapped in the slag. This has been observed visually as honey-
combs in the solidified slag phase of the same sample.

Detailed microscopic investigations reveal that the microstructure of the carbon-depleted regions are highly porous with a dominant presence of silicate phases behind the dense MgO layer (Figures 52(a) and (b)). These silicate phases extend into the carbon-bearing region of the brick crucible to a depth of 1 to 2 mm. Carbon, MgO grains (particularly the fines) and silicates do not show any regular pattern of distribution throughout this zone. In contrast, the necks which bridge the MgO grains, constituting part of the dense layer, appear almost free of silicate. The results of microprobe analysis will be given later.

The location of the dense layer follows the slag/refractory interface contour or the outer surface when reacted with iron oxide-containing slags. The location of the MgO layer in the empty crucible specimens decarburized by air (Section 4.6.1) follows the boundary of the remaining carbon.

A comparison of the features of the dense MgO layer and the decarburized zone in Figures 52(a), (b) and (c) is fruitful. The dense MgO layer with slag V (CaO/\text{SiO}_2 = 2) is relatively thick and uniform, and a well-defined boundary exists. The layer with slag N (CaO/\text{SiO}_2 = 1), on the other hand, is very thin, poorly-defined and of less uniform thickness. The layer with slag C (CaO/\text{SiO}_2 = 1.5) is well-defined but thin at locations between the coarse MgO grains. It is further noticed in the figure that the dense layer with slag V shows extensive cleavage cracks and almost no refractory attack. With slags of N and C, the dense layer is free of cleavage cracks and
the attack is considerable.

4.7.3 **Crucibles Reacted with Iron Oxide-Free Slags**

Figure 53 shows micrographs of thin sections from carbon-bearing crucibles reacted with iron oxide-free slags T (10% Al₂O₃) and U (15% Al₂O₃-8% MgO) in the air atmosphere at 1600°C for 2 hours. Carbon near the surface which was covered by slag has not been attacked and no decarburized zone has formed. Instead, the slag which is a weak oxidizing agent for carbon, has penetrated through the defects and pores. The depth of slag penetration into the specimen is ~3 to 4 mm.

In the slag phase near the hot face, fine opaque spherical and angular particles are noted in addition to gas bubbles. The spherical particles are believed to be the metal droplets and the particles of angular shape to be carbon disrupted from the matrix of the brick. Slag T is very corrosive to the silicate bond of the brick due to the presence of alumina while MgO-containing slag U is far less deteriorous (Figure 53). The extent of disintegration of MgO grains from the brick and the subsequent dispersion of the MgO grains and subgrains in the slag phase by these iron oxide-free slags is much smaller than for the iron oxide-containing slags of the previous section.

4.7.4 **Crucibles Reacted with Iron Oxide-Containing Slag in Reducing Atmosphere**

Figure 54 shows micrographs of thin sections of a carbon-bearing crucible reacted with slag D (15% Al₂O₃) in the graphite container for 30 minutes at 1600°C. The microstructure is characteristically similar to that of the specimen reacted with slag T (Figure 53(a)) of the prev...
ference noted is that the slag/refractory interface is better defined due probably to far less attack. This may be expected for the shorter reaction time of 30 minutes in this case.

Neither a decarburized zone nor a dense MgO layer has been observed in these crucibles in reducing atmospheres. Figure 54(b) is a micrograph taken from the same thin section as Figure 54(a) but under crossed nicols. The light area in the brick surrounding the slag/brick interface is observed to be a silicate phase originating in the slag.

4.8 ELECTRON MICROPROBE ANALYSIS

Figure 55 shows results of microprobe analysis for the constituent elements in a pitch-impregnated brick sample coked at 1600°C in a graphite container for 30 minutes. It will be used as a reference when the results of other reacted specimens are discussed. On the whole, the concentration profile is remarkably similar to Figure 45(a). However, sporadic rises of pointed intensity of Fe are noticeable unlike the pitch-free specimen. Working conditions of the microprobe were 100 m.a. beam current, 15 KVA beam voltage and 150 n.a. specimen current.

4.8.1 Empty Crucible in Flowing Air Atmosphere

Figure 56 shows the microprobe analysis of a carbon-bearing brick crucible heated at 1600°C in an air atmosphere for 2 hours. The profile is still similar to Figures 45(a) and 55 (carbon-free and coked samples). Like Figure 55, sporadic rises of pointed intensities of Fe are noted. No obvious change in concentration profile, particularly Mg and Si, are observed over
4.8.2 Crucibles Reacted with Iron Oxide-Containing Slags

Figure 57 shows the microprobe analysis along the line G, H and I (which are labelled in Figure 51(b)) over a well-defined dense layer formed in a carbon-bearing crucible reacted with slag C (10% Al₂O₃) for 2 hours at 1600°C in an air atmosphere. At the right end of the strip charts, the bundles of high intensities of Ca, Si, Al, Mn and Fe are for the outer regions of the specimen penetrated by slag. It is noticed that the concentration gradient of Ca, Si and Al changes abruptly at the slag/dense MgO layer interface. In a similar fashion to Figure 45(b), there are steep concentration gradients of Mn and Fe downward into the dense MgO layer. This is considered to arise from an iron oxide-stained MgO grain in the microstructure. The use of the tracer Al₂O₃ in the slag and the result in Figure 57 leads to an important conclusion, i.e. the slag penetration has been stopped at the dense layer and the dense layer of MgO is impermeable as far as the slag is concerned.

Figure 58 is the result of probe analysis along the lines D, E and F over a decarburized zone which is apparently void of a dense layer (Figure 51(a)). This specimen was from a carbon-bearing crucible reacted with slag N (CaO/SiO₂ = 1) in an air atmosphere for 2 hours at 1600°C. At the right end of the strip charts, the bundles of lines correspond to high concentrations of Ca and Si in the slag phase. In comparison with Figure 57, a gradual concentration gradient of Ca and Si has extended into the decarburized zone of the brick. However,
4.8.3 Crucibles Reacted with Iron Oxide-Free Slags

Figure 59 shows the results of microprobe analysis along the lines J, K and L of Figure 53(a) over the slag/refractory interface region. This specimen was from a carbon-bearing brick crucible reacted at 1600°C in an air atmosphere for 2 hours with iron oxide-free slag T (10% Al₂O₃). At the right ends of the strip charts, bundles of high intensities of Al, Mn, Ca and Si are from the slag phase in the crucible specimen. In contrast with the iron oxide-containing slag-reacted crucibles, the depth of slag penetration into brick is about 3 mm. This is in good agreement with microscopic observation of Section 4.6.3.

4.8.4 Crucibles Reacted with Iron Oxide-Containing Slag in Reducing Atmosphere

Figure 60 shows the microprobe analysis of a carbon-bearing brick crucible reacted with slag D (15% Al₂O₃) in a graphite container at 1600°C for 30 minutes. This figure is surprisingly similar to Figure 59. Slag has penetrated the brick through the carbon-bearing matrix. However, the depth is shallow.

It would be helpful if the experimental procedure for this particular series is outlined. When the graphite container (holding a brick crucible with slag D in it) was placed in the Globar furnace at 1600°C, the furnace temperature was lowered to approximately 1000°C due to chilling effect of the crucible assembly. Then, approximately 5 hours were required to reach 1600°C. Most of iron oxide and possibly Mn oxide have been reduced to respective metallic state long before significant at1 on the specimen could take place.
4.9 **SUMMARY OF CRUCIBLE TESTS WITH CARBON-BEARING BRICK**

The presence of carbon in the BOF magnesite brick increases the slag resistance of BOF refractories. Without iron oxide in the slag, the carbon-bearing brick crucible was penetrated by slag through the matrix which contains carbon. No decarburized zone was formed. With iron oxide in the slag, a decarburized zone as well as a dense MgO layer was formed. Slag penetration stopped at slag/dense MgO layer interface, as verified by microprobe analysis. This indicates that the dense MgO layer is impermeable to slag. The dense MgO layer with a high basicity slag was relatively thick and well-defined whilst the same layer for a low basicity slag was poorly-defined and not continuous. This shows the significance of the slag basicity on refractory performance. However, the severity of slag attack shown with carbon-free brick is about the same as for carbon-bearing brick specimens.
CHAPTER V
DISCUSSION

5.1 INTRODUCTION

As indicated in the literature survey, very little work has been reported on the attack of magnesia brick by $\text{Al}_2\text{O}_3$-containing slags. Phase equilibrium data are relevant and may be used as a guide in assessing refractory/slag reactions. However, their usefulness is limited by the large number of components involved in practical situations and the present case is no exception. Present knowledge of the properties of molten slags of compositions relevant to industrial practice, i.e., density, surface tension and viscosity, is very limited. Data available on $\text{Al}_2\text{O}_3$-containing slags are for compositions that prevail in the blast furnace, i.e., acidic and less oxidizing compared with the slags used in the present work. In view of the imprecision of the knowledge of the physical and chemical properties of phases involved and the nature of measurements in the present work, interpretations will be qualitative in nature.

5.1.1 $\text{Al}_2\text{O}_3$-$\text{MgO}$-Containing Slag in Steelmaking

Alumina and magnesia will flux CaO and $\text{C}_2\text{S}$ in steelmaking with an identical adverse effect on refractory service. The fact that alumina-containing slags attack the dicalcium silicate ($\text{C}_2\text{S}$) bond can be seen from the CaO-$\text{SiO}_2$-$\text{Al}_2\text{O}_3$ ternary phase
Dicalcium silicate and alumina have eutectics at 1470°C, 1455°C and lower. MgO additions moderate the detrimental effect of Al₂O₃.

The use of alumina as a steelmaking flux is readily understood from Figures 62(a) through (h) in the monograph by Muan and Osborn. The most important feature of these constant Al₂O₃ sections of the CaO-SiO₂-MgO-Al₂O₃ system is the presence in each plane of relatively low liquidus temperatures (~1500°C). This area is seen to extend into "basic" parts of the system, where the SiO₂ content is 10 to 30% (depending on the level which the plane represents). Low silica is an important requirement in basic steelmaking where the primary slag function is desulfurization and dephosphorization.

The liquidus surface is very steep and temperatures are high especially in the primary phase field magnesia (Figures 62(a) through (h)). Slags used in the present work have some solubility for magnesia, as shown in Figure 63. and a positive temperature coefficient for magnesia solubility. The low melting eutectics occur at relatively small concentrations of MgO in the pseudo-ternary diagrams of C-S-M-A. Recently, Glasser and Marr investigated two quarternary compounds in the C-A-M-S quarternary system. They concluded that the two compounds, designated Q and R, are thermodynamically stable to their incongruent melting temperatures of 1379 and 1315°C, respectively, with approximate composition Q - 42.2% CaO, 45.4% Al₂O₃, 4.1% MgO, 8.2% SiO₂ and R - 40.5% CaO, 48% Al₂O₃, 9.4% MgO, 2.1% SiO₂.

It is apparent that...
Figure 61: Phase diagram for the system CaO-Al₂O₃-SiO₂. (12)
62: at quiet temperatures in the
Figure 63: Solubility of magnesia in CaO-FeO-SiO₂ slags at 1600°C. (66)

Figure 64: Relation between viscosity of basic open-hearth slags and temperature. (58)
MgO to calcium silicate BOF steelmaking slags is expected to potentially replace CaF$_2$ as a flux to facilitate slagmaking by effectively dissolving CaO and C$_2$S without an adverse effect on the service life of MgO refractories.

5.1.2 Carbon-Free Refractory and Slag as a Single System

Magnesite brick consists of periclase grains, silicate bond and carbon phase (in case of pitch-bearing brick) with a level of porosity (apparent porosity of 16.5% in carbon-free brick used in this work). The composition of the bond of the magnesite brick, whose chemical analysis was given in Table 4, is given in the following table as both part of the brick and the bond. The MgO component of the bond has been estimated using the method by Rigby et al.(68) based on the assumption that the Al$_2$O$_3$ and Fe$_2$O$_3$ in the magnesite brick form spinels with the MgO for CaO/SiO$_2$ mole ratios below 2 and make up the brick bond.

<table>
<thead>
<tr>
<th></th>
<th>As part of Brick</th>
<th>Bond Only</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>2.4%</td>
<td>47.1%</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.3%</td>
<td>25.5%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.2%</td>
<td>3.9%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.9%</td>
<td>17.3%</td>
</tr>
<tr>
<td>MgO</td>
<td>0.3%</td>
<td>5.9%</td>
</tr>
<tr>
<td></td>
<td><strong>5.1%</strong></td>
<td><strong>100.0%</strong></td>
</tr>
</tbody>
</table>

The composition of the bond phase coincides with a typical steelmaking slag. This fact has been pointed out by Richardson(69) as follows:

"Some reactions which occur during the firing of these refractories would, in other circumstances such as
steelmaking, be called slag formation and where the slag ends and the refractory begins might not be easy to define."

As shown above, the carbon-free magnesite brick used in this work has an apparent porosity of 16.5%. The slag can therefore penetrate into the interior along the pore channels and silicate networks as soon as the brick specimen is immersed in a molten calcium silicate slag. From the secondary slag source within the specimen, therefore, the spread of slag to the rest of the specimen through the matrix will occur relatively slowly.

Figure 27 shows an almost constant penetration of slag (A, B, C, D, E, F, J, K, L, N, P, Q and R), i.e., 1.45 gm/cm³, equivalent to 15.2% by volume. This value is close to the porosity of the brick (16.5%). A comparison of Figures 26 and 27 indicates that the elongation and penetration have roughly a similar trend. The penetration of slag was influenced by the elongation as the more elongated specimens provide more space for slag penetration. On the other hand, the limited penetration of slag indicates that only a fraction of the void space which is connected to the surface has actually filled with slags. In summary, the extent of slag penetration into the specimens in the present work depends mainly on the properties of the slags.

The penetrating slag combined with the as-fired brick bond constitutes a new mineralogical system. From the density and components of the brick bond, the new bond system may be
Original Bond 0.15 gm/cm³ in the brick
Slag Penetration 0.45 gm/cm³ in the brick
Slag-Penetrated Bond 0.60 gm/cm³ in the brick

From this approximation, it may be said that the resultant system has a composition which is closer to that of the slag than to the initial bond.

5.1.3 Attack of Carbon-Free Refractories by Slag

Most of the slags used in this work can flux the matrix of the brick and weaken its bond; the more Al₂O₃ in MgO-free slags the worse the situation (Figure 22). Alumina in the slag caused disruption of the matrix and the collapse of the brick specimens (Figure 32). Such morphology of refractory wear has been also observed in industrial practice with electric-arc furnace steelmaking linings. (41, 42, 70) MgO additions to Al₂O₃-containing slags moderates the detrimental effects of Al₂O₃ (Figures 22 and 35).

As the result of direct contact of the multi-phases in refractories and molten slag at 1600°C (Section 5.1.2), chemical reactions will occur, unless the phases are saturated with one another. Since the CaO/SiO₂ ratio of the slags used is mainly 1.5 with additives as listed in Table 5, the slags are capable of dissolving more MgO. If, in practice, the required MgO can be supplied from an external source, such as burned dolomite, this should reduce refractory wear.

The brick specimens contain the silicates C₂S and C₃MS₂ as the major constituents of the bond. When sufficient Fe₂O₃ and Al₂O₃ are present, it is conceivable that such a bond may be liquid at 1600°C or close, at least, to its melting point.
In either case it may join the penetrating slag to give a liquid phase. The dissolution of the silicate phase which bonds the periclase grains together will result in brick disintegration. This dissolution (erosion) may be more serious than the simple dissolution of periclase grains (corrosion) as in the case of the silicate-bonded MgO brick. Generally, corrosion and erosion may occur simultaneously and differentiation of these two modes of attack depends on their relative magnitude. For instance, a lack of deep penetration of MgO-containing slag may be indicative of a chemical reaction taking place, even though this slag has comparable physical properties to the master slag, which demonstrated far deeper penetration (Figure 23).

Microscopic examination of reacted brick specimens indicates that Al$_2$O$_3$ in the slag reacts mainly with the silicate bond to form Ca-Al-silicate compounds with low melting points and high fluidity at steelmaking temperatures. Therefore, the silicate bond loses its role as the bond. This is confirmed by microprobe analysis (Figure 45(b)) which clearly shows that Si, Ca and Al are mainly located in the bond whilst Fe and Mn coexist with MgO, in the coarse grains and fines of the matrix. This trend is in good agreement with that of magnesite brick itself. (2,14)

The picture is quite different for the specimen immersed in an acidic slag N (CaO/SiO$_2$ = 1). In this case the MgO grains as well as matrix are heavily attacked. The periclase corrosion product is monticellite (CMS), which is low melting and highly fluid (Figure 42).
5.1.4 Capillary Penetration of Slag into Carbon-Free Brick

Extensive slag/refractory reaction requires the penetration of slag into the brick by one or more of the following steps: (1) capillary action, (2) liquid state diffusion, and (3) solid state diffusion. In view of the rate of penetration observed in the 30 second experiments, it is evident that the capillarity effect must be the dominating mechanism.

According to Bikerman, the horizontal depth \( d \) of penetration of a uniform liquid of viscosity \( \eta \), surface tension \( \gamma \), and contact angle \( \theta \) between meniscus and capillary of radius \( r \), at time \( t \), is given by

\[
d^2 = \frac{r \gamma \cos \theta}{2\eta} t
\]  

(5.1)

In a similar manner, the vertical height \( h_t \) of climb at time \( t \) is given by

\[
t = \frac{8\eta}{r^2 \rho g} \left( h_\infty \ln \left( \frac{h_\infty}{h_\infty - h_t} \right) - h_t \right)
\]  

(5.2)

where \( h_\infty \) is the final height of the meniscus and \( \rho \) the density of the liquid. Equation (5.2) may be approximated, with the assumption that \( h_\infty >> h_t \), to the simplified form:

\[
h_t^2 = \frac{r \gamma \cos \theta}{2\eta} t
\]  

(5.3)

which has the same functional form as Equation (5.1). Hence, the horizontal depth of slag penetration and the vertical height of slag climb in the early stages may be described in the same manner.

Slag penetration through the tortuous and varying pores of a brick specimen may not be described accurately by the above equations. Furthermore, when the slag reacts
with the wall of the capillary, its viscosity near the capillary wall may differ from that of its bulk. The assumption that an equilibrium composition is maintained locally at the solid/liquid interface during the slag reaction and hence the viscosity of slag near the wall is different from that of bulk, was used by Christensen and Bang (72) to rationalize their observations of slag absorption into a porous ceramic.

However, after some time of reaction at a given temperature, the penetration distance of various slags into one type of refractory is proportional to the quantity \((\gamma \cos \theta / \eta)^{1/2}\). A decrease in viscosity or contact angle and an increase in surface tension will result in deeper penetration. The application of Equations (5.1) and (5.3) will be discussed in the following sections.

5.2 EFFECTS OF COMPOSITIONAL CHANGE IN AGGRESSIVENESS OF SLAG

This section will discuss, in detail, the experimental results of Chapter III based on previous work and established theories involved. By monitoring the slag compositional changes, efforts will be made to follow the penetration of slag into the brick, the slag/bond and slag/MgO grain reactions, and the resulting refractory attack.

5.2.1 The Detrimental Effects of \(\text{Al}_2\text{O}_3\) in Slag

In slags which contained 10% or more \(\text{Al}_2\text{O}_3\), no brick specimens survived the 5 minute tests (Figure 22). As shown in Figures 26 and 27, slag penetration and elongation increased with increasing \(\text{Al}_2\text{O}_3\) content in slag. \(\text{Al}_2\text{O}_3\) in the slag composition in this work is...
brick.

The addition of Al₂O₃ caused a decrease of slag viscosity as a result of depression of liquidus temperatures (Figure 61). For compositions more basic than the orthosilicate, the viscosity changes are more likely due to changes in liquidus temperature. With the exception of slag N (CaO/SiO₂ = 1), a CaO/SiO₂ ratio of 1.5 (Table 5) was used throughout.

As temperature increases, the viscosity of a liquid decreases, i.e., \( \log \eta = A/T + B \), where \( A \) and \( B \) are constants whose value depends on the particular liquid being considered. \( T \) is the temperature. An illustration of the effect of temperature on the viscosity of an open hearth slag is shown in Figure 64.\(^{(58)}\) This clearly shows a drastic decrease in viscosity from 8 poise to less than 1 for a temperature increase of 50°C.

The surface tension of a slag is intimately related to the type of oxygen bonding present within it and hence to the related features of basicity and constitution. For normal liquids, the surface tension decreases fairly uniformly with increasing temperature. However, the surface tension of silicate melts increases with temperature at high silica concentrations, and decreases at low concentrations.\(^{(74)}\) The magnitude of temperature dependence seems moderate. Surface tension data for the CaO-Al₂O₃-SiO₂ system is not available for the composition range of steelmaking slags but is available for blast furnace slags.\(^{(75)}\) According to this, the surface tension decreases slightly with increasing Al₂O₃/CaO ratio at constant silica. From temperature and composition considerations re-
the surface tension may be reduced but not significantly.

With no pronounced change of surface tension, the wetting angle between magnesia and the silicate slag can be lowered significantly by the presence of \( \text{Al}_2\text{O}_3 \) (Figure 65).\(^{11}\)

Consideration of all the three parameters involved in Equations (5.1) and (5.3) indicates that two parameters out of the three are changing in favor of enhancing capillary absorption of slag into the brick with \( \text{Al}_2\text{O}_3 \) additions to the Ca-silicate slags studied in the present work.

With increasing \( \text{Al}_2\text{O}_3 \) in the slag, both penetration and refractory disruption increased (Figure 32). The elongation and break-off phenomena seemed to result from the creation of void space by localized creep and separation of the matrix.

Microscopic observations show that the addition of \( \text{Al}_2\text{O}_3 \) to the calcium silicate slags has no effect on the dissolution of magnesia. All \( \text{Al}_2\text{O}_3 \)-containing slags show marked formation of Al-Ca-silicate compounds such as gehlenite \( (\text{C}_2\text{AS}) \) or melilite \( (\text{C}_2\text{AS}-\text{C}_2\text{MS}_2 \text{ solid solution}) \) widely spread out. The high degree of reaction and dissolution of the silicate matrix creates large voids in some areas. Hence it can be concluded that \( \text{Al}_2\text{O}_3 \) deteriorates the bond phase making the silicates highly fluid.

Therefore, attack of magnesite by \( \text{Al}_2\text{O}_3 \)-containing slags is probably a combination of lower viscosity with initial MgO dissolution, the lowering of dihedral angle and the production of the highly fluid liquids. Magnesia in the slag would tend to decrease rather than increase the dihedral angle and to
Figure 65: The effect of CaO/SiO₂ ratio on the dihedral angle between the periclase grains at 1725°C in periclase-silicate containing: (11)

A. No addition.  D. 1% Al₂O₃.
B. 5% Cr₂O₃.  E. 1% Al₂O₃, 17% Cr₂O₃.
C. 5% Fe₂O₃.  F. 5% Al₂O₃.

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<th>Pt.</th>
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<th>MgO</th>
<th>Al₂O₃</th>
<th>Temp</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>C, M</td>
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<td>33.0</td>
<td></td>
<td>2300</td>
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<td>B</td>
<td>M, MA</td>
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<td>55.0</td>
<td>1000</td>
<td>2030</td>
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<td>MA, A</td>
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<td>98.0</td>
<td></td>
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<td>D</td>
<td>C, C₃A</td>
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<td>41.0</td>
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<td>E</td>
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<td>50.0</td>
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<tr>
<td>F</td>
<td>Ca₃A, CA</td>
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<td>53.0</td>
<td></td>
<td>1400</td>
</tr>
<tr>
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<td>66.5</td>
<td>1590</td>
<td>1590</td>
</tr>
<tr>
<td>H</td>
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<td>6.2</td>
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<tr>
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<td>6.7</td>
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<td>Corundum</td>
<td>100.0</td>
<td>2050</td>
<td></td>
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</tbody>
</table>

* Eutectic.

Figure 66: System CaO-MgO-Al₂O₃; (18)
the marked effect of adding Al₂O₃ to the slag, it is felt that the contribution of the third mechanism of attack, production of highly fluid liquids at the expense of bond, is paramount.

5.2.2 Beneficial Effects of MgO in Slags

Addition of MgO to the master slag substantially reduced slag climb and sample elongation (Figures 22 and 26).

MgO additions to Al₂O₃-free steelmaking slags in the range of 5 to 7% lowers the fusion temperature of the slag and probably decreases its viscosity so speeding up the slagmaking.\(^{(9,62)}\) The bulk viscosities of these MgO-containing slags may be lower or comparable to those of the master slag for MgO contents of 5, 8 and 13%. Furthermore, magnesia in the slag will make it more compatible with periclase, hence, lowering the wetting angle. However, the experimental results show that this type of slag penetrates less than the master slag.

Tadsen\(^{(61)}\) reported that near the saturation point of MgO in slag, a further increase of MgO rapidly increases the viscosity and melting point of the slag. A slag with initial MgO will require less additional MgO from the brick than the master slag requires, so a shorter distance of penetration or a shorter time of reaction will be required to reach an MgO level sufficiently high to give the higher viscosity values. At the front of the penetrating slag through the brick pores, a high viscosity will pertain and solidification might even result in this location. The shallow penetration of MgO-containing slags (Figure 23) may thus be explained. The physical penetration of slag by capillarity is thus affected by chemical
reactions taking place along the pore channels, as pointed out by Christensen and Bang.\(^{(72)}\)

Microscopically, coarse grains of periclase were unattacked by the slag. The external surface of these grains were stained yellow due to MW (magnesiowustite) formation. MgO-containing slags show a similar morphology (Figure 31) to that of the master slag, but the spreading of iron oxide is more uniform and the crystallization better developed compared with the master slag case. This may be the result of MgO acting as a crystallizer or a more completely molten slag, or a combination of both.

These considerations help to explain why MgO-saturated slags from calcined dolomitic lime are successful in BOF steel-making practice, particularly from the standpoint of refractory performance.

5.2.3 The Combined Effects of Al\(_2\)O\(_3\) and MgO Additions

MgO additions to Al\(_2\)O\(_3\)-containing slags beyond certain levels are beneficial. With relatively lower contents of up to 8% MgO in the Al\(_2\)O\(_3\)-containing slags as shown in Figure 22, the effect of MgO additions was not pronounced.

The addition of Al\(_2\)O\(_3\) to high lime slags will cause the formation of calcium aluminates. The fluxing action of these compounds on MgO can be readily appreciated from the CaO-Al\(_2\)O\(_3\)-MgO ternary phase diagram (Figure 66).\(^{(18)}\) No fewer than four invariant points exist at the CaO-Al\(_2\)O\(_3\)-rich portion of this diagram (at ~ 7% MgO). The temperatures of these invariant points are from left to right 1450, 1345, 1345, 1370 and...
grain at 1600°C will cause the production of liquids of compositions dictated by these invariants. Hence, in the presence of Al₂O₃-containing slag, MgO will be dissolved from the brick to give highly fluid liquids which can penetrate down the increasingly enlarged channels. The increased fluidity associated with its superheating is evidenced by the excessive creep of these samples. If, on the other hand, sufficient MgO is contained in the initial slag to place the overall composition beyond the series of invariant points (~7%), any subsequent dissolution of MgO from the brick will result in a reduction of the liquid content of the refractory, i.e., partial freezing will occur as the liquidus surface in the MgO field is very steep. Hence, a relatively small amount of MgO dissolution will lead to a substantial reduction in liquid levels and possible blockage of previously open channels.

5.2.4 The Effect of Oxidation State of Slag

The oxidation state of the slag seems not to influence the slag resistance of refractory specimens (Figure 22). A marked difference of slag climb is, however, observed depending on the oxidation state of the slag in terms of iron oxide. Without Al₂O₃ in the slag, climb by the more oxidizing slag is higher than for the less oxidizing slag. With Al₂O₃ in the slag, the reverse is true. This behavior was confirmed by microscopic investigation. A lower degree of reaction was noted between the matrix and the Fe₂O₃-containing slag Q (10% Al₂O₃) than for the FeO-containing slag C (10% Al₂O₃) (Figures 38 and 32).

not the dihedral angle^{10,14} but also
the fusion point of calcium silicate slags in a fashion similar to Al₂O₃. The surface tension of iron oxide decreases with increasing oxidation state and hence ferric oxide is weakly surface active. Therefore, the effect of Fe₂O₃ is similar to Al₂O₃ for slag penetration into carbon-free brick. This may explain the enhanced slag penetration of slag P (17% Fe₂O₃) as compared to slag A (17% FeO).

There are presently no data to explain the reduced climb by the more oxidizing Al₂O₃-containing slags. Two ternary phase diagrams are interesting in this regard. The FeO-SiO₂-Al₂O₃ system shows the formation of a low-melting compound, fayalite, in the FeO-SiO₂-rich phase field whilst the FeO·Fe₂O₃-SiO₂-Al₂O₃ system does not contain any low melting compounds. Hence, Fe₂O₃ depresses the liquidus of C-S slags less than FeO so leading to a lower decrease of viscosity for more oxidizing slags. This is reflected by the elongation suffered by brick specimens in these two slag types (Figure 26), i.e., a smaller elongation with Fe₂O₃ than with FeO slags.

5.2.5 Effects of Basicity of Slag

In the low basicity slag N (CaO/SiO₂ = 1), the brick specimen broke during the 5 minutes reaction time, whereas it survived up to 100 minutes in the medium basicity slag A (CaO/SiO₂ = 1.5) (Figures 21 and 22). These two slags showed comparable heights of slag climb (Figure 26).

From the standpoint of viscosity change due to melting point depression, the viscosity of the low basicity slag must be lower than that of the medium basicity slag and hence more
the low basicity slag is so acidic that the structural consideration of the $\text{SiO}_2$-rich network must be taken into account.

It is reasonable to expect a higher viscosity for the low basicity slag (N) than for the medium basicity slag (A). The same consideration may also be true for the change of surface tension, i.e., a lower surface tension for the low basicity slag. The dihedral angle between MgO and the slag will be lower with the low basicity slag (Figure 65). Considering that only one parameter of the three parameters involved in Equation (5.3), i.e., the dihedral angle, is changing in favor of enhanced capillary absorption of slag into the brick, the result is quite justifiable.

Microscope observations show the highest degree of matrix dissolution and pericalse corrosion in the specimen reacted with the low basicity slag N ($\text{CaO}/\text{SiO}_2 = 1$). MgO fines in the matrix have disappeared completely in some areas and well-crystallized monticellite (CMS) is in evidence. There are many voids but less brick disruption than for the high $\text{Al}_2\text{O}_3$ slags.

Brick attack by the low basicity slag seems mainly to be dissolution of periclase grains. For instance, the broken end of this specimen was pointed (Figure 22), whereas other broken specimens exhibited the irregular shape of disruption or separation along the matrix with periclase grains protruding (Figure 22). Voids around the edge of periclase grains are considered to be created by the dissolution of periclase grains plus creep due to the specimen weight and the penetrated slag. The creep taking place in this particular specimen is well illustrated.
of CMS is indicative of the corrosion of periclase in this acid slag.

Although the matrix suffered a high degree of dissolution, the viscosity of the reaction product might be high enough so as not to loosen the periclase grains from the matrix. This is in contrast to the high-$\text{Al}_2\text{O}_3$ slag in which disruption or separation of the periclase grains is dominant as the attack mechanism of brick. This indicates that periclase corrosion took place but at an insignificant rate. Otherwise, a substantial disruption would result as CMS is a low-melting compound (Table 1) and a highly fluid liquid at 1600°C.

The results obtained using a low basicity slag clearly illustrate the significant influence of the basicity of the slag on the life of basic steelmaking linings. This is a well-known fact. This is even more evident for carbon-bearing magnesite brick as will be seen in the following sections.

5.2.6 The Effects of Iron Oxide in the Slag

Iron oxides in calcium silicate slag lowers considerably the melting point of the silicate. For this reason iron oxides as mill scale are added as flux to expedite slagmaking in the initial stage of BOF steelmaking. They effectively dissolve the $\text{C}_2\text{S}$ formed at the lump lime and slag interfaces. The chemical and physical properties of $\text{FeO}$ and $\text{MnO}$ are similar. (77) Recently, Beechan and Steger (78) reported that manganese oxide as a flux is more beneficial for refractory service than $\text{CaF}_2$.

In the penetration of slag into brick specimens, the depth of iron-manganese oxides penetration is much less than the
periclase grains, coarse and fine, in contact with the initial slag are stained from yellow to brown. Subgrain disintegration is generally observed in the slag/brick interface region. This is confirmed by microprobe analysis (Figure 45) and is a good illustration of the preferential reaction of Fe and Mn oxides with MgO to form MW (magnesiowustite) and MF (magnesioferrite) and MnO-MgO-FeO solid solutions.

A differential penetration depth of the slag components has been observed in practice by many investigators for electric-arc furnace and open-hearth linings. For instance, Spencer et al. reported that iron oxide attack from slag is restricted to a penetration of ~40mm from the hot face of the brick whilst slag CaO and SiO₂ showed marked penetration to a depth of ~100mm. Some have associated this with the phenomenon of "slabbing" frequently observed in practice with carbon-free linings.

The slag/grain interface always shows an iron stain of considerable depth, reaching as much as 1mm in some cases (as measured by microprobe scan) (Figure 57). This is also true for Mn. A similar observation was made by Kriek et al. for magnesite linings in a rotor steelmaking furnace. They suggested that FeO and MnO in the penetrating slag go into solid solution in the MgO of the brick, causing the grain to expand and break into smaller subgrains which ultimately dissolve in the slag. This work also showed a disintegration of magnesia grains into subgrains in the slag/brick interface region. The subgrains are invariably iron stained. The overall morphology
cription but there seems no way to confirm their suggested mechanism.

It is considered anyhow that dissolution of MgO in the slag may be invariably preceded by the formation of solid solutions of MgO, FeO and MnO as an intermediate step.

5.3 SUMMARY OF SLAG ATTACK ON CARBON-FREE MAGNESITE BRICK

The mechanism of slag attack of carbon-free magnesite brick is matrix disruption rather than dissolution of MgO grains for the slag compositions \((\text{CaO/\text{SiO}_2} = 1.5)\) used in this work. An exception was the low basicity slag N \((\text{CaO/\text{SiO}_2} = 1)\). With increasing \(\text{Al}_2\text{O}_3\) in the slag, both penetration and refractory disruption increased. This is thought to be the result of the formation of Ca-Al-silicates of low melting points and high fluidities at steelmaking temperatures. MgO additions beyond certain levels to \(\text{Al}_2\text{O}_3\)-containing slags are beneficial, as a result of the rapid increase of viscosity associated with the increase of fusion point of such slags near their saturation points with MgO. A low basicity slag is as detrimental to refractories as a high \(\text{Al}_2\text{O}_3\) slag \((10\% \text{Al}_2\text{O}_3)\). This is due not only to matrix dissolution but also to corrosion of the periclase grains by the acidic slag to form low-melting compounds. With respect to the oxidation state of the slag, there appears to be different slag penetration behavior but no obvious difference in the aggressiveness of the slag.

5.4 PITCH-BEARING MAGNESITE BRICK
refractories greatly increases their slag resistance. This improved slag resistance is the result of limited penetration by silicates into the brick when carbon remains in the interior (contrast the deep penetration in the case of the carbon-free brick).

In the literature, the beneficial effect of the presence of carbon has been explained in terms of the following mechanisms:

Mechanism I: The nonwetting of carbon by slags.\(^{(21,23,25)}\)

Mechanism II: A pressure buildup due to the evolution of carbon monoxide.\(^{(26,81)}\)

Mechanism III: The formation of a dense MgO layer behind the hot face.\(^{(27,28,29)}\)

An attempt will be made to clarify the role of carbon in BOF refractories partly based on the results of present work.

5.4.1 **Slag Penetration into Carbon-Bearing Brick**

Experimental results definitely show that iron oxide-free slags have penetrated the carbon-bearing matrix of brick crucibles (Figure 53). With substantially reduced slag penetration and without oxidation of the carbon in the brick, there was almost no refractory attack. However, the depth of penetration of slag into the carbon-bearing brick matrix is restricted to surface regions (Figures 53 and 54) as compared with the deep penetration of the carbon-free brick (Figures 23 and 25). This may be due, in part, to the substantially reduced porosity of the brick by the presence of carbon serving as a filler material. Based on the results mentioned above and reports on AOD practice\(^{(37)}\), the validity of Mechanism I will be
It has been established in the literature that not all carbon types are nonwetted by silicate slags. Derge\(^{(82)}\) reported that the wetting or nonwetting character of carbon by silicate slags depends on the physical form of the carbon in relation to the carbidic reaction of the electric-arc furnace finishing slag. He observed that carbon obtained from lamp filaments or crushed electrodes was readily wet by the slag but crushed graphite was not. Ford and Greenhalgh\(^{(83)}\) presented numerical values for the contact angle of molten silicate oxides on graphite thus:

<table>
<thead>
<tr>
<th>Molten Slags</th>
<th>Atmosphere</th>
<th>Temperature</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO-(\text{Al}_2\text{O}_3)-SiO(_2) (2:1:2)</td>
<td>(\text{N}_2)</td>
<td>1330°C</td>
<td>160°</td>
</tr>
<tr>
<td>CaO-(\text{Al}_2\text{O}_3)-SiO(_2) (2:1:2)</td>
<td>(\text{N}_2)</td>
<td>1455°C</td>
<td>30°</td>
</tr>
</tbody>
</table>

From the above table it can be seen that molten alumino-silicates wet or do not wet graphite, depending on temperature. Certainly, they wet graphite when the possibility of interfacial reactions exist, for example, silica and graphite.\(^{(83)}\)

Metallic manganese has been detected by microprobe analysis at the slag/brick interface region in a carbon-bearing magnesite brick crucible reacted with iron oxide-free slag T (6.3% MnO), as shown in Figure 59. This is evidence of interfacial reaction between the silicate slag and carbon.

Baker et al\(^{(37)}\) reported that the carbon failed to retard the slag penetration appreciably in the AOD (Argon Oxygen Decarburization) vessel lined with carbon-bearing MgO brick. Even though conditions in commercial practice are complex, their data are consistent with the results of the present work as evidence against Mechanism I.
If the carbon in a BOF brick cannot stop the slag penetration, it certainly moderates significantly the attack by corrosive, non-oxidizing slags. Iron oxide-free slag T (10% Al₂O₃) is more corrosive to the refractory than iron oxide-free slag U (15% Al₂O₃-8% MgO). This confirms the detrimental effect of Al₂O₃ in the silicate slag previously shown for the carbon-free brick in immersion tests. This may be the result of insufficient slag/ceramic contact. Iron oxide is recognized as an effective solvent for almost every oxide including MgO (Kraner (80) and Limes et al (84)). Iron oxide is also one of the sources of oxygen for brick decarburization which will facilitate the slag attack of the refractory.

5.4.2 Pressure Buildup by Evolution of Carbon Monoxide

The partial pressures of CO and Mg(g) in equilibrium with MgO(s) and C(s) at different temperatures have been calculated based on established thermodynamic data (85) and are tabulated in Table 7. Isolated system was assumed, i.e., total pressure = \( p_{\text{Mg}} + p_{\text{CO}} = 2 p_{\text{Mg}} = 2 p_{\text{CO}} \). No measurement of the partial pressures of the gaseous species in the interior of the specimens was carried out.

Table 7: Calculated partial pressures of Mg(g) and CO in contact with carbon.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Total Pressure ( PCO = PMg )</th>
<th>Total Pressure ( PCO = 1 atm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>0.004</td>
<td>1.0000003</td>
</tr>
<tr>
<td>1400</td>
<td>0.015</td>
<td>1.000060</td>
</tr>
<tr>
<td>1500</td>
<td>0.057</td>
<td>1.000807</td>
</tr>
<tr>
<td>1600</td>
<td>0.181</td>
<td>1.008230</td>
</tr>
<tr>
<td>1700</td>
<td>0.515</td>
<td>1.066400</td>
</tr>
<tr>
<td>1750</td>
<td>0.835</td>
<td>1.175000</td>
</tr>
<tr>
<td>1800</td>
<td>1.322</td>
<td>1.438000</td>
</tr>
</tbody>
</table>
For an isolated system, the total pressure at temperatures up to 1750°C is less than atmospheric, as shown in the second column of Table 7; therefore, there will not be any outward massive flow of gases. These values are similar to those of Brezny and Landy (29) and Carniglia (36). When magnesium vapor is eliminated from the gas phase by reaction, it causes the $p_{CO}$ to build up to the ambient value. For this situation, i.e., assuming $p_{CO} = 1$ atm., the total pressure of such a binary gas mixture is shown in the third column of Table 7.

In this work (at 1600°C), there was no evidence of bulge or rupture near the dense MgO layer indicating pressure buildup. However, Pickering and Batchelor (27) reported such fissuring at 1750°C in a laboratory test. For all conceivable rates of bulk gaseous flow as the result of pressure gradient in the macroscopic sense, it is unlikely that the flowing gas could significantly affect the penetration of slag due to the capillarity driving force into the interior of the brick. Therefore, it is difficult to support the claim that Mechanism II is the sole or even significant cause for the beneficial effects of carbon in BOF refractories.

5.4.3 The Formation of Dense MgO Layer in Decarburized Zone

At high temperatures, the carbon in BOF refractories can be removed by oxidizing agents originated from the atmosphere ($O_2$, $CO_2$, etc.) or slag ($FeO$, $SiO_2$, etc.). In the absence of external oxidants or when their supply is limited, decarburization by the components of the ceramic structure, i.e., MgO, $Fe_2O_3$, $SiO_2$, etc. may become important. In the experiments, was decarburized by flowing air on the
outer surface and by slag on the inner surface, except of those cases with iron-free slags. Within each decarburized zone, a region devoid of carbon located between the specimen surface (or the front of penetrated slag) and the carbon-bearing interior, a dense and essentially continuous layer of MgO was identified (Figures 51 and 52). The existence of such a dense MgO layer was first reported by Herron et al\(^ {21} \) and later by Leonard and Herron\(^ {28} \) using slag as the oxidizing agent and by others\(^ {27, 29, 86} \) for oxidizing atmospheres. The only report of observation of dense layer in specimens taken from the BOF is Howe et al\(^ {30} \) in 1976.

The significance of the existence of a dense MgO layer is clarified for the first time in Figures 51(b), 52(b) and 57. Using Al\(_2\)O\(_3\) as the tracer, the results of microprobe analysis demonstrate that the dense MgO layer stopped slag penetration. Even though the region right behind the dense layer is highly porous and rich in silicate, there is no evidence of slag penetration therein. The fact that carbon in BOF refractories under oxidizing atmospheres and/or in contact with oxidizing slags can last many hours may well be due to the dense layer being impermeable to liquid slag and gases. This leads to the conclusion that Mechanism III (Section 5.4) is the most likely explanation for the improved slag resistance of carbon-bearing BOF refractories.

5.4.3.1 The Mechanism of Formation of the Dense MgO Layer

The formation of appreciable Mg vapor as the result of MgO reduction by carbon at high temperatures under flowing
by many authors.\(^{(27,28,29,86)}\) Under this condition, the
following reaction

\[
\text{MgO} + \text{C} \rightarrow \text{Mg(g)} + \text{CO}
\]  \(\text{(5.4)}\)

was the only important reaction taking place and the non-
equilibrium state was maintained by removing the gaseous pro-
duct with the flow of inert or reducing gas. After certain
time of reaction, a decarburized zone can be observed but no
dense layer of MgO. In inert atmospheres, the overall reaction
rate is considered controlled by diffusion of the reaction pro-
duct from the reaction site into the main gas stream, at least
in the early stage.\(^{(86)}\)

Pickering and Batchelor\(^{(27)}\) and others\(^{(29,86)}\) have reported
the oxidation of Mg vapor by oxidizing gases such as air and CO\(_2\)
and the precipitation of MgO at locations between the sources
of these reactants by the following reactions:

\[
\text{Mg} + \text{CO}_2 \rightarrow \text{MgO} + \text{CO}
\]  \(\text{(5.5)}\)

or

\[
\text{Mg} + \frac{1}{2} \text{O}_2 = \text{MgO}
\]  \(\text{(5.6)}\)

The fact that the dense MgO layer has been formed with iron-
containing slags with no direct contact between the penetrating
slag and carbon in the present work, strongly implies the fol-
lowing chemical reaction occurs:

\[
(\text{FeO}) + \text{CO} \rightarrow \text{Fe} + \text{CO}_2
\]  \(\text{(5.7)}\)
in parallel with Reactions (4) and (5).

A more elaborate model of the kinetics and mechanism of
the formation of the dense MgO layer will be given in the next
chapter.
5.4.3.2 The Effect of the Slag CaO/SiO₂ Ratio on the Attack of the Dense MgO Layer

No refractories last forever, even in the presence of a dense MgO layer impermeable to both slag and oxidizing gas. Therefore, certain segments must be destroyed constantly and repaired by new layer formation at a distance back into the brick. The destruction of the dense MgO layer may be due to a number of factors, i.e., dissolution, erosion, spalling and breaking as the result of pressure buildup. Figures 51 and 52 show that the thickness of dense layer is sensitive to the CaO/SiO₂ ratio. This result clearly suggests that dissolution of the MgO by the penetrated slag is the dominant cause of the destruction of the dense layer. The capacity for dissolving MgO by a silicate slag drastically decreases with increasing CaO/SiO₂ ratio, as shown in Figure 63. The dissolution of MgO in the slag could cause a break-through, so allowing slag to penetrate the porous region behind the dense layer. Once direct contact between the sources of oxygen (the slag) and magnesium vapor is established, the building of a new dense layer of MgO will commence. The establishment of a new layer in the rear of the destroyed one will be dealt with in detail in the next chapter.

Extensive cleavage cracks (indicative of grain growth) and zero attack in the dense layer formed with a high basicity slag (CaO/SiO₂ = 2) indicate that sintering between and within the coarse MgO grains has taken place. On the other hand, the absence of cleavage cracks and considerable attack on the dense layer with low and medium basicity slags (CaO/SiO₂ = 1 and 1.5)
time for sintering or grain growth to occur. This clearly shows the significance of slag basicity from the standpoint of refractory performance as well as the metallurgical aspects of steelmaking.

5.4.3.3 The Relative Thickness of the Decarburized Zone and Dense MgO Layer

The mechanism of the destruction of a dense MgO layer has not yet been proposed. It has been claimed that in actual practice a quasi-steady state thickness of decarburized zone will develop because of the balance between the diffusion-limited layer growth and normal refractory wear. However, little observation of the existence of the dense layer has been reported from practice (Section 5.4.3) and this work has revealed that the thickness of the dense layer depends on the corrosiveness of slag. Therefore, a study of quasi-steady state formation of a dense MgO layer is carried out to determine the mechanism of its destruction.

Consider pitch-impregnated magnesite brick, whose pore network is an integral part of its structure. It is assumed that carbon in the brick functions only to reduce MgO and that the Mg(g) is subsequently oxidized to form the dense MgO layer. To simplify the discussion, a one-dimensional system of unit cross-sectional area perpendicular to the hot face is considered.

---

Figure 67: Schematic diagram for decarburized zone and
The system under consideration is shown in Figure 67, for quasi-steady state conditions. At \( t = t_1 \), the carbon boundary is at \( x = X_2 \) and dense layer boundary at \( x = X_1 \). At \( t = t + dt \), the carbon boundary is at \( x = X_2 + dX_2 \) and the dense layer boundary is at \( x = X_1 + dX_1 \).

Assuming that all the open pores are filled completely with pitch, the mass of carbon, \( \pi \), after coking a volume of \( dV_2 \) will be

\[
\pi = \varepsilon_a \rho_p \phi dV_2
\]

(5.8)

where \( \varepsilon_a \) = apparent porosity of burned brick, \( \rho_p \) = density of pitch and \( \phi = \) carbon yield after coking.

The loss of MgO weight by the reducing agent carbon in the volume of \( dV_2 \) may be expressed by

\[
\text{Loss of MgO} = \pi \frac{M_m}{M_c} \varepsilon_a \frac{M_m}{M_c} \rho_p \phi dV_2
\]

(5.9)

where \( M_m \) = molecular weight of MgO and \( M_c \) = atomic weight of carbon.

The increase in porosity, \( \Delta \varepsilon \), by such a loss of the MgO, will be

\[
\Delta \varepsilon = \varepsilon_a \frac{M_m \rho_p \phi}{M_c \rho_l}
\]

(5.10)

where \( \rho_l \) = density of the dense MgO layer.

The porosity, \( \varepsilon \), of the decarburized zone is

\[
\varepsilon = \varepsilon_a + \Delta \varepsilon = \varepsilon_a (1 + \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_l})
\]

(5.11)

Now, the amount of MgO removed from \( dV_2 \) is used to fill the pores in \( dV \) in the decarburized zone, a \( \varepsilon \), to
form a dense layer and, from the law of conservation of mass,

\[ \varepsilon_a \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_\ell} dV_2 = \varepsilon_a (1 + \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_\ell}) dV_1 \]  

(5.12)

For the unit cross-sectional area, assumed \( dV_1 \) and \( dV_2 \) may be substituted by \( dX_1 \) and \( dX_2 \), respectively,

\[ \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_\ell} dX_2 = (1 + \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_\ell}) dX_1 \]  

(5.13)

or

\[ \frac{dX_1}{dX_2} = \frac{1}{(1 + \frac{M_m}{M_c} \frac{\rho_p \phi}{\rho_\ell})} < 1 \]  

(5.14)

which indicates that \( dX_1/dX_2 \) is independent of time and porosity \( \varepsilon \) but sensitive to properties of pitch \( \rho_p \) and \( \phi \) and indirectly to coking procedures.

The thickness of decarburized zone, \( z \), is the difference between \( X_2 \) and \( X_1 \), i.e.,

\[ dz = d(X_2 - X_1) = dX_2 - dX_1 \]  

(5.15)

Combining Equations (5.14) and (5.15),

\[ dz = \left( \frac{\rho_\ell}{\rho_p \phi} \frac{M_c}{M_m} \right) dX_1 \]  

(5.16)

and

\[ \int dz = \left( \frac{\rho_\ell}{\rho_p \phi} \frac{M_c}{M_m} \right) \int dX_1 \]  

(5.17)

with the initial condition that

\[ \text{at } t = 0, \ X_1 = z = 0 \]  

(5.18)

After the integration of Equation (5.17) and satisfying Equation (5.18), the thickness of decarburized zone at time \( t \) and the accumulative thickness of \( MgO \) up to \( t \),
$X_1$ are as follows:

$$z = \left( \frac{\gamma \varphi}{\rho_0} \frac{M_c}{N_m} \right) X_1$$  \hspace{1cm} (5.19)

Since $X_1$ increases monotonically with increased reaction time, the analysis suggests that $z$ would increase with time if the assumed mechanism is reasonable. The observed values of $z$ reported in the literature are $\approx 0.6$ mm. In this work, $z$ has been measured as $\approx 2$ mm. Hence the gradual and continuing formation of the dense MgO layer and decarburized zone as analyzed in this section is unlikely to be operative. An alternative approach will be given in the following section.

5.4.3.4 The Destruction and Rebuilding of Dense MgO Layer

Once a dense "layer" of MgO is formed, based on experimental observation (Figures 51 and 52), it is impermeable to liquid slag. It is reasonable to assume it is also impermeable to gas. If the slow processes of solid state diffusion of FeO and MnO through the MgO layer can be neglected, the chemical transport reactions which move MgO across the decarburized zone, would stop upon completion of the dense MgO layer, i.e., the oxidizing gas and magnesium vapor cannot now meet to continue formation of more MgO for the growth of the dense layer. It is clear now that the assumption that the steady chemical transport reactions can be maintained as described in the last section is questionable.

To simplify the analysis, assume that each dense MgO layer has a life time of $t_L$.

$$t_L = t_1 + t_2$$
where $t_1$ is the time it takes to build a mature dense MgO layer and $t_2$ is the time it takes for its destruction. As discussed in Section 5.4.3.2, of the many potential causes leading to the destruction of the dense layer, the dissolution of MgO in the slag seems to be the most important. The events between time zero and $t_1$ will be the subject of the next chapter. A brief outline of the possible events during the period of $t_2$ are given below.

After a certain thickness of dense MgO layer is reached and becomes impermeable to slag and gases, further growth of this layer ceases. Now the process of destruction begins. The destruction is probably the result of the failure of the thinner sections of the dense layer between the native large periclase grains. The penetration of slag through such holes into the highly porous region in the decarburized zone will follow. The direct exposure of the oxidizing slag to the magnesium vapor-containing gas will trigger rapid MgO(s) precipitation at the slag/gas interface. Further generation of Mg(g) by MgO reduction and pressure buildup due to the accumulation of CO will follow. The vanguard of the streams of slag flowing through the network of void space in the decarburized zone, would experience more fine MgO precipitation and its dissolution in the slag together with FeO reduction by Mg(g) and CO. The accompanying changes of slag composition will lead to higher viscosities and even solidification. Therefore, in narrow enough passages, the advance of the slag may be stopped. The building of a new dense MgO layer will begin and proceed at a diminishing rate of oxidizing.
FeO) meeting magnesium vapor decreases as the dense MgO layer grows. Such self-healing of the impermeable MgO layer would make the BOF lining behave chemically as a thin crucible of high purity MgO.

The fact that all authors noticed the existence of a decarburized zone but few reported the observation of the dense MgO layer in BOF refractories after service demands certain comments. It should be pointed out that the dense layer was noticed first in the laboratory in 1967 and in industrial operation in 1976 after changing slagmaking practice (30) (Section 2.5.4.3). There are several possibilities for the non-observation or reporting of a dense MgO layer in the early work: (1) slag too acid or corrosive to magnesia, resulting in a high rate of consumption of MgO at the front of slag penetration; (2) the slag was too high or too low in oxidizing power to sustain a fast rate of MgO formation, or (3) a combination of both the above. One should be reminded that in the early microscopic studies the investigators were unaware of the dense MgO layer, hence, did not search for it. In view of the fact that steel-making slag is very aggressive in the early stages of the blow, i.e., is very oxidizing and rather acid, it is not surprising that specimens examined by the early investigators had no dense MgO layer.

The sequence of events in a BOF brick during service are, decarburization, slag penetration and failure of the slag-penetrated and carbon-free portions of the brick. There is always a portion of the refractory which is essentially decarburized but not significantly penetrated by slag (the decarburized zone).
Hence, the penetrating slag containing iron oxide does not contact the carbon as reported in the present work and in the literature. The reaction of decarburization always results in an increase in volume of gaseous phase with oxidant from either gaseous or condensed phases. When the brick is covered and penetrated by slag, the source of oxygen (other than MgO) for decarburization and the formation of the dense MgO layer in the interior of refractories, would be slag. It is of interest to consider a hypothetical case in which an oxidizing slag and carbon are in contact at one time. At the moment chemical reaction between the carbon and slag is allowed to proceed, the newly generated carbon monoxide and the recession of the carbon boundary separates the remaining carbon and slag. The change in slag composition, i.e., a decrease in FeO and MnO and an increase in MgO content results in increased viscosity which helps maintain this separation.

The dissolution of MgO in slags may be the major cause of failure of the dense MgO layer in the tests here reported. The region of the decarburized zone flooded by slag as the result of break-through of the dense layer, should be attacked in the same manner as a carbon-free brick in an immersion test. With improved slagmaking practice, i.e., having more basic slag earlier, it is expected that the dense MgO layer would form under the conditions of BOF operation presently prevailing in North America. It is to say that we may assume that the wear of specimens of carbon-bearing refractories in the present work is similar in nature to that of BOF brick in steelmaking shops. The effective life of BOF which
therefore a very thin layer of MgO. At any moment, there will be many local break-throughs of this dense MgO layer. Each break-through is followed by slag penetration and subsequent reestablishment of new segment of dense MgO layer and the wear of the newly penetrated portion of decarburized zone as discussed previously. The process of formation and destruction of the dense MgO layer will repeat itself all during steelmaking with a net result of having the location of dense layer moving further back towards the cold face of the lining in a BOF. With more corrosive slags, the process will proceed at a faster rate and result in more rapid lining wear.
CHAPTER VI

A THEORETICAL STUDY ON THE FORMATION OF THE DENSE MgO LAYER

6.1 INTRODUCTION

The direct identification of the dense MgO layer after exposure of BOF refractories to oxidizing atmospheres and/or slag in the present work and in the literature is certainly acceptable. It may be considered as the cause for improved slag resistance of pitch-bearing brick and for the preservation of carbon in the brick for many hours at steelmaking temperatures.

The dense MgO layer is constantly being destroyed, most likely by penetrating slag, and reestablished in nearby locations. The mechanism of its destruction is not very clear (Section 5.4.3.2) but its formation definitely involves gaseous mass transport and chemical reactions (Section 5.4.3.1). In this chapter, a mathematical model is devised to study the influence of various steelmaking process parameters on the formation of the dense layer and some of the consequences. No attempt will be made to analyze mathematically the dissolution of the MgO layer in slags.

6.2 THE SYSTEM

The system consists primarily of the decarburized zone, across which a gradient of oxygen potential is maintained. This is a region where no solid carbon exists, i.e., two boun-
daries with constant oxygen potential. At the inner boundary it is maintained by solid carbon and at the other one by external conditions, i.e., the composition of the penetrating slag or the atmosphere.

Since the whole system is normally less than one centimeter, isothermal conditions are assumed at steelmaking temperatures.

It is a one-dimensional system and the coordinates are on a moving frame, with the origin at the inner boundary of the decarburized zone.

\[
\begin{array}{c}
\text{Carbon-Bearing MgO} \\
\text{Decarburized Zone} \\
\end{array}
\]

**Figure 68**: Schematic diagram of Mg-CO\(_2\) reaction model in BOF lining.

At \(x \leq 0\), there is solid carbon in the refractories.

\(x > 0\), solid carbon does not exist.

\(x = x_L\), oxygen potential in the gaseous phase is independent of reaction time.

\(x > 0\), the porous solid in this region is of uniform structure and permeable to gaseous species.

\(x < 0\), is impermeable to gases.
The assumption that the porous solid in the region \(0 < x < x_1\) is uniform implies that a new dense MgO layer is being presently established. At \(x = x_1\), the penetration of slag stops. As the reaction proceeds, in the region where MgO forms as the result of the gaseous reaction, the porosity, permeability and mass transfer fluxes will decrease with increased reaction time until complete sealing of the dense layer and termination of reactions under consideration. At any location in the region, \(0 < x < x_1\), in principle, the porous structure and hence the rates of mass transfer and chemical reaction are functions of the reaction time. Before the separation of sources of Mg vapor and oxygen by the dense layer, the system is always at an unsteady state.

In order to simplify the system to the extent that a mathematical analysis is tractable, it is assumed that time is not an explicit variable. The phenomena under investigation is the formation (or the repairing) of the dense layer from beginning to completion. In reality what actually happens can only be described, for example, by a movie. The attempt which will be made here only concerns a few still pictures assuming quasi-steady state and under quasi-steady state, time is not a variable explicitly. The model is only valid for the case that the coordinates are on a moving frame and for a very short period of time during which steady state is an acceptable assumption. Each mathematical solution is only a still picture in the movie.
6.3 CHEMICAL REACTIONS IN THE SYSTEM

Chemical reactions will be considered according to the reaction site in the system in the following three categories (no reaction in the regions \( x < 0 \) and \( x_c < x \) will be considered).

(a) \( x = 0 \): The boundary of the system is defined based on the availability of solid carbon at \( x = 0 \), therefore, the reactions should be considered as decarburization.

\[
C + CO_2 \rightarrow 2CO \quad (6.1)
\]

\[
C + MO \rightarrow CO + \text{Suboxide or metal vapor} \quad (6.2)
\]

Due to the fact that CaO, SiO_2 and Al_2O_3 (1) usually form stable compounds during firing of the brick, (2) are in limited quantities in the raw materials, and (3) are chemically stable, reaction (6.2) may be simplified to

\[
C + MgO \rightarrow CO + Mg(g) \quad (6.3)
\]

Reaction (6.3) may take place in the following ways:

\[
C + MgO(s) \rightarrow Mg(g) + CO \quad (6.4)
\]

and

\[
C + MgO(g) \rightarrow Mg(g) + CO \quad (6.5)
\]

It has been reported that under flowing inert atmosphere conditions, the observed reaction rate of gasification of magnesium does not depend on the properties of magnesia including its specific surface but is sensitive to the properties of the carbon including its specific surface. (86) It is obvious that it is a gas/carbon reaction, therefore, reaction (6.5) is a chemical equation representing the mechanistic step and the following reaction is maintained at its equilibrium:

\[
MgO(s) \rightarrow MgO(g) \quad (6.6)
\]

In the literature, the decarburization rate of BOF refrac-
tories by CO₂ in the early stages, when the resistance associated with mass transfer in porous solid is relatively insignificant, is high in comparison with later stages, i.e., reaction (6.1) is not inherently slow at 1600°C nor is it likely to be a rate-limiting step in the overall reaction. A similar conclusion may be reached for reaction (6.5) because of the fast reaction rate observed in flowing inert atmospheres. For the modelling of reactions in 0 < x < x_l, therefore, reactions (6.1) and (6.5) are assumed to be at the equilibrium state. The individual decarburization rates of reactions (6.1) and (6.5) will be computed from the outward flux of magnesium vapor and inward flux of carbon dioxide, both at x = 0, respectively.

(b) x = x_l: The system is defined by the criterion that at x_l the oxygen potential of the gases remains time-independent for the duration under consideration. The length of duration of the quasi-steady state is assumed acceptable but may be rather short. However, it will become clear later on in this chapter that this assumption imposes no significant limitations on the validity of the analysis for the present purposes.

The source of oxygen may be the atmosphere or the slag. The location of x = x_l would be the external surface of the refractory in the case of oxidizing atmosphere or the front of the penetrating slag. Since carbon monoxide is being generated at x = 0 and not being consumed over the region x < x_l, for a given oxygen potential, the partial pressure of CO₂ will be orders of magnitude bigger than that of O₂. In summary, the condition of the model at x = x_l is that at x = x_l is time-
independent for the duration considered.

(c) $0 < x < x^*_2$: In this region the gaseous phase contains CO, CO$_2$, Mg and MgO molecules and the reversible reaction is

$$\text{Mg}_g + \text{CO}_2 \rightleftharpoons \text{MgO}_g + \text{CO} \quad (6.7)$$

and the gas/solid reaction is (6.6) which is considered to be fast and not rate-limiting. The reactants of (6.7) are generated at two boundaries of the system, i.e. at $x = 0$ and $x = x^*_2$, respectively. Reaction (6.7) will maintain the concentration gradients of these species in the system. The maximum value of the product of the partial pressures of Mg$_g$ and CO$_2$ will be located a distance away from the boundary of the system.

The forward reaction rate of (6.7) will vary over the location in the system as well as boundary condition. If chemical Equation (6.7) is accepted as the proper mechanistic presentation, and there is no reason against it, based on the Mass Action Law the following rate expression is proposed for this gaseous reaction:

$$\frac{d(\text{CO})}{dt} = -\frac{d(\text{Mg})}{dt} = -\frac{d(\text{CO}_2)}{dt} = k(\text{Mg})(\text{CO}_2) - k^*(\text{MgO})(\text{CO}) \quad (6.8)$$

or

$$\frac{d\text{pCO}}{dt} = -\frac{d\text{pMg}}{dt} = -\frac{d\text{pCO}_2}{dt} = \frac{k}{RT} \text{pMg} \cdot \text{pCO}_2 - \frac{k^*}{RT} \text{pMgO} \cdot \text{pCO} \quad (6.8a)$$

6.4 FORMULATION OF THE MODEL

The purpose of this mathematical modelling is to study the reaction of the dense MgO layer formation, hence, the basis of the model is reaction (6.7) and Equation (6.8). The overall reaction, as viewed from the surroundings of the system, is decarbonization to give gaseous products with oxygen from an ex-
ternal source. It is conceivable that this gasification could create a gradient of total pressure throughout the system. No assumption will be made concerning the values of total pressure in the system.

Under isothermal and non-isobaric conditions there are four independent variables for the gaseous phase, i.e., \( p_{\text{CO}} \), \( p_{\text{CO}_2} \), \( p_{\text{Mg}} \) and \( p_{\text{MgO}} \). The combination of their values, through Equation (6.8a), determines the reaction rate for the formation or reduction of MgO at every location within \( 0 < x < x_f \). As the equilibrium for the sublimation of MgO, reaction (6.6) has been assumed throughout the system, therefore, \( p_{\text{MgO}} \) is a constant for a given temperature and independent of time and location within the system. Three relationships, hence, are required to determine the remaining three unknowns, \( p_{\text{CO}} \), \( p_{\text{CO}_2} \) and \( p_{\text{Mg}} \) as functions of \( x \) but not of time explicitly.

(a) The Quasi-Steady State of Decarburization

Carbon is being gasified by reactions (6.1) and (6.5) at \( x = 0 \) and transported in the positive \( x \)-direction leaving the system. With the assumption that the accumulation of gaseous carbon-containing compounds at any location due to change of total pressure or size of system can be neglected in comparison with the corresponding fluxes, a simple relationship can be obtained. Carbon, therefore, irrespective of the nature of the gaseous molecules, must be transported at a constant rate in the \( x \)-direction. For the case where the carbon-containing gases are CO and \( \text{CO}_2 \) and a one-dimensional system (which means the sectional area is not a function of \( x \)), the following can be given:
\[ J_{\text{CO}} + J_{\text{CO}_2} = 0 \text{ for } 0 \leq x \leq x'_f \]  

(6.9)

where J's are fluxes with positive value which represent the positive x-direction; \( \theta \) is the rate of decarburization, a positive constant under given conditions.

(b) Stoichiometric Requirement

It is reasonable to assume that there is no reaction other than (6.7) involving Mg(g) and CO\(_2\) in the region of \( 0 < x < x'_f \) where there is no source or sink of oxygen and carbon. The only cause for the variation of fluxes of Mg and CO\(_2\) as a function of x is due to chemical reaction (6.7). It is obvious that the stoichiometric relationship in (6.7) must be observed. The changes of flux of Mg and CO\(_2\) over the same locality and duration must be equal, then

\[ \frac{d}{dx} J_{\text{Mg}} = - \frac{d}{dx} J_{\text{CO}_2} \text{ for } 0 \leq x \leq x'_f \]  

(6.10)

where J's are in mole per unit area per unit time and the negative sign is because these two fluxes are of opposite signs in this model.

The mathematical expression of fluxes, assuming low bulk flow is essentially carbon monoxide due to the low total pressure gradient, is of the form of simple Fick's law. Another justification is that over the region, \( 0 < x < x'_f \), it is a porous solid of about 15-20% porosity so that diffusion would be the dominant mechanism for mass transfer. Then, these are

\[ J_{\text{Mg}} = - \frac{D_{\text{Mg}}}{RT} \frac{dp_{\text{Mg}}}{dx} \]  

(6.11a)

\[ J_{\text{CO}_2} = - \frac{D_{\text{CO}_2}}{RT} \frac{dp_{\text{CO}_2}}{dx} \]  

(6.11b)
\[ J_{CO} = - \frac{D_{CO}}{RT} \frac{dp_{CO}}{dx} \]  
(6.11c)

where \( D_i \) is the effective diffusivity of \( i \) species in porous solid. The above three equations are uniquely related through the stoichiometry of reaction (6.7) such as Equation (6.10).

(c) **No Accumulation of Gases in the System**

Another independent relationship which is being sought in this section can be obtained as follows:

\[ \frac{dJ_{Mg}}{dx} = -\frac{dJ_{CO_2}}{dx} = \text{chemical reaction rate} \]  
(6.12)

Then, substituting Equations (6.8a) and (6.11b) into the above equation,

\[ \frac{dp_{CO_2}}{dx^2} = \frac{k}{D_{CO_2}(RT)} \left( p_{Mg} \cdot p_{CO_2} - \frac{1}{K} p_{MgO} \cdot p_{CO} \right) \]  
(6.13)

where \( K \) is the equilibrium constant of gaseous reaction (6.7).

Finally, three equations are established, i.e., Equations (6.9), (6.10) and (6.13), for determining the three unknown \( p_{CO}, p_{CO_2} \) and \( p_{Mg} \) as functions of \( x \) over the region, \( 0 \leq x \leq x_L \).

6.5 **MATHEMATICAL OPERATIONS AND BOUNDARY CONDITIONS**

(a) **Rewriting Equation (6.9)**

\[ -D_{CO} \frac{dp_{CO}}{dx} - D_{CO_2} \frac{dp_{CO_2}}{dx} = \theta RT \]  
for \( 0 \leq x \leq x_L \)  
(6.14)

Assuming \( D_{CO} = D_{CO_2} = D_{Mg} = D \) and knowing \( \theta \) is independent of \( x \), Equation (6.14) can be integrated as follows:

\[ (p_{CO} + p_{CO_2}) = -\frac{\theta RT}{D} x + C_1 \]

The integration constant can be determined only when one value of \( (p_{CO} + p_{CO_2}) \) is known for a known value of \( x \). With the following boundary condition:
At $x = 0$, $p_{CO} = p_{CO}^{(o)}$ and $p_{CO_2} = p_{CO_2}^{(o)}$

Equation (6.14) becomes

$$p_{CO} + p_{CO_2} = -\frac{\theta RT}{D} x + p_{CO}^{(o)} + p_{CO_2}^{(o)}$$  \hspace{1cm} (6.15)

The sum of partial pressures of carbon oxides decreases linearly with the increase of $x$ up to at least $x < x_k$.

(b) Rewriting Equation (6.10) and making use of the fact that $D_{Mg} = D_{CO_2} = D$ in an isothermal system, it becomes

$$\frac{d^2p_{Mg}}{dx^2} = -\frac{d^2p_{CO_2}}{dx^2}$$  \hspace{1cm} (6.16)

Then,

$$p_{Mg} + p_{CO_2} = C_2 x + C_3$$  \hspace{1cm} (6.17)

where $C_2$ and $C_3$ are integration constants to be determined.

The boundary conditions are

At $x = 0$, $p_{Mg} = p_{Mg}^{(o)}$ and $p_{CO_2} = p_{CO_2}^{(o)}$, and

at $x = x_k$, $p_{Mg} = p_{Mg}^{(l)}$ and $p_{CO_2} = p_{CO_2}^{(l)}$

Therefore,

$$C_3 = p_{Mg}^{(o)} + p_{CO_2}^{(o)}$$

and

$$C_2 = \frac{1}{x_k} (p_{Mg}^{(l)} - p_{Mg}^{(o)} - p_{CO_2}^{(o)})$$

After replacing $C_2$ and $C_3$ by the above expressions,

$$p_{Mg} + p_{CO_2} = \frac{x}{x_k} (p_{Mg}^{(l)} + p_{CO_2}^{(l)} - p_{Mg}^{(o)} - p_{CO_2}^{(o)}) + p_{Mg}^{(o)} + p_{CO_2}^{(o)}$$  \hspace{1cm} (6.18)

(c) Equation (6.13) contains all three dependent variables, $p_{CO_2}$, $p_{Mg}$ and $p_{CO}$, therefore, cannot be solved as it is. From Equations (6.15) and (6.18), $p_{CO}$ and $p_{Mg}$ may be expressed as functions of $p_{CO_2}$, $x$ and other parameters. After substituting these expressions for $p_{CO}$ and $p_{Mg}$ in Equation (6.13), it becomes:
\[
\frac{d^2 P_{CO_2}}{dx^2} = -c p_{CO_2} + p_{CO_2} \left( \frac{x}{x_k} (p_{Mg}^{(x)} + P_{CO_2}^{(x)}) - p_{Mg}^{(o)} - P_{CO_2}^{(o)} \right) + \\
p_{Mg}^{(o)} + P_{CO_2}^{(o)} + \left( \frac{P_{MgO} \cdot \theta \cdot RT}{KD} \right) x - \frac{P_{MgO}^{(o)}}{K} (P_{CO_2}^{(o)} + P_{CO_2}^{(o)})
\] (6.19)

Equation (6.19) has been solved numerically with the aid of a CDC 6400 computer. \( p_{CO} \) and \( p_{Mg} \) as functions of \( x \) were obtained through Equations (6.15) and (6.18) after solving Equation (6.19).

6.6 NUMERICAL METHODS AND CHOICE OF VALUES FOR PARAMETERS

Since no analytical solution was available for Equation (6.19), which is a 2nd-order ordinary differential equation, it was solved by Runge-Kutta numerical method using CDC 6400 computer. This type of formula is among the most widely used program for the numerical solution of ordinary differential equations due to its simplicity of programming associated with a reasonable accuracy. For a given set of boundary values, \( p_{CO_2}^{(o)} \) and \( p_{CO_2}^{(x)} \), the computation was carried out from one boundary to the other. This process was repeated by changing a starting slope of one boundary at \( x = 0 \) until the calculated value of the other boundary corresponds to the given value. The size of the step chosen was 0.001 cm. This size was found to yield reasonably accurate results considering that a trial with a step size of 0.0001 cm yielded about an order of 10^-3 deviation from that with a step size of 0.001 cm.

For the Equation (6.19) to be useful, a proper selection of numerical values of the parameters in this equation is required. As shown in the equation, the required numerical values for boundary conditions and parameters involved are
\( p_{Mg}^{(0)}, p_{Mg}^{(\ell)}, p_{CO_2}^{(0)}, p_{CO_2}^{(\ell)}, p_{CO}^{(0)}, K, D, \ell, \theta, \) and \( k. \)

Since there were no measurements from which to estimate \( p_{CO} \) in decarburized zone of a BOF lining, an ambient value and hence an atmospheric pressure was taken as \( p_{CO}^{(\ell)} \) at \( x = x_\ell \), which is not necessary explicitly. This is quite reasonable from the thermodynamic calculation shown in the third column of Table 7, Section 5.4.2. The \( p_{CO} \) at \( x = 0 \) was estimated from \( p_{CO}^{(\ell)} = 1 \) and from the Equation (6.15). Once the values of \( p_{CO} \) are set at both boundaries, \( p_{Mg} \) and \( p_{CO_2} \) were readily calculated at both boundaries based on the equilibrium relationships as discussed in Section 6.3, using JANAF Thermochemical Tables. (85) For the \( p_{CO_2}^{(\ell)} \) estimation, in particular, the activities of iron oxide in the slag \( a_{FeO} \) at \( x = x_\ell \) was necessary. The values of this parameter used in evaluation were 0.075 and 0.150, respectively. The value for \( K \) of 4.6 \( \times 10^{-8} \) at 1600°C was also calculated in a similar way.

In fact, \( p_{Mg} \) and \( p_{CO_2} \) are so small in the system in comparison with \( p_{CO} \) that \( D's \) were estimated on the basis of binary mixtures of \( CO-CO_2 \) using the following formula and literature data, (88)

\[
D_{ij(eff)} = \frac{D_{ij} \epsilon}{\tau}
\]

where \( D_{ij(eff)} = \) effective interdiffusivity, \( \epsilon = \) porosity or void fraction, and \( \tau = \) tortuosity. For example,

\[
D_{CO-CO_2(eff)} = \frac{(4)(0.20)}{2} = 0.4 \text{ cm}^2/\text{sec. at 1600°C}
\]

The thickness of a decarburized zone \( (X_\ell) \) and the rate of decarburization \( (\theta) \) used in computation were estimated at 0.4 cm and \( 2.9 \times 10^{-7} \) mole/sec·cm², respectively, from liter-
ature\((3,36)\) as well as from this work.

Specific reaction rate constant, \(k\), in Equation (6.19), which is for reaction (6.7), was arbitrarily given for three different temperatures, as shown below, since no data are available. The coefficient on the left hand side of Equation (6.19) is \(DRT/k\). Because simple numbers were given for \(DRT/k\), the resulting \(k\)'s for different temperatures are listed as follows:

<table>
<thead>
<tr>
<th>Specific Rate Constant ((\text{cm}^3/\text{mole} \cdot \text{sec}))</th>
<th>Temperature ((^\circ \text{C}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.09 (\times) (10^6)</td>
<td>1500</td>
</tr>
<tr>
<td>4.42 (\times) (10^6)</td>
<td>1600</td>
</tr>
<tr>
<td>9.31 (\times) (10^6)</td>
<td>1700</td>
</tr>
</tbody>
</table>

6.7 Computational Results

The numerical solutions of Equation (6.19) with parameters described in the last section are shown in Figures 69 and 70. They are partial pressures of \(\text{Mg}\) and \(\text{CO}_2\) at three different temperatures of 1500, 1600 and 1700\(^{\circ}\)\(\text{C}\) against dimensionless distance, \(x/x_\chi\). In fitting the curve to the chosen boundary values, the fluxes of \(\text{CO}_2\) at \(x = 0\) were the only adjustable parameter. \(p_{\text{CO}}\)'s have not been included in the figures because of their being off-scale. Figure 71 is the rate of formation of magnesia against the dimensionless parameter, \(x/x_\chi\), which has been evaluated using Equation (6.13) with the same partial pressure distribution shown in Figures 69 and 70.

Table 8 shows the calculated fractions of oxidation of carbon by oxidants \(\text{MgO}\) and \(\text{CO}_2\), respectively, for the case of \(a_{\text{FeO}} = 0.075\) at \(x = x_\chi\). As has been shown in Section 6.3(a),
Figure 69: Partial pressures of Mg(g) and CO$_2$ at $a_{FeO} = 0.075$ versus dimensionless distance.
Figure 70: Partial pressures of Mg(g) and CO₂ at a₁FeO = 0.150
Figure 71: Rate of MgO formation versus dimensionless distance.
solid carbon, which is available at \( x = 0 \), may be oxidized by MgO as well as CO\(_2\) molecules. For a given rate of decarburization under a quasi-steady state condition, the rate is the sum of rate of Mg formation and that of decarburization by CO\(_2\) by Equation (6.9),

\[
(J_{Mg})_x = 0 + (J_{CO_2})_x = 0 = 0
\]

The second term in the left hand side is the contribution of CO\(_2\) to the oxidation of carbon, which is again closely related through Equation (6.11b) to \( (dp_{CO_2}/dx)_x = 0 \). This is the adjustable parameter in computation.

**Table 8: Fractions of Decarburization by MgO and CO\(_2\)**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( MgO + C \rightarrow Mg + CO )</th>
<th>( CO_2 + C \rightarrow 2CO )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500(^\circ)C</td>
<td>0.03</td>
<td>0.97</td>
</tr>
<tr>
<td>1600(^\circ)C</td>
<td>0.74</td>
<td>0.26</td>
</tr>
<tr>
<td>1700(^\circ)C</td>
<td>0.998</td>
<td>0.002</td>
</tr>
</tbody>
</table>

### 6.8 DISCUSSION

A comparison of Figures 69 and 70 clearly shows the effects of temperature and/or activity of iron oxide in the slag on the distribution of \( p_{Mg} \) and \( p_{CO_2} \) across the decarburized zone. The effect of temperature on \( p_{Mg} \) is extremely large compared with that on \( p_{CO_2} \) for a fixed value of activity of iron oxide in the slag and constant \( p_{CO} \) at \( x = x_f \). With increasing temperature and activity of iron oxide of the slag, the maximum rate of MgO formation increases and happens at a location closer to the slag front, as shown in Figure 71. The failure of a dense layer will allow slag to penetrate the brick
oxidizing slag to magnesium-containing gas will trigger rapid MgO(g) precipitation at the slag/gas interface and stop further penetration of slag. This situation may partly explain the absence of direct contact between carbon and penetrating slag.

The rate of formation of MgO or the dense layer is proportional to the product of $p_{Mg}$ and $p_{CO_2}$ at any location in the system. Higher temperatures, with the activity of iron oxide in the slag within a range of desirable values, will therefore result in a more intensive effort to establish or repair the dense MgO layer. On the other hand, the rate of the destruction of this layer due at least to the mechanism of MgO dissolution will be enhanced at higher temperatures and with more acid slags. Under these conditions slags are more fluid and capable of dissolving more MgO.

Even though the presence of iron oxide in the slag, as the source of oxygen, is essential to the formation of a dense layer and the reaction rate can be increased by the increase of activity of iron oxide, as clearly shown in this chapter, it has to be qualified in the following way. When the activity of iron oxide is too high, hence, very large $p_{CO_2}$ at $x = x_C$, the decarburization at $x = 0$ will be mainly done by $CO_2$. Therefore, the partial pressure of magnesium vapor and the rate of formation of the MgO layer will be very low at normal steelmaking temperatures.

The important process parameters involved in the building and repairing of the dense MgO layer are temperature and oxygen potential at $x = x_C$, or the activity of iron oxide in the
If the assumption, on the other hand, that the destruction of the dense layer is mainly due to the dissolution of MgO in the penetrating slag, then, the solubility of MgO, which is a function of slag composition and temperature and the viscosity of slag, are the important parameters. In order to maximize the slag resistance of BOF refractories, based on the results in present work, the temperature and the activity of iron oxide should be at their optimum values and the slag should be as basic as possible.
CHAPTER VII
CONCLUSIONS

From laboratory studies on the attack of carbon-free and carbon-bearing magnesite refractories by synthetic steelmaking slags at 1600°C and theoretical analysis, the following conclusions may be drawn.

7.1 CARBON-FREE REFRACTORIES

1. The attack of carbon-free magnesite brick by steelmaking slags is consistent with the mechanism of matrix disruption rather than dissolution of MgO grain for all slags except slag N.

2. Al₂O₃ in the slag is detrimental to magnesite refractories, i.e., with increasing Al₂O₃ in the slag, both penetration and disruption increased. The experimental results suggest that this is mainly the result of formation of Ca-Al-silicates, which are low melting and highly fluid at steelmaking temperatures.

3. MgO additions beyond certain levels to Al₂O₃-containing slags are beneficial, i.e., MgO moderates the detrimental effect of Al₂O₃ in the slag. The interpretation of this result is that it is due to the rapid increase of viscosity associated with the increase of fusion point of the slag near its saturation with MgO, an explanation consistent with the phase diagrams.
available in the literature.

4. Silica in the slag with insufficient accompanying lime, i.e., slag N with CaO/SiO₂ = 1, is detrimental to the basic refractories studied. This is due not only to brick matrix dissolution but also to corrosion of the periclase grain by forming low melting silicate compounds.

7.2 CARBON-BEARING REFRACTORIES

1. The beneficial effect of the presence of carbon in BOF magnesite refractories has been verified to be mainly due to the formation of a dense MgO layer. Such a layer is formed by the reduction of the MgO by carbon, with subsequent transport and reoxidation of the Mg vapor. Its precipitation near the front of penetrating slag gives a dense MgO layer. There is no evidence in the present work to support that the non-wetting nature of carbon by slags or pressure buildup due to decarburization gases play significant roles in the "slag resistance" of BOF refractories.

2. Different segments of the dense layer are being constantly formed and destroyed by dissolution in the slag. The region of the decarburized zone flooded with slag as a result of the local break-throughs of the dense layer are attacked in the same manner as the carbon-free brick.

3. There are competitive reactions for decarburization and the oxidants are MgO and CO₂. CO₂ is the dominant oxidizing agent at lower temperatures or when the iron oxide activity in the slag is high.

4. Decarburization with MgO is considered to be still
beneficial compared to that with CO₂, even if it fails to produce a dense MgO layer due to the presence of very corrosive slags. The Mg vapor will reduce FeO and become part of penetrating slag as MgO. This results in an increased viscosity and retardation of further slag penetration.

5. To maximize the slag resistance of BOF refractories, the temperature and activity of iron oxide in the slag should be at their optimum values and the slag should be as basic as possible.
FUTURE WORK

The scope of this work covered many aspects of refractory problems in several types of steelmaking vessels. This investigation was designed to clarify the overall view of the behavior of steelmaking slag - basic refractory systems. The future work, as an extension of this thesis, may be directed towards quantitization and generalization of the understanding established in this project. Several topics are listed below:

1. Establishing the optimum values of temperature and oxygen potential at the hot face to result in the maximum rate of formation of the dense MgO layer in BOF bricks.

2. Investigating the kinetics of dissolution of the dense MgO layer by slags of various compositions.

3. Studying the kinetics and mechanism of slag attack of basic brick by varying brick properties, i.e., chemical composition, firing conditions, bonding, pore structure, carbon content, etc.

4. Investigating the causes for (a) unusual long lining life (over 7600 heats) of BOF at Nippon Steel\(^6\)\(^3\) and (b) the excessive wear in AOD with lining life generally less than 100 heats.
APPENDIX

The investigations on the reactions between acid refractories and iron-manganese alloys have been carried out by the author before the commencement of the work on basic bricks. As discussed in Chapter I, Introduction, p. 2, for simplifying the presentation, this portion of thesis work in the form of a reprint of a published article is attached here as an Appendix.
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Figure 21: Carbon-free magnesite brick specimens, from left, after immersion in master slag (46% CaO, 30% SiO₂, 17% Fe₂O₃, and 7% MnO) for 20, 40, 60, 80, and 100 minutes in that order.
Figure 22: Carbon-free magnesite brick specimens, from left, fresh specimen, and those of 5 minute immersion in slags A, B, C, D, E, G, H, J, K, L, N, P, Q and R in that order (Table 2, page 58, for slag composition).
Figure 23: Partially sectioned carbon-free magnesite brick specimens, from left, fresh specimen, and those of 30 second immersion in slags A, B, C, D, E, F, G, H, J, K, L, N, P, Q and R in that order (Table 5, page 58, for slag composition).
Figure 24: Partially sectioned carbon-free magnesite brick specimens, from left, fresh specimen, and those of 5 minute immersion in slags A, B, C, D, E, F, G, H, J, K, L, N, P, Q and R in that order (Table 5, page 58, for slag composition).
Figure 25: Carbou-free magnesite brick specimens reacted at 1550°C, from left, after 5 minute immersion in slags A, C and F; partially sectioned specimens after 30 seconds in slags A, C and F; and partially sectioned specimens after 5 minutes in slags A, C, and F: slag A (master slag), slag C (10% Al₂O₃), and slag F (15% Al₂O₃ - 8% MgO).
Figure 26: Specimen elongation and slag climb vs. slag composition.
Figure 27: Slag penetration vs. slag composition.
Figure 28: Magnesite brick fragments which remained in slag D (15% Al₂O₃) for another 30 minutes at 1600°C after 5 minute immersion test; dark areas are slag phases and MgO grains have suffered slag penetration along the subgrain boundaries (15X).
Figure 29: Photomicrographs (33X) of...
Figure 30: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in slag A (master slag); brown regions are slag-penetrated matrix and light areas are void spaces.

Figure 31: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in slag K (8% MgO); brown regions are slag-penetrated
Figure 32: Thin section photograph (4.2X) of carbon-free specimen after 30 seconds immersion in slag C (10% Al₂O₃); brown regions are slag-penetrated matrix and light areas are void spaces.

Figure 33: Ca-Al-silicate compound (dendrites) developed in the matrix of carbon-free brick specimen after 5 minute immersion in slag C (84X).
Figure 34: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in slag F (15% Al₂O₃-8% MgO); brown regions are slag-penetrated matrix and light areas are void spaces. The thin section has been made from the portion remaining in the specimen holder.

Figure 35: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in slag G (10% Al₂O₃-13% MgO); brown regions are slag-penetrated matrix and light areas are void spaces.
Figure 36: Ca-Al-silicate compound (dendrites) developed in the matrix of carbon-free brick specimen after 5 minute immersion in slag C (84X).

Figure 37: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in Fe₂O₃-containing slag F (48% CaO, 30% SiO₂, 17% Fe₂O₃, 7% MnO); brown regions are slag-penetrated matrix and
Figure 38: Thin section photograph (4.2X) of carbon-free specimen after 5 minute immersion in Fe₂O₃ slag Q (10% Al₂O₃); brown regions are slag-penetrated matrix and light areas are void spaces. The thin section has been made from the portion remaining in the holder.

Figure 39: Thin section microphotograph (84X) showing dendritic crystallization in the matrix of cylindrical carbon-free brick specimen after 5 minutes in Q (10%).
Figure 40: Thin section photograph (4.2X) of cylindrical carbon-free specimen after 30 second immersion in Fe₂O₃ slag R (15% Al₂O₃-8% MgO); brown regions are slag-penetrated matrix and light areas are void spaces.

Figure 41: Thin section photograph (4.2X) of carbon-free specimen after 30 second immersion in slag N (CaO/SiO₂ = 1).
Figure 42: Monticellite (CMS) developed in the matrix of carbon-free brick specimen after 5 minute immersion in slag N (CaO/SiO$_2$ = 1); 84X.
Figure 43: Thin section photographs (4.2X) of cylindrical carbon-free brick specimen which has been withdrawn by standard procedure after 30 second immersion in slag H. (a) in plain light and (b) under crossed nicols. Brown regions are Fe- and Mn-rich slag-penetrated outer layers. Bright areas are the matrix penetrated mainly by silicate of slag.
Figure 44: Thin section photographs (4.2X) of cylindrical carbon-free brick specimens which have been withdrawn immediately after (a) 30 second and (b) 5 minute immersions in slag G (10% Al₂O₃-13% MgO).
Figure 45: Composite strip charts of electron microprobe analysis over cross-sections of cylindrical carbon-free brick specimens; (a) as-received and (b) after 30 second immersion in slag H (distance from the surface of the specimen).
Figure 46: Cross-sections of carbon-bearing brick crucibles tested in air atmosphere for 2 hours, from left, without slag, with slags C, T and N at 1600°C and with slag V at 1650°C in that order.

Figure 47: Cross-sections of carbon-bearing brick crucibles tested at 1600°C in air atmosphere for 2 hours, from left, without slag and with slags T and U in that order.

Figure 48: Cross-sections of carbon-bearing brick crucibles at
Figure 49: Thin section photograph (4.2X) of pitch-impregnated magnesite brick coked in a graphite container at 1600°C for 30 minutes.

Figure 50: Thin section photograph (4.2X) of crucible wall made of carbon-bearing magnesite brick maintained in air atmosphere at 1600°C for 2 hours; carbon-bearing central region is surrounded by light decarburized zones and thin white layers are noticed at the boundaries between these two regions.

Figure 51: Carbon-bearing magnesite brick crucibles reacted in air atmosphere for 2 hours with slag N (a) and slag C (b) at 1600°C and slag V (c) at 1650°C.
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Figure 53: Thin section photographs (4.2X) of sectioned crucible wall made of carbon-bearing brick reacted with (a) iron oxide-free slag T (10% $\text{Al}_2\text{O}_3$) and (b) U (15% $\text{Al}_2\text{O}_3-3\% \text{MgO}$) in air atmosphere at 1600°C for 2 hours.

Figure 54: Thin section photographs (4.2X) of sectioned crucible wall made of carbon-bearing brick in
Figure 55: Composite strip charts of microprobe analysis over a pitch-impregnated magnesite brick sample coked at 1600°C for 30 minutes in a graphite container (distance from the surface of the specimen).

Figure 56: Composite strip charts of microprobe analysis over a carbon-bearing magnesite brick sample tested in air atmosphere at 1600°C for 2 hours (distance from the surface of the specimen).
Figure 57: Composite strip charts of microprobe analysis along the line GHI of Figure 51(b) over a well-defined dense MgO layer formed in a carbon-bearing magnesite brick crucible reacted with slag C in air atmosphere at 1600°C for 2 hours; slag, right and refractory, left.

Figure 58: Composite strip charts of microprobe analysis along the line DEF of Figure 51(a) over a decarburized zone without dense MgO layer in a carbon-bearing magnesite brick crucible reacted in N at °C for 2 hours...
Figure 59: Composite strip charts of microprobe analysis along the line JKL of Figure 53(a) over the slag/refractory interface region in a carbon-bearing magnesite brick crucible reacted with slag T at 1600°C in air atmosphere for 2 hours, slag, right and refractory, left.

Figure 60: Composite strip charts of microprobe analysis along the line ABC of Figure 54(a) over the slag/refractory interface region in a carbon-bearing magnesite brick crucible reacted with slag D at 1600°C in a graphite container for 30 minutes; slag, right and refractory, left.