THE KINETICS OF THE REACTIONS BETWEEN SILICA AND ALUMINO-
SILICATE REFRACTORIES AND MOLTEN IRON ALLOYS
THE KINETICS OF THE REACTIONS BETWEEN SILICA AND ALUMINO-SILICATE REFRACTORIES AND MOLTEN IRON ALLOYS

By

SID EDWARD FELDMAN, B.Sc.

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TITLE: The Kinetics of the Reactions Between Silica and Alumino-Silicate Refractories and Molten Iron Alloys

AUTHOR: Sid Edward Feldman, B.Sc. (McMaster University)

SUPERVISOR: Professors W-K. Lu, P.S. Nicholson and A.E. Hamielec

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ABSTRACT

The rate of corrosion of silica and alumino-silicate refractories in Armco iron and iron-carbon melts was measured. An interpretation of the rate data required an experimental investigation of the kinetics of the reactions between iron oxide and silica, and carbon and silica.

A standard "immersion" technique was used under both static and dynamic conditions. The corrosion of the refractories in Armco iron melts was initially controlled by a chemical reaction process but changed rapidly to a steady-state, diffusion-controlled process. A liquid silicate product layer built up at the interface during the induction period. The steady-state rate of corrosion was independent of the oxygen content of the melt and was also found to be a linear function of the peripheral velocity of the refractory specimen. The rate of corrosion for the various refractories was measured and found to be controlled by diffusion of iron and oxygen in the silicate layer.

The rate of corrosion of these refractories in carbon-saturated iron melts was also studied. The rate was found to be independent of the silicon concentration and the carbon concentration in the melt (in the range 2.3% C to saturation). The rate was independent of the rate of rotation of the refractory specimen. The results were interpreted in terms of chemical reaction control at the refractory/metal interface, with the dissociation of silica proposed as the controlling reaction. The rate was found to be strongly temperature dependent indicating reaction control.

This experimental investigation has provided new insights into the mechanism of corrosion of silica and alumino-silicate refractories in iron melts.
ACKNOWLEDGEMENTS

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TO MY PARENTS
CHAPTER 1

INTRODUCTION

In the modern steelmaking industry, the destruction of refractories by molten metals and slags is a major concern. Despite advances in refractory technology and the development of new and improved refractory materials, refractory attack continues to cause serious problems in steelmaking processes.

In general, steelplant refractories are heterogeneous mixtures of inorganic oxides in crystalline and glassy forms, containing a variable amount of porosity. In view of the complexity of these composites, it is not unexpected that the reactions between refractories and molten metals and slags are complex in nature. Past studies of the kinetics of these reactions have been characterized by a diversity of opinions as to the reaction mechanisms and the controlling steps in these mechanisms. Due to the high temperatures normally encountered in steelmaking and the low diffusivities associated with molten metals and slags, it is generally believed that these reactions are transport-controlled. However, it has been found that certain reactions are possibly controlled by chemical reaction mechanisms.

The purpose of the present study was to investigate the kinetics of the attack of silica and alumino-silicate refractory materials by molten iron and its alloys. Under carefully controlled conditions, the reaction mechanisms and the rate-controlling steps have been studied and some new insight into the overall process has been obtained.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

One of the major problems in modern steelmaking is the attack of refractories by molten metals and slags. This attack is quite severe and results in the costly destruction of ladle refractories, furnace linings, refractory runners and nozzles, and other refractory surfaces. In addition, the cleanliness of the steel is influenced by refractory attack since the latter is a primary source of non-metallic inclusions. The purpose of this chapter is to review much of the work which has been done to study the attack of silica and alumino-silicate refractories by molten metals and slags.

2.2 The Nature of Refractory Attack

Refractory attack is the result of chemical corrosion and physical erosion of the refractory by the melt. The corrosion of refractories is due to the chemical reactions which take place between the components of the melt or slag and the refractory material, resulting in the eventual destruction of the refractory. The physical erosion of refractories can take place in systems where there is relative motion between the molten metal or slag and the refractory. In this case, the melt mechanically removes a portion of the refractory due to the forces applied to the surface by the melt. Quite often refractory attack is a result of combined chemical corrosion and physical erosion. In such situations physical erosion will compliment the corrosion by making available fresh refractory surfaces.
which are susceptible to chemical reaction with the melt, and conversely, the chemical attack will weaken the structure of the refractory to facilitate further erosion.

Very little work has been done to study the nature of the physical erosion of refractories. Most attention has been directed towards the problem of corrosion. For this reason, much of the literature on the subject of refractory attack deals solely with the chemical corrosion aspect.

2.3 Reactions Between Refractory and Melt

The reactions between refractory materials and molten metals and slags usually result in the formation of a product with a low melting point which is normally liquid at steelmaking temperatures.

2.3.1 Refractory/Metal Reactions

The initial step in the reaction, in the case of molten metals, is the reduction of the refractory oxides by elements dissolved in the metal. In the case of silica and alumino-silicate refractories the reaction can be written as:

\[ \text{SiO}_2 (\text{solid refractory}) + X = \text{Si} + \text{XO} (s, l, \text{ or gas}) \]  

where the underlined symbols represent elements in solution in the molten alloy. The product of this reaction, XO, can be a solid, liquid, or gas. In most steel/refractory reactions, however, this product is a liquid at steelmaking temperatures.

Under certain operating conditions, the initial step in a metal/ refractory reaction is the oxidation of the melt to form a liquid oxide:

\[ X + \frac{1}{2} O_2(g) = (\text{XO})_l \]

(2)
In either case, the second step in the reaction is the fluxing of the refractory material by the liquid oxides produced in reactions (1) and (2), to form a low melting point product:

$$\text{SiO}_2 \text{(solid refractory)} + (\text{XO}) = \text{liquid silicate}$$  \hspace{1cm} (3)

The continuous fluxing of the refractory will eventually lead to its destruction.

A large number of workers have investigated the reactions between silica and alumino-silicate refractories and molten iron alloys. Wahlberg and Fredholm\(^{(1)}\) examined the reaction products formed during the interaction of molten steel and fire-clay brick. They found that the corrosive action of the steel was due to the reaction between manganese in the steel and silica in the brick, leading to the formation of manganese oxide and silicon. The manganese oxide in turn dissolved the brick material to form a manganese-aluminum-silicate. Morton and Carter\(^{(2)}\) studied the reactions between siliceous and fire-brick refractories and steels with various manganese and silicon contents. They concluded that the manganese oxide, formed in the reaction between the brick and melt, had a greater fluxing power than iron oxide for alumino-silicate refractories. They also showed that high silica refractories were more susceptible to attack than fire-brick refractories.

The stabilities of various chamotte and alumina refractories, in cast iron melts, open hearth iron, and high manganese steel, were determined by Andronov and Netronin\(^{(3)}\). An increase in either the temperature or the manganese content of the iron was observed to accelerate the destruction of the refractory. The mechanism of the attack was believed to be the oxidation of manganese and iron by silica in the refractory with the subsequent interaction of these oxides with the refractory to form a liquid slag. In a similar study, Colligan et al\(^{(4)}\) showed that the attack of alumina, fused silica, zircon, and zirconia refractories by molten steel alloys was due to the
fluxing of the refractory materials by the oxides of various elements in
the alloys, namely manganese, iron, and chromium. The attack was
found to be most severe with fused silica, zircon, and alumina refractories,
and only slight with zirconia. Rait et al.\(^{(5, 6)}\) investigated the corrosion
of casting pit refractories by high manganese steel. They concluded
that the free quartz in siliceous firebrick was reduced by manganese in
the steel to form manganous oxide which then fluxed the brick to form a
slag.

Maekawa and Nakagawa\(^{(7, 8)}\) measured the corrosion of chamotte
bricks (63\% \(\text{SiO}_2\), 34\% \(\text{Al}_2\text{O}_3\)) by molten steel. They found that the
rate of corrosion was influenced by the silicon, manganese, and iron
oxide content of the steel with silicon inhibiting, and manganese and
iron oxide promoting corrosion. If elements with a greater affinity for
oxygen were present in the steel, the rate of corrosion was observed
to decrease. They therefore concluded that the corrosion reactions taking
place were:

\[
\text{SiO}_2 \text{ (in brick)} + 2 \text{ Fe} = 2 \text{ (FeO)} + \text{ Si}
\]

\[
\text{SiO}_2 \text{ (in brick)} + 2 \text{ Mn} = 2 \text{ (MnO)} + \text{ Si}
\]

\[
x \text{ SiO}_2 \text{ (in brick)} + y \text{ (FeO)} + z \text{ (MnO)} = \text{(SiO}_2\text{)}_x \cdot \text{(FeO)}_y \cdot \text{(MnO)}_z \text{ (slag)}
\]

In this work it was shown that the corrosion of the refractories by molten
iron and iron oxide increased greatly when the manganese content of the
steel was low. In a similar study, Isomo et al.\(^{(9)}\) demonstrated that as
the manganese/silicon ratio in steel increased, the rate of corrosion
increased. Post and Luerssen\(^{(10)}\) determined that the cleanliness of steel,
which is a function of refractory attack, was influenced greatly by the
manganese and silicon contents of the steel.

Tanoue and Ikeda\(^{(11)}\) studied the reactions at 1600°C between silica,
fire-clay, and high alumina refractories and steels containing manganese, chromium, nickel-manganese, and manganese-aluminum. The liquid steel was observed to attack the silica of the refractories when the silicon content of the steel was lower than the equilibrium concentration which was given by expressions obtained by the authors from this work:

\[
\text{Mn steel: } [\text{Si\%}] = 0.72 \left[ \text{Mn\%} \right]^2
\]
(7)

\[
\text{Cr steel: } [\text{Si\%}] = 0.00135 \left[ \text{Cr\%} \right]^2
\]
(8)

\[
13\% \text{Cr, 18\% Cr-Mn steel: } [\text{Si\%}] = 0.55 \left[ \text{Mn\%} \right] + 0.043 \left[ \text{Cr\%} \right]^2
\]
(9)

\[
18\% \text{Cr - 9\% Ni-Mn steel: } [\text{Si\%}] = 0.72 \left[ \text{Mn\%} \right] + 0.043 \left[ \text{Cr\%} \right]^2
\]
(10)

In general these authors found that the rate of attack decreased with an increase in the silicon content of the metal.

In a series of tests, Minowa et al\(^{12-18}\) used crucibles manufactured from various refractory materials to study the reactions between these refractories and steels containing manganese, silicon, aluminum, carbon, chromium, and nickel. All these elements except silicon and nickel increased the rate of reduction of silica from the refractories. In a similar type of investigation, Novakhatsky and Ershov\(^{19}\) examined the kinetics of the interaction of solid silica with melts containing carbon, manganese, and aluminum. The primary reaction was the reduction of the silica by these elements.

Suzuki et al\(^{20}\) and Narita et al\(^{21}\) used rotating-refractory samples immersed in melts of stainless steel to determine the corrosion resistance of various types of nozzle refractories. The zircon and zirconia refractories proved to be far superior to silica, fire-clay, or alumina refractories in terms of corrosion resistance.

It would appear from the literature that refractory attack by molten
iron alloys results, in general, from the oxidation of iron and alloying elements to form liquid oxides which in turn flux the refractory brick. Manganese oxide and iron oxide seem particularly harmful to silica and alumino-silicate refractories.

In the non-ferrous metal industry, the corrosion of refractories by molten metals is also a serious problem. The reactions between the refractories and metals are quite similar to those taking place in steel-making systems.

Ignatova et al.\(^{(22)}\) investigated the attack of alumino-silicate refractories by molten tin. The attack was due to the formation of low melting compounds associated with the reaction between the silica in the refractories and the oxides of tin.

Brondyke\(^{(23)}\) studied the reactions between molten aluminum and alumino-silicate refractories and found that the silica was reduced by the aluminum to form alumina and silicon which dissolved in the melt. They postulated the following reaction:

\[
3 \text{SiO}_2 + 4 \text{Al} = 2 \text{Al}_2\text{O}_3 + 3 \text{Si}
\]  

(11)

In a similar study, the reactions between vitreous silica and molten aluminum were observed by Standage and Gani\(^{(24)}\).

The interfacial reactions of various metals (Be, Mo, Nb, Ni, Si, Ti, and Zr) with dense oxide specimens (Al\(_2\)O\(_3\), BeO, MgO, ThO\(_2\), and TiO\(_2\)) were investigated at temperatures up to 1800°C by Economos and Kingery\(^{(25)}\). At 1800°C, the systems Be-Al\(_2\)O\(_3\), Be-MgO, Si-Al\(_2\)O\(_3\), Si-ZrO\(_2\), Si-MgO, Nb-BeO, and Ti-MgO formed new phases which were not soluble in the oxides or the metals, with the resultant formation of interfacial layers. In the systems Ti-BeO, Ti-Al\(_2\)O\(_3\), Ti-TiO\(_2\), Ti-ZrO\(_2\), Ti-MgO, Zr-Al\(_2\)O\(_3\), Zr-TiO\(_2\), Zr-MgO, Be-TiO\(_2\), Si-BeO, Si-ThO\(_2\), Nb-BeO, Nb-ThO\(_2\), and Nb-TiO\(_2\), corrosion of the oxide interface by the metal, due to a solution process, was observed.
2.3.2 **Refractory/Slag Reactions**

Extensive investigations have been carried out on the chemical aspects of refractory/slag attack. In the case of this attack, it has generally been observed that the oxide constituents of the slag combine with the oxide components of the refractory to form low melting products.

In a series of papers, Towers\(^{(26, 27)}\) reviewed some of the work done to study the nature of slag/refractory attack and the variables which affect the rate of this attack. Barrett et al\(^{(28-31)}\) have investigated the dissolution of single crystals of alumina, magnesia-alumina spinel, and magnesia in a variety of silicate slags. In similar studies, Cooper et al\(^{(32, 33)}\) measured the rates of dissolution of sapphire, alumina, mullite, anorthite, and silica in a calcium-aluminum-silicate slag. The dissolution rates and their temperature dependence were found to be controlled by transport within a liquid boundary layer. At lower temperatures, alumina was less susceptible to attack than the other refractory materials tested.

Isomo et al\(^{(9)}\) investigated the corrosion of fire-clay and high alumina refractories in contact with molten steelmaking slag. The amount of corrosion was observed to increase with temperature and time, and was independent of the reaction atmosphere. A comparison study, in which the corrosion of these refractories by molten steel was measured, showed that the attack by the slag was much more severe than the attack by molten steel.

Forster and Knacke\(^{(34)}\) studied the dissolution of dolomite, sillimanite, and silica bricks in a calcium-aluminum-silicate slag. The chemical composition of the slag and the bricks, the texture and moisture content of the bricks, the temperature, and the agitation of the melt, were all shown to have some influence on the stability of the bricks with respect to the slag.
2.4 Controlling Processes

In general, the path followed by refractory/metal or refractory/slag reactions may consist of a series of consecutive steps as follows:

(a) The transport of material to the reaction interface.
(b) The chemical reaction at the interface.
(c) The removal of reaction products from the interface.

The overall reaction rate will be controlled by the slowest of these steps. In the case of refractory/slag attack it has been found by a majority of investigators that the rate of attack is transport-controlled. In a review of the subject, Cooper and Kingery (35) discussed previous work on the corrosion of refractories by liquid slags and concluded that the transport process was rate-controlling. This was said to be due to the low diffusion coefficients and the effective thickness of the product layer associated with the diffusion processes.

Experimentally the transport process has been shown to be rate controlling in the work of Cooper et al. (32, 33). In a series of tests, Barrett et al. (28, 29) studied the dissolution of single crystals of sapphire and corundum in silicate slags. It was found that the dissolution rates were diffusion controlled. In more recent work (30, 31) these authors have shown that the reaction rate initially was controlled by a chemical process. However, the rate became diffusion controlled after only a very short time. In this same work, the dissolution of magnesia in sodium silicate melts was shown to be chemical reaction-controlled.

Flood and Seltveit (36) studied the dissolution of corundum and magnesia-alumina spinel in sodium borate melts. The rate of corrosion was affected by the properties of the boundary layer between the refractory and the melt, and by the ability of this layer to permit diffusion or penetration of the reacting ions. In these experiments the rate determining process was thought to be cation diffusion through the boundary layer. The
rate of dissolution of fused quartz in ferrous-silicate slags was measured by Reeve (37) who concluded that the dissolution rate was controlled by the mass transfer of the dissolving species through the liquid boundary layer. In a similar study, Kovalenko et al. (38) rotated disks of iron oxide and mullite in fused enamels and measured the dissolution rates at various temperatures. At 1600°C the rates of dissolution were governed by diffusion processes. However, at lower temperatures, the rates of dissolution of the iron oxide and mullite were governed by the kinetics of chemical reactions and the role of diffusion was insignificant.

In the case of refractory/metal reactions there exists a diversity of opinions as to the rate-controlling processes and it is apparent that further research is needed in this field. This problem will be discussed in greater detail later in this work.

2.5 Equilibrium and Kinetic Studies of Refractory Attack

The extent of the chemical reaction between a refractory and molten metal or slag at a fixed temperature is controlled by the kinetics and limited by the thermodynamics of the system. Thermodynamics determines the equilibrium state which the system will approach and the kinetics determines the rate at which this equilibrium state is approached.

2.6 Equilibrium Studies

In the study of reactions between refractories and molten metals or slags, the use of phase-equilibrium diagrams has become increasingly important. These diagrams provide a basis for predicting the effect of temperature, composition, and atmosphere on the reaction between the refractory and melt. Much work has been done on the determination of the
phase equilibrium diagrams for silica and alumino-silicate refractory systems by Muan and his co-workers \cite{39-41} and diagrams for most common ceramic systems are now available \cite{42,43}.

These phase diagrams have certain limitations in their ability to predict the extent of refractory attack. Most of the diagrams have been compiled using pure oxide materials and represent equilibrium conditions. In practice the refractory/melt system will consist of a large number of oxides which are not pure and are not at equilibrium. The phase diagrams also do not provide any information regarding the properties of the phases formed, for example viscosity or density, nor do the diagrams help determine the rate at which the reactions take place. With these limitations in mind, phase diagrams can still play an integral role in the study of refractory attack.

The use of phase-equilibrium diagrams can be illustrated by considering the $\text{Al}_2\text{O}_3-\text{SiO}_2$ system which encompasses the whole composition range of alumino-silicate refractories including high purity silica brick (greater than 96\% $\text{SiO}_2$), fire-clay brick (up to 69\% $\text{SiO}_2$ and 30\% $\text{Al}_2\text{O}_3$), and high alumina brick (greater than 50\% alumina). This diagram is shown in Figure 1. The effect of the addition of small amounts of alumina to silica brick is apparent from the diagram. A relatively small amount of alumina present as an impurity in silica brick can cause liquid formation at a temperature as low as 1590\degree C. From the diagram it can also be seen that the most refractory alumina-silica mixtures are those whose compositions lie in the range between mullite ($\sim72\% \text{Al}_2\text{O}_3$) and alumina. In this composition range, a liquid phase does not appear below 1840\degree C. In the case of fire-clay bricks, some liquid begins to form at 1590\degree C. The amount of liquid formed at or above this temperature decreases with increasing alumina content of the fire-clay brick.

Iron oxide can cause severe damage to silica and alumino-silicate refractories. The effect of iron oxide on silica brick can be seen from Figure 2. A slight amount of iron oxide can cause liquid formation
Figure 1: Phase Diagram for the System $\text{SiO}_2$-$\text{Al}_2\text{O}_3$. 
Figure 2: Phase Diagram for the System Iron Oxide - SiO₂ In Contact with Metallic Iron.

Figure 3: Phase Diagram for the System Iron Oxide - SiO₂ in Air.
at a temperature as low as $1178^\circ C$. This diagram has been compiled under atmospheres with relatively low oxygen potentials. The effect of an oxidizing atmosphere on the attack of silica refractories by iron oxide can be seen in Figure 3 which shows that the lowest temperature of liquid formation rises from $1178^\circ C$ for an atmosphere with $P_{O_2} \sim 10^{-9}$ atm. to $1455^\circ C$ in air ($P_{O_2} = 0.21$ atm.). Also as the oxygen partial pressure is increased the silica content of the liquid which is formed decreases. Thus the ability of iron oxide to flux silica brick is greatly enhanced when iron oxide is in its lowest oxidation state, i.e., as a basic oxide.

An important feature of the silica-iron oxide system is the region of two immiscible liquids which is found at the silica end of the phase diagram (Figures 2 and 3). Fortunately for silica brick, this region of immiscibility influences the relative amounts of solid and liquid in the two-phase region beneath it. Upon application of the lever rule to this solid-liquid region, it is evident that the solid/liquid ratio changes very little with increasing temperature at any constant composition and with increasing iron oxide composition at a constant temperature. As can be seen from Figures 2 and 3, the effect of oxygen partial pressure is quite significant in extending the limits of the two-liquid region of the silica-iron oxide system from a maximum iron oxide composition of approximately 40% under highly reducing conditions to a 70% maximum in air. Due to these properties of silica brick, it is important that this refractory be used in oxidizing rather than reducing conditions in service.

Alkalis also have a strong fluxing action on silica brick, with a small amount of alkali causing liquid to form at a temperature as low as $769^\circ C$. The $Na_2O-SiO_2$ system is shown in Figure 4.

The effect of the addition of iron oxide to an alumino-silicate refractory will depend on the oxygen partial pressure of the atmosphere. Figures 5 and 6 show the phase relations at liquidus temperatures in the system iron oxide - $Al_2O_3 - SiO_2$ in contact with metallic iron and air respectively. As can be seen in Figure 5, a fire-clay brick under reducing
Figure 4: Phase Diagram for the System $\text{Na}_2\text{O} - \text{SiO}_2$ (where h = high, l = low, Trid. = tridymite, Crist. = cristobalite, Qtz. = quartz, $N_2\text{S} = \text{Na}_4\text{SiO}_4$, $NS = \text{Na}_2\text{SiO}_3$, $NS_2 = \text{Na}_2\text{Si}_2\text{O}_5$, L = liquid).
Figure 5: Phase Relations at Liquidus Temperatures in the System Iron Oxide - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ in Contact with Metallic Iron.
Figure 6: Phase Relations at Liquidus Temperatures in the System Iron Oxide - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ in Air.
conditions can form a liquid with iron oxide at a temperature as low as 1210°C. If, however, the refractory contains a larger amount of alumina such that it is initially composed of corundum and mullite, liquid will not form until a temperature of 1380°C is reached. As demonstrated in Figure 6, the formation of a liquid in a fire-clay brick in air does not begin until a temperature of 1380°C is reached. Similarly, a high alumina brick will withstand temperatures up to 1460°C in air before the refractory is fluxed by iron oxide to form a liquid phase.

2.7 Kinetic Studies

While a great deal of work has been done concerning the equilibrium aspect of the reactions associated with refractory attack, very little has been published on the rates of these reactions. In any kinetic study the rate will depend on a number of variables. The aim, therefore, of any kinetic study is to measure the reaction rate under carefully controlled conditions such that the rate can be related to the variables of study.

2.7.1 Experimental Techniques for Studying the Kinetics of Refractory Attack

A number of methods are available in the literature to study the attack of refractories by molten metals and slags. Two of these methods most commonly used are the "crucible" method and the "immersion" method.

(i) The Crucible Method

This technique involves the preparation of a crucible from the refractory material to be tested. The alloy or slag is added to the crucible and the system is heated to the required temperature. The rate of attack can be determined by analyzing the melt and expressing the change in
composition, due to the dissolution of the refractory, as a function of time. It is also possible to determine the rate by observing the dimension change, volume change, and weight change of the crucible as a function of time. This method has been used successfully in a number of studies of refractory/metal and refractory/slag attack as in the work of Maekawa et al\textsuperscript{(7, 8)} and Minowa et al\textsuperscript{(12-18)}.

(ii) The Immersion Method

Using this method, the test refractory may be different shapes and forms, for example cylindrical rods, spheres, disks, entire bricks, or perhaps actual refractory objects used in service (for instance nozzles). The specimen is immersed in the melt for a predetermined length of time. The rates of attack, as in the case of the crucible method, can be determined by measurement of weight, volume, or dimension changes or by measuring the change in composition of the melt as a function of time. Barrett et al\textsuperscript{(28-31)} and Cooper et al\textsuperscript{(32, 33)} used this method to study the dissolution of refractory materials in silicate slags. Snow and Shea\textsuperscript{(44)} used a variation of this method to study the attack of nozzles in open hearth ladles. For their tests, various types of steels were teemed through nozzles manufactured from fire-clay and other refractory materials. The rate of attack was determined by measurement of the change in the bore diameter of the nozzle. Colligan et al\textsuperscript{(4)} also used an "immersion" method to study the reactions between molten steels and various refractories.

An advantage of the "immersion" method is that the effect of agitation on the reaction rate can be studied by rotation of the refractory specimens in the melt. Although agitation can be introduced in the "crucible" method by stirring of the melt, it is difficult to determine the exact hydrodynamic condition of the system with this method. With the "immersion" method, however, careful control of the hydrodynamics of the system can be obtained by controlling the rotation speed of the
refractory specimen. Cooper et al.\(^{(32, 33)}\), Lakatos and Summingskold\(^{(45)}\), and Flood and Seltveit\(^{(36)}\) rotated cylindrical refractory specimens in molten slags and glasses to study the effect of agitation on the reaction rates. Suzuki et al.\(^{(20)}\) and Narita et al.\(^{(21)}\) also used this method to observe the reactions of cylindrical specimens of fire-clay, siliceous, high alumina, zircon, and zirconia refractories with various steel melts.

2.7.2 Variables Affecting Refractory Attack

(a) Physical Properties of the Refractory and Melt

It has been found that the reaction between refractories and molten metals or slags depends to a certain extent on the physical characteristics of the melt and the refractory. Increased porosity of the refractory results in an increase in the effective surface area of the refractory and a subsequent increase in the rate of attack by the melt. Also the pore structure and permeability of the refractory will determine the ability of the melt to penetrate the interior of the refractory where dissolution processes can take place and weaken the entire refractory structure.

A number of authors have reported the effects of porosity and permeability on the rate of refractory attack. Vago and Griffith\(^{(46, 47)}\) rotated zircon refractories in molten glasses. They determined that there was a direct relationship between the apparent porosity and the loss in volume of the refractory. It was also noted that pure and homogeneous specimens were attacked to a lesser degree than coarse-grained and uneven specimens. Minowa et al.\(^{(16)}\) observed that the rate of attack of alumina crucibles by carbon dissolved in iron increased with the porosity of the crucible. Whittaker and Seddon\(^{(48)}\) and Laing et al.\(^{(49)}\) found that fusion-cast refractories exhibited a much better resistance to glass corrosion than those moulded or slip cast. The lowering of the porosity of refractories by using higher firing temperatures decreases the rate of attack by molten
metals, as discussed in papers by Snow and Shea\textsuperscript{(44)} and Novikov\textsuperscript{(50)}. Suzuki \textit{et al}\textsuperscript{(20)} also observed that the high temperature firing of refractories improved their corrosion resistance to molten steel. In reviewing the literature, it was generally noted that the greater the porosity of the refractory, the greater the attack by the melt.

Norton\textsuperscript{(51)} suggested that surface tension and wettability had some effect on refractory attack. It has been proposed\textsuperscript{(52)} that the optimum condition for reducing slag attack on refractories is a high contact angle with a high interfacial energy. Comeforo and Hursh\textsuperscript{(53)} measured the wetting of alumino-silicate refractories by molten glass, using the sessile-drop method to determine the contact angle. In comparing these results with another study\textsuperscript{(54)} to observe the penetration of the glass into the refractory, the authors found that the rate of penetration of the glass into the refractory was more strongly dependent on the contact angle than on the pore size. The surface tension, interfacial energy, and contact angles in various liquid metal-solid ceramic systems have been measured at elevated temperatures by a number of authors\textsuperscript{(55-62)}, using a sessile-drop method. In general, it has been observed that the surface tension of the metals and the wettability of the metal-ceramic systems were strongly dependent upon the atmosphere and the presence of impurities or alloying elements in the metals.

Another factor which greatly influences the rate of attack is the viscosity of the melt and the reaction product. In a review, Rait and Green\textsuperscript{(63)} reported the work done on this subject prior to 1940. In a later work, Van Gijn\textsuperscript{(64)} showed that the corrosive action of slag on porous refractories was mainly determined by its viscosity. In particular, he found that the rate of penetration into the pores depended on the viscosity. Endell and his co-workers\textsuperscript{(65, 66)} observed a linear relationship between corrosion and the kinematic viscosity of the slag, with the attack varying inversely with the kinematic viscosity. Fehling\textsuperscript{(67)} proposed an empirical equation to express the rate of slag attack;
\[ e = \text{const} \frac{S_T}{\eta} \left( \frac{T}{r} \right)^{2/3} \left( \frac{\rho \sin \alpha}{\lambda} \right)^{2/9} V_s^{1/9} \]  

where \( e \) is the rate of corrosion perpendicular to the reaction surface in cm sec.\(^{-1}\), \( S_T \) is the solubility of the refractory in the slag, \( r \) is the molecular radius, \( \eta \) is the viscosity of the slag, \( \rho \) is the density of the slag, \( \alpha \) is the angle of inclination to the wall, \( \lambda \) is the length of the wall, and \( V_s \) is the volume of slag supplied per unit area per unit time. The work of Fettke and Stewart\(^{(68)}\) showed that Endell's equation could be used successfully to compare calculated values of the rate of slag attack with actual experimental values.

The viscosity of the reaction product will also affect the rate of attack. In situations where the reaction product is quite viscous, a build-up of a thick product layer could occur thus diminishing the rate of attack\(^{(69)}\). Barham and Barrett\(^{(31)}\) have shown that the magnitude of the viscosity of the reaction product can determine whether or not the rate of dissolution of a refractory in a slag is diffusion-controlled or reaction-controlled.

(b) **Reaction Atmosphere**

The gas phase present in the refractory/metal or refractory/slag system will determine to a great extent the reactions which take place between the metal, slag, and refractory. In examining the attack of chamotte bricks by molten steel and slags, Maekawa and Nakagawa\(^{(8)}\) considered the effects of atmosphere on the rate of attack. They found that oxygen in the atmosphere promoted corrosion. Isomo et al\(^{(9)}\) in a similar study showed that the rate of attack of alumino-silicate refractories by molten steel was strongly influenced by the atmosphere, whereas the rate of slag attack was independent of the atmosphere. The reaction of molten steel with silica sand was studied by Van Vlack\(^{(70)}\).
Under oxidizing conditions a large amount of iron oxide was formed which dissolved a considerable amount of silica. Colligan et al.\(^{(71)}\) investigated the reactions between steel and silica sand under controlled CO\(_2\)/CO atmospheres. The reaction proceeded with iron being oxidized by the atmosphere and this oxide reacting with the silica sand to form an iron silicate liquid. Under conditions where the carbon dioxide to carbon monoxide ratio was quite small, no silicate liquid was formed, and iron and quartz were the only phases present. Minowa et al.\(^{(12)}\) observed that the products from the reaction between molten iron and alumina depended on the oxygen partial pressure of the atmosphere with an iron spinel, hercynite, formed at partial pressures of oxygen of 1.9 \times 10^{-9} \text{ atm. or higher. When melted in air, hematite was formed. In a similar study, Broklof f et al.\(^{(72)}\) used a controlled H\(_2\)O/H\(_2\) - Ar atmosphere to examine the reactions between alumina and molten iron. Solid hercynite, FeAl\(_2\)O\(_4\), was the product resulting from the equilibration of molten iron and alumina below 1700°C.}

(c) Hydrodynamics of the Refractory/Melt System

A study of the effect of agitation on the rate of attack is important. In many practical situations the melt is in relative motion with respect to the refractory surface. Thus, some sort of agitation used in the experimental system will help simulate refractory attack under service conditions. Also, by studying the effects of agitation, some knowledge can be gained of the rate-controlling step in the reaction between the refractory and melt. In transport-controlled reactions, the hydrodynamics of the system has a definite influence on the rate of reaction, whereas for the chemical reaction-controlled cases, the rate should be independent of the hydrodynamics of the system.

A number of authors have used agitation to study the rate of refractory/metal reactions. Snow and Shea\(^{(44)}\) measured the decrease
in diameter of nozzle refractories after steel had been teemed through the nozzles. No attempt was made, however, to correlate the rate of teeming with the rate of attack. Suzuki et al (20) and Narita et al (21) rotated cylindrical refractory specimens in molten steels to measure the rates of attack. The effect of rotation on the rates was not taken into account. Novokhatsky and Ershov (19) used rotating silica disks to measure the kinetics of the interaction of silica and carbon, manganese, and aluminum dissolved in an iron melt. The experiments established that variation of the rotation speed of the specimens, in the range 0 - 600 r.p.m., did not affect the rates of the reactions investigated. From this they concluded that the rates were chemical reaction-controlled.

Simkovich et al (73) studied the effect of rotating cylindrical alumina rods in carbon-saturated iron melts. The rate of dissolution was greatly increased by rotation of the rods and it was thus concluded that the rate was diffusion-controlled.

Much work has been done in refractory slag systems to determine the relationship between the rate of attack and agitation. The rates of attack of alumina, mullite, anorthite, and silica refractories by calcium-aluminum-silicate slags were found to be dependent on the square root of the rotation velocity of the specimens, by Kingery et al (32, 33). From these results, the authors concluded that the reaction rates were controlled by transport within the liquid boundary layer. Similarly, Reeve (37) and Kovalenko et al (38) showed that the rates of dissolution of silica and iron oxide, respectively, in silicate melts were dependent on the rotation velocities of the refractory samples and that the rates were transport-controlled.

(d) **Temperature**

The dependence on temperature of the rate of attack of refractories by molten metals or slags is very important. Temperature not only affects the thermodynamic properties of the refractory/melt system.
but also has a strong influence on the kinetics of the reactions. The kinetic parameters such as diffusivity, viscosity, and chemical reaction rate constants are all, in general, temperature dependent. Furthermore, the physical properties of the refractory and the melt, the influence of the reaction atmosphere, and the hydrodynamics of the system are all dependent upon the temperature. In general, it has been found that refractory attack is a thermally-activated process and, therefore, temperature is an important variable in any such study.

2.8 Reaction of Refractory Materials with Molten Iron

Although many studies have been made of the reactions between refractories and molten iron alloys, few people have examined the reactions with pure liquid iron. The reactions which can take place in such a system are as follows:

\[
\text{Fe(}l\text{)} + \frac{1}{2} \text{O}_2 (\text{atmosphere}) = (\text{FeO})_s \tag{12}
\]

\[
\text{SiO}_2 (\text{refr}) + \text{Fe}(l) = (\text{FeO})_s + \text{Si} \tag{13}
\]

\[
x\text{SiO}_2 (\text{refr}) + y(\text{FeO})_s = (\text{SiO}_2)_x (\text{FeO})_y (\text{slag}) \tag{14}
\]

The first reaction will take place only under conditions which are sufficiently oxidizing to form the oxide. The second will be limited by the concentration of silicon in the melt. If the silicon concentration is at or above the equilibrium value, reaction (13) will not proceed, but instead the reverse reaction will occur.

Many equilibrium studies have been carried out to determine the products formed when iron oxide reacts with silica or alumino-silicate refractories. Some of this work has already been reviewed in a previous
section (2.6). The works of Bowen and Schairer (74) in the FeO-SiO₂ system, Muan et al (39-41) in the Al₂O₃-SiO₂-iron oxide and FeO-Fe₂O₃-SiO₂ systems, and Darken's (75) studies in the Fe-Si-O-C system are of immeasurable help in studying the reactions between molten iron and alumino-silicate refractories.

Studies of the kinetics of the reactions between alumino-silicate refractories and pure molten iron have not been actively pursued although many authors have studied the kinetics of the reactions of these refractories with molten iron alloys. In general, it has been found that the rate of attack is a function of the oxygen content of the melt and the reaction atmosphere. Colligan et al (76) heated compacts of pure iron and silica sand under atmospheres controlled by various CO₂/CO mixtures. They found that the iron was oxidized to form liquid iron oxide which wetted the silica sand. This iron oxide reacted with the silica to form a liquid silicate. Although no quantitative information concerning the rate of the reaction was obtained, they were able to draw some general conclusions, namely that the rate of slag formation depended upon the time, temperature, and the oxidizing level of the atmosphere. They also showed that under extremely reducing conditions the rate of attack was negligible.

Van Vlack (70), in studying the reaction between molten iron and a silica sand mould, determined that the reaction proceeded with the oxidation of the molten iron to produce a molten iron oxide slag, which in turn fluxed the silica sand. The rate of attack was said to increase with increasing oxidation potential of the atmosphere. Maekawa et al (7, 8) evaluated the effect of oxygen in the atmosphere on the attack of alumino-silicate refractories by molten iron. The corrosion of chamotte bricks was observed to be promoted by a longer reaction time.

2.9 Reaction of Refractory Materials with Iron-Carbon Alloys

Studies of the reduction of silica and alumino-silicate refractories
by iron-carbon alloys constitute a large part of the work done on refractory/metal reactions. The opinions regarding the reactions which take place in these systems and the associated rate-controlling steps are diverse. In general, the methods used to study these reactions are similar to those discussed earlier. In addition, many investigations have been carried out in which the rates of reaction between molten slags and iron-carbon alloys have been measured.

The reduction of refractory oxides by carbon dissolved in iron usually takes place according to the following reaction:

\[
XO_{(s \text{ or } \ell)} + C = X + CO_{(g)}
\]

As discussed in an earlier section, the rate of this reaction is controlled by transport processes, chemical reaction, or in some cases a combination of these two. Much of the work on the refractory/iron-carbon system has been carried out to determine the controlling step or steps in the reaction.

Fulton and Chipman\(^{(77,78)}\) studied the kinetics of silica reduction by carbon in iron. They reacted a lime-alumina-silica slag with carbon-saturated iron and measured the rate of reduction of silica from the slag, taking as the overall reaction:

\[
(SiO_2)_{\text{slag}} + 2 C_{\text{graphite}} = Si + 2 CO_{(g)}
\]

They obtained an apparent activation energy for the observed rate to be 130 Kcal/mole, and found that the rate was nearly independent of stirring. They concluded that the rate was controlled by the slow step or steps in the chemical reaction. The controlling step was thought to be the breaking of silicon-oxygen bonds or the removal of oxygen by carbon either at the slag/metal interface or the metal/crucible interface. Schumann\(^{(79)}\), in discussing the work of Fulton and Chipman, suggested that the data could be interpreted to show that the rate of reduction was transport-controlled with the transport of oxygen across the liquid metal boundary.
layer at the slag/metal interface, the controlling step. Ward \(^{(80)}\) stated that the activation energy necessary to break four silicon-oxygen bonds was 104 Kcal/mole and thus the activation energy obtained by Fulton and Chipman would be compatible with the suggestion of chemical control.

Turkdogan et al \(^{(81)}\) also investigated the reduction of silica from silicate slags by carbon-saturated iron. In their experiments, carbon monoxide was impinged on the slag/metal interface. They concluded that the rate-controlling step in the reduction of silica from the slag was the desorption of silicate ions at the slag/metal interface to form a vacant site plus silicon and oxygen in the metal. They also found that the rate of reduction decreased when impingement of carbon monoxide was halted. They stated that under these conditions the transport of oxygen from the slag/metal interface to the graphite walls of the crucible was the rate-controlling step.

Novokhatsky and Ershov \(^{(19)}\) examined the reduction of disks of solid silica in iron-carbon alloys with compositions ranging from 1.0 to 4.9% carbon. They found that sample rotation speeds of up to 600 r.p.m. did not affect the reduction rate and, therefore, the reaction was stated to be chemical reaction-controlled.

Grimble \(^{(82)}\) showed that the rate of reduction of silica from silicate slags was independent of the stirring rate and yielded an activation energy of 125 Kcal/mole. He concluded that the reaction rate was chemically-controlled and proposed that silicon monoxide, SiO, was formed as an intermediate product in the reaction. In a similar study, Sotnikov et al \(^{(83)}\) determined that the rate of reduction of silica was independent of mixing in either the slag or metal phase.

Wojcik \(^{(84)}\) investigated the reactions between tubes of silica and pyrex, and carbon-saturated iron, which was drawn up into the tubes by capillary action. The results indicated that the rate of reduction of the quartz tubes was chemical reaction-controlled while the reduction of the pyrex tubes was diffusion-controlled.
The reactions between silica and manganese oxide and carbon dissolved in liquid iron were studied by Shurygin and Kryuk (85). They rotated disks of the refractory materials in iron-carbon melts at speeds of from 1 to 400 r.p.m. They observed that the rate of reduction of manganese oxide was three to four times faster than the reduction of silica and that both rates were independent of stirring. They concluded that the overall rates of reduction were controlled by chemical reactions rather than by diffusional processes. In similar experiments, Barmin et al. (86) rotated solid manganese oxide samples in iron-carbon melts. They found that the rate of manganese oxide reduction was independent of the rotation of the sample and was limited by one of the following steps:

(a) adsorption of carbon on the surface of the manganese oxide crystals
(b) the electrochemical reactions: \[ \text{Mn}^{2+} + 2e^- = \text{Mn} \quad \text{O}^{2-} + C + 2e^- = \text{CO} \]
(c) the formation of CO bubbles and their removal.

Rawling and Elliott (87) investigated the transfer of silicon from blast furnace type slags to carbon-saturated iron. They concluded that the diffusion of oxygen in the metal phase to the gas/metal interface was controlling at 1600°C and lower temperatures, while at higher temperatures the reaction could possibly have become chemical reaction-controlled. The dissociation of complex silicate ions was suggested as the possible rate-limiting step at the higher temperatures. In a similar system, Adachi et al. (88) found that the rate of silica reduction was increased by stirring of the slag phase and suggested that the rate was controlled by diffusion of silicon in the slag.

Simkovich et al. (73) rotated cylindrical alumina rods in carbon-saturated iron and determined the rate of dissolution. The rate was greatly increased by rotation of the rods and the authors concluded that the diffusion of aluminum from the alumina/metal interface was the rate-controlling step. In a similar system they studied the rate of reduction
of silica rods. The results of these experiments were inconclusive. However, the authors suggested that the rate of reduction was probably controlled by mass transport.

The rates of reduction of several refractory materials by iron-carbon alloys under a vacuum were obtained by Tiberg. Bars of the refractory materials were immersed in the metal bath and the rates of reduction were determined by measuring the change in diameter of the rods. He showed that the rates of reduction were a function of the pressure of the system. For the reduction of the silica refractories, he concluded that the rate of reduction was controlled by the diffusion of oxygen from the oxide surface into the metal.

Maas and Abratis and Abratis et al determined the rates of reduction of fire-clay bricks, high alumina bricks, and basic bricks in iron-carbon melts (0.5 to 2% C) at temperatures of 1500°C to 1600°C, under vacuum. Cylindrical rods made from the bricks were slowly rotated in the melts and the rates of reduction were obtained by measuring the changes in concentration of the elements in the melts. Silica in the glassy phase of the fire-clay bricks and high alumina bricks was reduced by the carbon leaving a reaction layer of corundum on the surface of the sample. They also showed that the rate of silica reduction varied with the square root of time and concluded that the rate was transport-controlled. They suggested that diffusion of gaseous silicon monoxide and carbon dioxide (formed as intermediate compounds) in the pores of the corundum reaction layer controlled the overall reduction rate.

Sharma determined the rate of reduction of solid silica crucibles by carbon-saturated iron, by measuring the amount of carbon monoxide evolved in the reaction. He concluded that the rate of reduction was controlled by the transport of oxygen in the liquid metal.

Minowa et al measured the amount of carbon monoxide evolved when silica and alumina crucibles were allowed to react with an iron-carbon alloy at temperatures from 1200 - 1600°C. They found
that the amount of carbon monoxide produced in the reaction increased linearly with the reaction time. They also found that the reaction rate decreased with an increase in the pressure of the system. An apparent activation energy for the reduction of silica was calculated to be 50.8 Kcal/mole and for the reduction of alumina, 59.0 Kcal/mole.

The question has been raised as to whether the silica reduction reaction:

\[ \text{SiO}_2(s) + 2 \text{C} \rightarrow \text{Si} + 2 \text{CO} \quad \text{(g)} \quad (17) \]

is purely chemical in nature, in which case electrons are transferred directly between the reacting atoms, or electrochemical in nature in which case electrons are transferred via electronic conductors many atomic distances.

Wagner\(^{(93)}\) considered the electrochemical contribution to a chemical reaction at a slag/metal interface, and also the electrochemical reduction occurring at a second interface (the slag/crucible interface) due to a local cell mechanism. The reaction at the slag/metal interface was said to involve the discharge of oxygen and silicon ions:

\[ 2 \text{(O}^{2-}\text{)} - 4e = 2 \text{O} \]

\[ \text{(Si}^{4+}\text{)} + 4e = \text{Si} \]

It was suggested that these reactions occurred at adjacent sites such that electrons were transferred directly between the sites and the reaction was chemical in nature rather than electrochemical. Grimble et al.\(^{(82, 94)}\) studied the electrochemical nature of silica reduction by carbon-saturated iron due to the local cell mechanism, using a graphite crucible to hold the melt and slag. They proposed that the overall reaction (17) could occur by an electrochemical mechanism with the following reactions taking
anodic reaction at the slag/crucible interface,

\[ 2 \text{C}^- + 2 (\text{O}^2-) - 4e = 2 \text{CO}_g \]

cathodic reaction at the slag/metal interface,

\[ (\text{Si}^{4+}) + 4e^- = \text{Si} \]

with the electron transfer taking place through the graphite crucible.

Their work showed that at lower temperatures (below 1370°C) the local cell effect predominated and even at 1450°C, approximately 50% of the silica reduced was by an electrochemical mechanism and the remainder by a chemical reaction. At higher temperatures (above 1530°C) there was found to be no local cell contribution to the overall reduction kinetics.

In a similar system, Aurini\(^{(95)}\) established the existence of the local cell electrochemical mechanism but showed that its contribution to the overall rate of silica reduction was negligible. In this same work, he found that the kinetics of silica reduction by carbon-saturated iron was chemical reaction-controlled with the rate-controlling step being the decomposition of silica at the slag/metal interface.

The literature pertaining to the attack of refractory materials by carbon-saturated iron expresses the many different opinions held by various authors as to the reactions which take place and the steps or steps controlling the kinetics of these reactions. It is obvious from their work that the reactions and rate-controlling steps depend on the physical state of the refractory material and the melt, the arrangement of the apparatus, and the experimental technique.

In the case of systems used to study the reaction of a carbon-saturated iron melt and a silicate slag, the nucleation of carbon-monoxide bubbles most often occurs at the walls of the crucible. In these systems,
due to a large diffusion distance (from the slag/metal interface to the crucible wall), it is not unusual to find that the reaction is controlled by diffusion phenomena. If, however, gas bubbles are introduced to the slag/metal interface, they serve as nucleation sites greatly shortening the diffusion lengths, such that the reaction could become chemical reaction-controlled.

Many authors have bubbled gases into both the slag and metal phases to demonstrate the effect of agitation on the reaction rate. In these cases it is necessary to examine whether or not the effect of agitation, due to the added gas bubbles, is masked by the turbulence caused by gas evolution during the reaction between the melt and the slag. In the experiments in which agitation is achieved by mechanical stirring of the melt and slag, it is necessary to control the rate of stirring at such a level that the melt/slag interfacial area will not be affected.

In the reaction between a solid refractory material and a carbon-saturated iron melt the physical properties of the refractory are quite important in determining the rate of reaction and the step controlling this reaction.
CHAPTER 3

EXPERIMENTAL APPARATUS

3.1 Introduction

The major portion of this work was carried out in a carbon resistance furnace. A description of this furnace and other equipment used in the experiments is presented in this chapter.

3.2 The Carbon Resistance Furnace

The furnace was operated from a three-phase power supply. The heating element was made up of six carbon rods, 1/2" diameter x 9" in length, arranged in a cage construction as shown in Figure 7. These rods were set in pairs into a carbon base consisting of three segments. The tops of the rods were connected in a "star" arrangement by a carbon ring. A graphite radiation shield, 6" O.D. x 5 1/2" I.D. x 10" long, was positioned around the heating element. This radiation shield was electrically insulated from the carbon base blocks by a ring of refractory brick, 1/2" thick. Power to the heating element was supplied through three water-cooled copper conductors which screwed into the carbon base.

The furnace design is shown in Figure 8. The heating element with its radiation shield was contained in a vacuum-tight steel casing, 17" in diameter x 1/2" wall thickness x 20" in height. The furnace was lined with refractory insulating brick. The top and base plates were bolted to flanges welded onto the furnace casing. Each plate was fitted with a water-cooled O" ring to provide a gas-tight seal. The top plate was also fitted with 6" long, single-ply stainless steel bellows to allow expansion and contraction.
FIGURE 7. CARBON HEATING ELEMENT.
Fig. 8 - Schematic diagram of apparatus: 1) furnace shell; 2) thermocouple; 3) carbon elements; 4) furnace tube; 5) drive shaft; 6) viewing port; 7) sealing cap; 8) graphite specimen holder; 9) specimen; 10) reaction crucible and melt; 11) pyrometer; 12) insulating refractory; 13) roller bearing; 14) sampling hole.
of the reaction tube during furnace operation. The bellows had a water-cooled "O" ring assembly to maintain a gas-tight fit with the reaction tube.

Two horizontal holes were drilled through the steel casing and refractory brick lining. These holes passed between the resistance elements at the level of the constant temperature zone. Two recrystallized alumina sheaths, 7/8" O. D. and 5/16" O. D., closed at one end, were positioned in these holes such that they touched the reaction tube. An optical pyrometer was sighted on the closed-end of the larger sheath and a thermocouple was inserted in the other. Gas-tight fittings were made with the furnace casing by means of a water-cooled "O" ring for the sighting tube and a swagelock fitting for the thermocouple sheath. An additional two holes were drilled in the casing and refractory brick to serve as inlet and outlet gaskets for the gas used to protect the heating element.

3.3 The Reaction Tube Assembly

The reaction tube was a MV30mullite tube (McDaniel Refractory Co.), closed at one end, of dimensions, 1 3/4" O. D. x 1 1/2" I. D. x 20" long. The tube was centered between the heating elements by the "O" ring assembly of the bellows. A refractory insulating brick pedestal was fitted in the bottom of the reaction tube to support a crucible during the experiments. The top of the reaction tube was fitted with a water-cooled brass cap which maintained a gas-tight fit with the reaction tube by means of an "O" ring. A number of roller bearings for a 5/16" drive shaft were set in the center of this cap. Reaction atmospheres were controlled by introducing and exhausting gases through two tubes set in this brass cap. A quartz window set in the cap allowed continuous observation of the melt. A 3/8" stoppered hole in the cap was used for taking samples from the melt.

The drive shaft was 15" long and was made from 5/16" drill rod. The graphite specimen holder was screwed onto this drive shaft. The shaft was passed through the roller bearings in the cap with two "O" rings maintaining a gas-tight seal about the shaft. Additional guidance for the
shaft was provided by another set of roller bearings positioned directly above the cap. A hollow-spindle, variable speed stirrer was attached to the shaft. The shaft could be raised or lowered during an experiment. The furnace, reaction tube, and drive shaft assembly are shown in Figure 8.

3.4 The Power Supply

The operating capacity of the heating element and the associated electrical equipment was 10KVA. The power supply was connected through a mercury relay switch to a 13.3 KVA Variac variable transformer and a 20:1 step-down transformer. All these components were designed for three-phase operation. The entire assembly is shown schematically in Figure 9.

3.5 Temperature Control and Measurement

The furnace temperature was measured with a Honeywell "Radiamatic" optical pyrometer. The radiation pyrometer signal was fed into a "Pyro-O-Vane" proportional controller and temperature indicator, and the control output signal operated the mercury relay switch. The pyrometer was sighted on the closed end of the 7/8" O.D. alumina sheath in contact with the furnace reaction tube.

A Pt/Pt-13% Rh thermocouple was also used to measure the temperature of the hot zone. This thermocouple was protected by the 5/16" O.D. alumina sheath extending into the hot zone. The thermocouple output served as a check on the optical pyrometer readings.

3.6 The Gas Supply

A nitrogen atmosphere was maintained in the furnace to prevent too rapid oxidation of the carbon elements. The nitrogen was first settles through heated copper turnings (725°C) and after circulating through the
Figure 9: Schematic Diagram of Power Components.
furnace was exited through a dibutyl phthalate bubbler and exhausted into the air. The gas used as the reaction atmosphere was also deoxidized over heated copper turnings (725°C) before entering the reaction tube.

3.7 Measurement of Rotation Speeds

The rotation speed of the drive shaft was measured by means of a "Strobomatic" stroboscope which was sighted on a small clamp on the drive shaft.
CHAPTER 4

EXPERIMENTAL TECHNIQUE

4.1 Material Preparation

4.1.1 Refractory Specimens

(i) Fused Silica

Two types of fused silica rod, translucent and clear, were obtained from the General Electric Company. The clear material was 99.98% pure and the translucent silica contained 99.93% silica. In both materials, alumina represented about two-thirds of the total impurity. The supplied 1/2" diameter rods were cut into 4" lengths with a diamond saw. The chemical and physical properties of the fused silica are summarized in Table 1.

(ii) "Shelrock" Silica

This material was supplied by Glasrock Products Inc. The production process involved the melting of 99.7% pure silica sand followed by slip casting of the ground product into the required rod shape, 1/2" diameter x 4" long. The properties of the "Shelrock" silica are summarized in Table 1.

(iii) Silica Brick

Refractory silica bricks (96% SiO₂) were obtained from General Refractories Ltd. A diamond core-drill was used to obtain 1/2" cylindrical specimens from the bricks. Chemical and physical properties of this high silica brick are shown in Table 2.
(iv) Fire-Clay Brick

This material was supplied by Kaiser Refractories Ltd. and had an approximate composition of 53% silica and 43% alumina. Cylindrical specimens were obtained from the brick with a diamond core-drill. Properties of the fire-clay brick are shown in Table 2.

(v) Alumina

Two types of alumina refractories were used. The first was in the form of high purity, recrystallized alumina rods, 1/2" diameter x 4" long, supplied by McDanel Refractory Company. Single crystals of sapphire (Linde) in rod form, 1/2" diameter x 4" long, were also used. Both these materials contained >99.7% Al₂O₃. The properties of the recrystallized alumina are shown in Table 3.

(vi) Magnesia

High purity fused magnesia rods, 3/4" diameter x 4" long, were obtained from the Norton Company. Properties of this material are shown in Table 3.

4.1.2 Crucible Materials

Two types of crucibles were used. For experiments carried out using Armco iron and iron-silicon alloys, high purity recrystallized alumina crucibles (McDanel Company), 1 1/4" I.D. x 1 3/8" O.D. x 2 1/2" high, were used. For experiments with carbon-saturated iron, graphite crucibles were employed. These crucibles were machined from 2" diameter graphite rod and had the dimensions: 1 3/16" I. D. x 1 7/16" O. D. x 3" high.
## TABLE 1

PROPERTIES OF FUSED SILICA AND 'SHELROCK' SILICA

<table>
<thead>
<tr>
<th>Type of Refractory</th>
<th>Chemical Composition</th>
<th>Bulk Density</th>
<th>Apparent Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent Fused Silica</td>
<td>98.98% SiO₂ (Al₂O₃ accounts for 2/3 of impurity, trace amounts of Na₂O, Fe₂O₃, CaO, TiO₂, K₂O, Li₂O.)</td>
<td>2.20 gm/cm³</td>
<td></td>
</tr>
<tr>
<td>Translucent Fused Silica</td>
<td>99.93% SiO₂ (Al₂O₃ is 2/3 of impurity, Fe₂O₃ and TiO₂ contents are higher than the transparent variety.)</td>
<td>2.10 gm/cm³</td>
<td></td>
</tr>
<tr>
<td>'Shelrock' Silica</td>
<td>99.7% SiO₂ (Al₂O₃ is major impurity)</td>
<td>1.92 gm/cm³</td>
<td>12-18%</td>
</tr>
</tbody>
</table>

## TABLE 2

PROPERTIES OF HIGH SILICA BRICK AND FIRE-CLAY BRICK

<table>
<thead>
<tr>
<th>Type of Refractory</th>
<th>CHEMICAL COMPOSITION (%)</th>
<th>Bulk Density</th>
<th>Apparent Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>High Silica Brick</td>
<td>95.7</td>
<td>.7</td>
<td>.8</td>
</tr>
<tr>
<td>Fire-Clay Brick</td>
<td>53.2</td>
<td>42.8</td>
<td>1.07</td>
</tr>
</tbody>
</table>
### TABLE 3

**PROPERTIES OF RECRYSTALLIZED ALUMINA AND FUSED MAGNESIA**

<table>
<thead>
<tr>
<th>Type of Refractory</th>
<th>CHEMICAL COMPOSITION (%)</th>
<th>Bulk Density</th>
<th>Apparent Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recrystallized alumina</td>
<td><strong>Al₂O₃</strong> 99.7</td>
<td>.12</td>
<td>.03</td>
</tr>
<tr>
<td>Fused Magnesia</td>
<td><strong>SiO₂</strong> .35</td>
<td>.5</td>
<td>99</td>
</tr>
</tbody>
</table>

### TABLE 4

**PROPERTIES OF METALS USED**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Cu</th>
<th>Cr</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Armco Iron</td>
<td>.015</td>
<td>.018</td>
<td>.005</td>
<td>.018</td>
<td>.005</td>
<td>.052</td>
<td></td>
<td>.078</td>
</tr>
<tr>
<td>Electrolytic 'Derby' Iron</td>
<td>.005</td>
<td>.0028</td>
<td>.001</td>
<td>.003</td>
<td>.004</td>
<td>.0054</td>
<td>.002</td>
<td>.076</td>
</tr>
</tbody>
</table>
4.1.3 Charge Materials

The Armco iron used was obtained commercially in the form of 1" diameter bar stock. An analysis of this material is given in Table 4.

Electrolytic "Derby" iron was also used in a number of the experiments. The analysis of this material is also given in Table 4.

Carbon-saturated iron was prepared by melting 10 lbs. of Armco iron in a graphite crucible in a 3KC open-air induction unit. Graphite chips were added to the melt to speed up saturation. The power was increased before casting to superheat the melt, which was then cast into split steel molds producing white cast iron ingots, 1" diameter x 7" long.

Iron-silicon alloys were also prepared in the 3KC induction unit. Armco iron was melted in a magnesia crucible and ferrosilicon added to the melt. The amount of ferrosilicon added was in excess of the amount calculated to give an alloy of the desired silicon content, to compensate for the silicon loss due to oxidation. The melt was cast into split steel molds to produce ingots, 1" diameter x 7" long.

4.1.4 Gases and Gas Mixtures

Standard laboratory grades of argon and nitrogen were supplied by Liquid Air Ltd. Mixtures of carbon dioxide and carbon monoxide were prepared by Matheson Ltd.

4.2 Specimen Holder and Sample Preparation

The specimen holder and specimen arrangement are shown in Figure 10. The specimen holder was machined from 1" diameter graphite rod.

The top of the refractory specimen was cut with a diamond saw to
produce four grooves at angles of 90° to each other. The refractory specimen was then press-fitted into the holder and positioned such that the grooves were aligned with the threaded holes in the specimen holder. Graphite screws were inserted and tightened to ensure that the specimen was held securely during the experiment.

4.3 **Sampling Technique**

Suction samples of the melts were obtained through 3mm I. D. silica tubes attached to an aspirator bulb. Using this technique, 1 to 2 gm samples were taken. Before the samples were analysed, they were surface ground and cleaned with acetone.

4.4 **Chemical Analyses**

4.4.1 **Silicon in Iron**

Samples of the melts were analysed for silicon by the standard perchlorate method.

4.4.2 **Oxygen in Iron**

A Leco oxygen analyser was used for all oxygen determinations. The sample was induction melted in a graphite crucible. The oxygen in the metal was evolved as carbon monoxide which was then oxidized to carbon dioxide. The amount of carbon dioxide produced was measured in a thermal conductivity cell and the actual oxygen content of the metal calculated with the aid of standards of known oxygen contents.
4.4.3 Carbon in Iron

A Leco carbon analyser was used for all the carbon analyses. Like the analysis for oxygen, the sample was induction melted with the carbon being oxidized to form carbon dioxide. The carbon dioxide was absorbed in a potassium hydroxide solution and the carbon content of the sample so determined.

4.5 Analysis of the Reaction Atmosphere

In order to measure the partial pressure of oxygen in the various reaction atmospheres, an oxygen probe was used. For this work a lime-stabilized zirconia electrolyte was used and the cell was made up as follows:

\[
\text{Pt} | \text{Cr}_2\text{O}_3 | \text{Lime-Stabilized Zirconia} | \text{Atmosphere of } P_{O_2} | \text{Pt}
\]

A description of the probe and its use are given in Appendix I.

4.6 Temperature Profile

The temperature profile of the carbon resistance furnace was determined by lowering and raising a Pt/Pt-13% Rh thermocouple in 1/4" steps, through the top cap into the reaction tube. Figure 11 shows a typical profile and it was found that the temperature did not vary more than \(\pm 5^\circ C\) over a 2" length at 1600\(^\circ C\).

4.7 Measurement of Refractory Specimens

Both diameter and weight changes were measured in the experiments.
FIGURE II. TEMPERATURE PROFILE AND POSITION OF CRUCIBLE.
Diameters were measured with a micrometer and weights with a Sauter microbalance. Details of the measuring and weighing techniques are given in Appendix 2.

4.8 Experimental Procedure

4.8.1 Static Experiments

Prior to the start of an experiment, the furnace was flushed with nitrogen. The desired amounts of metal to be charged were cut from the 1" diameter ingots and were surface ground, cleaned with acetone, and weighed; 200 gm samples were used in the case of Armco iron and iron-silicon alloys and 175 gms in the case of carbon-saturated iron. The metal charge was placed in the appropriate crucible, and the crucible and charge were lowered into position in the reaction tube.

The refractory specimen and specimen holder assembly was then set in place, and the argon flow to the reaction tube was started and the tube flushed for one hour. The temperature was then slowly increased to the desired operating temperature over a six hour period. Having reached the operating temperature, the furnace was held at that temperature for an hour. The drive shaft was then lowered placing the refractory specimen in a position directly above the melt. The shaft was held in this position for a few minutes to allow the specimen to attain a temperature as close as possible to that of the melt and then was lowered so that the specimen was immersed in the melt. This point was taken as time zero for the experiment. After the desired reaction time, the drive shaft was quickly raised thus removing the specimen completely from the melt. Suction samples of the melt were taken at the beginning and end of the reaction period. The furnace was cooled slowly to room temperature and the refractory specimen was removed, weighed, and measured.
4.8.2 Dynamic Experiments

The procedure for these experiments was similar except that the stirrer motor was utilized to rotate the specimen upon insertion into the melt.
CHAPTER 5

RESULTS

(A) Armco Iron As the Metal Phase

5.1 Fused Silica

5.1.1 Devitrification of Fused Silica Specimens

Preliminary experiments to study the attack on fused silica by Armco iron melts showed that the specimens underwent a devitrification process during the heating and cooling cycle. This devitrification was indicated by the formation of an opaque layer at the surface of each specimen. Dimensional measurements on devitrified specimens showed the process to be accompanied by a volume change. A number of experiments were carried out in which specimens of both the transparent and translucent varieties of fused silica were heated to 1600°C, without any melt present, and held at temperature for various lengths of time. The specimens were then cooled to room temperature and the diameter and weight losses were measured. It was observed that the transparent variety of fused silica devitrified more than the translucent silica. Also, upon cooling, the transparent silica cracked and shattered quite severely such that no quantitative measurements of the diameter changes or weight losses could be made. The translucent silica underwent a small amount of surface cracking upon cooling but these cracks did not affect subsequent measurements. In all the experiments with the translucent fused silica, no weight losses were observed. However, a definite change in diameter was measured for each specimen. This diameter change was constant for times up to 1 hour at 1600°C. At longer times the diameter change increased with...
increasing time. Table 5 shows the diameter changes due to devitrification for specimens held for various lengths of time at 1600°C. The tabulated values are the average values of several experiments and the reproducibility of the measurements was found to be good.

5.1.2 Static Runs

A series of runs was carried out in which specimens of translucent-fused silica were immersed in Armco iron at 1600°C in an argon atmosphere. Immersion times were varied from 1 minute to 3 hours. Examination of the reacted specimens showed that, in certain runs, a small amount of a greenish-yellow slag adhered to the specimens. In all the static runs, a certain amount of this slag material collected on the wall of the crucible, at the melt line.

After each run, the weight loss and the diameter change of the specimen was determined. The results of these static experiments are shown in Table 6. The diameter changes reported have been corrected for the devitrification shrinkage, and were averaged over the corroded sections of the samples. In general, it was observed that the extent of devitrification of the portion of the specimen in the melt was comparable to that portion above the melt. Each value of the surface area recorded was the average of the areas following devitrification and at the end of the experiment.

The results of the static runs are plotted in Figure 12, in which the weight loss/unit surface area is shown as a function of time. It can be seen that the attack commences immediately on immersion of the specimen. After a short period of time, the rate of attack decreases until eventually the attack proceeds at a very slow but constant rate.

5.1.3 Dynamic Runs

Translucent fused silica specimens were rotated in Armco iron melts at 1600°C, at various rotation speeds for times between 1 minute and
2 hours. The results of these runs are listed in Table 7 and plotted in Figure 13. The best straight line fit for each group of experimental data was determined by a least squares method described in Appendix 3. The diagram shows that in each case, following a relatively fast initial reaction, the rate of attack becomes independent of time. The rates of attack were obtained from the slopes of the linear portions of the lines and were determined to a 95% confidence level by the least squares method. The rates obtained are given in Table 10. From Table 10 and Figure 13, it can be seen that the rate of attack increases with the peripheral velocity of the specimen. Extrapolation of the linear portions of the curves to time zero showed that the initial reaction was approximately the same for each experiment and the magnitude of the initial reaction was independent of the peripheral velocity of the specimen. For the runs with fused silica in Armco iron the average value of the weight loss/unit surface area due to the initial attack was determined to be $2.24 \times 10^{-3} \pm 0.52 \times 10^{-3}$ gm/cm$^2$.

A second series of dynamic runs was carried out in which fused silica specimens were rotated in Armco iron melts at 1600°C for 1 hour, at rotation speeds ranging from 40 to 550 r.p.m.. The results of these runs are summarized in Tables 8 and 9 and are shown graphically in Figure 14. From the diagram it can be seen that the rate of attack is a linear function of the peripheral velocity. The results summarized in Table 9 show that the attack of each fused silica specimen was uniform over the whole wetted depth of the specimen. In Table 8, the weight loss/unit surface area measured for each specimen has been corrected to account for the initial reaction, as determined in the first series of dynamic runs. The second plot in Figure 14 shows the corrected rates, in terms of the corrected weight loss/unit surface area/hour, as a function of the peripheral velocity. The reaction rates, at the various velocities, determined from this curve should be equivalent to those determined from the slopes of the curves in Figure 13. Table 10 compares the experimental rates of attack obtained from the two series of dynamic runs and shows the close agreement between the results of these runs.
In all the dynamic experiments a greenish-yellow slag remained on the crucible wall, at the melt line, at the end of the run. The amount of this material formed was greater than was observed in any of the static experiments. X-ray diffraction analyses of this slag phase showed it to consist almost entirely of the iron silicate, fayalite (2 FeO·SiO₂). A small amount of cristobalite was also detected. Figure 15 is a photograph of the fused silica specimens showing the material as received, after devitrification, and after a rotation run in Armco iron.

5.1.4 Change in Melt Composition

Suction samples of the melt were obtained at the end of each experiment and analysed for silicon and oxygen. Although significant scatter was observed in the analytical results certain trends were evident. The oxygen content of the Armco iron dropped in most cases from an initial content of .075 % to levels between .02 and .05%. In most of the runs, the silicon content was found to increase with both the duration of the run and the rate of rotation. Reproducibility of the silicon analyses was quite poor, so that exact values of the silicon concentrations in the melts were not obtained.

5.1.5 Runs with Electrolytic Iron

To study the contribution to the measured attack of small amounts of impurities in the Armco iron, namely carbon and manganese, a number of static and dynamic runs were carried out in electrolytic "Derby" iron. The properties of this material are given in Table 4. The attack of the fused silica by the electrolytic iron was found to be comparable to that measured using Armco iron. The results of these experiments and the Armco iron experiments are compared in Table II.
5.1.6  **Effect of the Addition of Silicon to the Melt**

For this work iron-silicon alloys were prepared in the open-air induction unit. An alloy with a chemical analysis of 2.10% silicon was chosen for these experiments. Both static and dynamic runs were carried out with this alloy using fused silica specimens. The weight loss and diameter change measured in each experiment are shown in Table 12. From these results it can be seen that in all the runs no appreciable attack was measured. In a few of the runs a slight gain in weight was observed. In all the runs with the iron-silicon alloy no slag was found on either the specimens or the crucible walls.

5.1.7  **The Influence of the Reaction Atmosphere**

The effect of the reaction atmosphere on the attack of fused silica by Armco iron was studied by replacing the argon atmosphere normally used, with CO₂/CO reaction atmospheres. These mixtures had carbon dioxide contents ranging between 0.5% and 13.7%. Using these mixtures, the oxidizing potential of the reaction atmosphere, with respect to the melt, could be controlled. A stabilized zirconia probe was used to measure the oxygen activity in the reaction atmosphere. The results of static and dynamic experiments in Armco iron using these gas mixtures are listed in Table 13. Under highly reducing conditions (low carbon dioxide content mixtures) no attack of the specimen by the melt was measured and no slag phase was observed. As the carbon dioxide content of the gas mixture was increased, the attack increased. For the higher carbon dioxide mixtures the attack was generally comparable to or greater than the attack occurring in the argon atmosphere.
5.2 'Shelrock' Silica

5.2.1 Shrinkage Due to Sintering of the Specimens

Upon heating of the porous 'Shelrock' silica specimens (12-18% porosity), sizable decreases in diameter were observed, due to sintering of the refractory material. Specimens were heated to 1600°C and held at this temperature for various times and then taken to room temperature. Diameter changes were measured on the cooled samples. In all these experiments it was noted that most of the sintering process took place while the specimens were being heated to 1600°C and that the length of time that the specimens were held at this temperature did not seem to greatly affect the measured shrinkage due to sintering. It was also observed that the amount of sintering varied from specimen to specimen. Due to this shrinkage, the rates of static and dynamic attack were measured by weight loss measurements rather than diameter changes. However, diameters were measured to obtain values of the surface areas.

5.2.2 Static and Dynamic Runs in Armco Iron

Prior to carrying out the experiments, the grooved ends of the 'Shelrock' specimens were heated in a hydrogen-oxygen flame to pre-sinter the refractory material so that the specimens would not become loose in the specimen holders during the experiments. Several static experiments were performed in Armco iron at 1600°C in an argon atmosphere. In all these experiments the weight loss of each specimen was measured. The results of these experiments are shown in Table 14 and Figure 16. Each value of the surface area recorded in Table 14 is the mean of the area of the specimen following sintering, as determined by measuring the specimen above the melt line, and the area of the reacted portion of the specimen at the end of the experiment. As can be seen in Figure 16, a brief initial reaction period is evident followed by a period of decreasing rate of attack with the
attack eventually proceeding at a very low, but constant rate. The static attack of the 'Shelrock' silica specimens was slightly greater than the attack of fused silica under the same conditions.

The appearance of the reacted 'Shelrock' silica specimens differed from the fused silica specimens in that a thin greenish slag coating adhered to the surface of each of the specimens. Also in the runs with 'Shelrock' silica more slag was observed to collect at the crucible wall. X-ray diffraction analysis of this slag material showed it to consist mainly of fayalite.

Dynamic runs were also carried out and the results are shown in Table 15 and in Figure 17. The curves shown were drawn using a least squares method. The rate of attack at each rotation speed appears to be independent of time after a short initial reaction period has passed and the rate increases with increasing rotation speed. The rates were determined from the slopes of these lines and are shown in Table 17. The intercepts of these curves were used to approximate the magnitude of the initial reaction and an average value of $5.72 \times 10^{-3} \pm 0.55 \times 10^{-3}$ gm/cm$^2$ was obtained.

A second series of dynamic runs was carried out in which specimens were rotated for one hour at various rotation speeds. The results of these runs are shown in Table 16 and Figure 18. The attack is seen to be a linear function of the peripheral velocity. The results of these experiments were corrected for the initial reaction using the results of the first series of dynamic experiments, as shown in Table 16 and the second plot in Figure 18. The rates of attack determined from the two series of dynamic experiments are compared in Table 17 and the agreement is good. In all the dynamic runs the attack of the specimens was observed to be uniform over the whole reaction surface. Figure 19 shows a 'Shelrock' silica rod as received and a reacted specimen from a 1 hour rotation run in Armco iron at 265 r.p.m.

5.2.3 Influence of the Reaction Atmosphere

To test the effect of reaction atmosphere, dynamic and static runs
were carried out in various CO₂/CO mixtures as discussed in section 5.1.7. The results of these runs are shown in Table 13. Again, experiments carried out in mixtures with a low carbon dioxide content showed a negligible amount of attack, while the runs with mixtures of higher carbon dioxide contents showed an amount of attack equal to or greater than the attack in argon. No evidence of slag formation was found in the runs with the low carbon dioxide content mixtures. In the runs with higher carbon dioxide mixtures, a slag was formed as in the runs with argon.

5.3 Runs with High Silica Refractory Brick

5.3.1 Static and Dynamic Runs

Cylindrical samples of the brick material were obtained by core-drilling of the bricks. The surfaces of the samples prepared in this manner were relatively smooth. Static experiments in Armco iron at 1600°C were carried out. After each experiment the surface of the specimen was observed to be coated with a thin layer of a green slag. The specimen surfaces were much rougher than those of the unreacted specimens and it appeared that the glassy matrix portion of the brick had been attacked to a greater degree than the crystalline silica grain. The results of the static runs are given in Table 18 and in Figure 20. The shape of the curve is similar to those curves obtained in the earlier experiments with fused silica and 'Shelrock' silica, although the reaction does not appear to be as severe.

Two types of dynamic experiments were again performed. The results of runs at constant rotation speeds for various lengths of time are listed in Table 19 and shown graphically in Figure 21. The initial rapid reaction is observed once again, followed by a period during which the rate becomes independent of time. Values of the steady-state rates were obtained from the slopes of the lines and are given in Table 21. The
approximate magnitude of the initial reaction was estimated from the intercepts of the curves of Figure 21 and was found to be $1.75 \times 10^{-3} \pm 0.37 \times 10^{-3}$ gm/cm$^2$.

The results of 1 hour rotation runs at various rotation speeds are shown in Table 20 and Figure 22. A linear relationship is observed between the rate of attack and the peripheral velocity. Also shown in Table 20 are the measured values of the attack corrected for the initial reaction. In Figure 22, these corrected rates are also shown as a function of the peripheral velocity. The rates of reaction obtained from the two series of dynamic experiments compare favourably as shown in Table 21.

Figure 23 shows a few of the high silica brick specimens; as received, after a one hour rotation run in Armco iron, after a one hour static run in carbon-saturated iron.

5.4 Runs with Fire-Clay Brick

5.4.1 Static and Dynamic Runs

Static runs were carried out in Armco iron at 1600°C using cylindrical samples taken from the brick by diamond-core drilling. A greyish-black slag was produced during each run, some of which adhered to the surface of the specimen. A large amount of slag solidified on the specimen at the melt line. Figure 24 shows two of the reacted specimens and an unreacted specimen. The presence of this slag on the specimen surface made it difficult to measure weight losses and diameter changes. Two different methods were used to obtain the weight loss of each specimen and these methods are discussed in Appendix 2. The agreement between the values of the weight loss determined using these methods was quite good as can be seen from the results shown in Table 22 and in Figure 25. The amount of attack in the static experiments was much greater than the attack of the other refractory materials investigated under similar conditions.
As in the other systems, the attack, after a rapid initial reaction, decreases quickly, and proceeds at a constant low rate as can be seen in Figure 25.

Dynamic experiments were also carried out on this brick material. In all these runs a great deal of slag was observed, not only at the specimen surface but also at the crucible wall, at the melt line. The results of these dynamic experiments are listed in Tables 23 and 24 and illustrated in Figures 26 and 27. As can be seen in Figure 26, at a constant rotation speed the rate of attack is constant once the short initial reaction period has passed. The rate of attack at an average peripheral velocity of 20.65 cm/sec was found from the slope of the curve and was $74.85 \times 10^{-3} + 4.05 \times 10^{-3} \text{ gm/cm}^2/\text{hr}$. An estimate of the initial reaction was made from the value of the intercept of the least squares line. This value was found to be $23.52 \times 10^{-3} + 5.43 \times 10^{-3} \text{ gm/cm}^2$. Despite the scatter of the results due to the uncertainty in the weight loss measurements, Figure 27 shows that the rate of attack is a linear function of the peripheral velocity. The second curve in Figure 27 shows the measured rates corrected for the initial reaction as a function of the velocity. From this curve the rate of attack at a velocity of 20.65 cm/sec was found to be $76.28 \times 10^{-3} \text{ gm/cm}^2/\text{hr}$.

The results of the static and dynamic experiments in Armco iron with all the refractory materials investigated are summarized in Figures 28 and 29. As can be seen in Figure 29, there is very little difference in the rates of attack of fused silica, 'Shelrock' silica, and high silica brick at the same peripheral velocity. However, the rate of attack of fire-clay brick is much greater than the rate of attack of each of the other materials at the same peripheral velocity.

5.5  **Runs with Alumina and Magnesia Refractories**

Experiments were carried out to measure the rate of attack of
alumina refractory materials by molten Armco iron at 1600°C. Static runs for periods of up to 4 hours using both sapphire and recrystallized alumina specimens failed to produce any measurable attack. Dynamic runs at rotation speeds up to 300 rpm for periods as long as 48 hours were also completed with no attack being observed. Similarly, static and dynamic runs with fused magnesia specimens in Armco iron at 1600°C failed to produce any indication of attack.

(B) Carbon-Saturated Iron as the Metal Phase

5.6 Runs with Fused Silica Rods

In all the runs using carbon-saturated iron as the metal phase, a graphite crucible was utilized to contain the melt instead of an alumina crucible, in order to maintain a constant saturation of the melt with carbon. Experiments were carried out with fused silica specimens in carbon-saturated iron melts under both static and dynamic conditions. In all these experiments it was found that the specimens became badly distorted during the course of the runs. The distortion was most pronounced in the dynamic runs. The extensive deformation of the specimens during all these experiments made quantitative measurements extremely difficult. However, observation of the specimen surfaces indicated that some attack of the specimens by the melt had taken place. This attack was confirmed by the discharge of gas bubbles at the surface of the melt during each experiment. The bulk of the gas evolution appeared to be concentrated near the surface of the specimen. The evolution of this gas was observed to begin immediately upon immersion of each fused silica specimen in the melt.
5.7  Runs with 'Shelrock' Silica Rods

5.7.1  Static Runs

Unlike the runs with fused silica, the 'Shelrock' silica rods did not distort to any great extent during the runs in carbon-saturated iron. However, examination of the specimen surfaces showed that the surfaces became rougher and more irregular as the reaction time increased. This aspect of the attack will be discussed in a later section.

Kinetic data for the experiments in carbon-saturated iron was obtained by two methods of measurement. The weight loss of each specimen was determined by measurement of the specimen weight at the beginning and the conclusion of the experiment. Also, suction samples of the melt were taken at the end of each run, and analysed for silicon. The kinetic results from the static runs in carbon-saturated iron at 1600°C are shown in Table 25 and Figures 30, 31, 32, and 33. As can be seen from Figures 30 and 32, after a relatively short induction period, the weight loss of the specimen and the silicon concentration of the melt each become a linear function of time. The weight loss per unit surface area is also recorded in Table 25. For each of these values, the average of the surface areas at the beginning and end of each run was used. In Figure 31, the weight loss per unit surface area is seen to be a linear function of time after the initial reaction period has passed. Also in Table 25, the number of gram-moles of silicon transferred to the melt per unit surface area of the specimen are given for each run. These values were calculated on the basis of the silicon analysis and the average surface area for each run.

Figure 33 shows that this quantity is also a linear function of time. All the curves drawn in Figures 30 through 33 were determined by a least squares method.

The rate of attack of the 'Shelrock' silica rods in carbon-saturated
iron was obtained from the slopes of the kinetic curves in Figures 31 and 33, as determined to a 95% confidence level by the least squares method described in Appendix 3. The rates obtained from these two curves are given in Table 29. Since the 'Shelrock' silica material is relatively pure silica (99.7%), the two rates, obtained from the measurement of weight loss per unit area and the moles' silicon transferred per unit surface area, are equivalent. Measurement of the lengths of the specimens at the end of the runs showed that the lengths changed only slightly during the reaction. Thus in the determination of the rate of attack, the attack at the bottom surface of each specimen was neglected. The rate of attack of 'Shelrock' silica in carbon-saturated iron was much greater than the rate of attack of the same refractory material in Armco iron.

5.7.2 The Effect of Rotation of the Specimens

In order to determine the effect of rotation of the specimens a series of dynamic experiments was carried out at a constant rotation speed of 200 rpm and a temperature of 1600°C. The kinetic results of these runs are given in Table 26. It was again found that the weight loss, the weight loss/unit surface area, the silicon content of the melt, and the number of moles of silicon transferred to the melt/unit surface area, were all linear functions of time. An example of this linear relationship is shown in Figure 34. The rates of attack were obtained from the slopes of the kinetic curves as discussed in section 5.7.1. These rates are given in Table 29. It can be seen by a comparison of the rates from both the static and dynamic runs that rotation of the specimens did not increase the rate of reaction. This fact is clearly illustrated in Figure 35 in which both the static and dynamic results are plotted. In this diagram, no significant difference between the results of the static and dynamic runs is observed. Similarly plots of the other measured and calculated values in Tables 25 and 26 showed no difference between the results of the static and dynamic runs.
To further investigate the effect of agitation on the rate of attack a number of rotation runs were carried out at higher rotation speeds. The results of these runs are given in Table 26 and Figure 34. As can be seen from Figure 34, increasing the rotation speed does not increase the reaction rate.

In Figure 36, a few of the 'Shelrock' silica specimens, following attack by carbon-saturated iron, are shown.

5.7.3 The Effect of Temperature

To study the influence of temperature on the rate of attack, a number of static runs were also carried out at 1400 and 1500°C. The results of these runs are given in Table 27 and shown graphically in Figure 37. A linear relationship was again observed to exist between the measured and calculated values in Table 27 and time as illustrated in Figure 37. The rates determined from the kinetic data for these runs are given in Table 29. From these results it is obvious that the rate of attack of the 'Shelrock' silica by carbon-saturated iron is very strongly dependent on the temperature of the reaction with the rate of attack at 1600°C approximately twenty-five times greater than the rate of attack at 1400°C.

5.7.4 The Effect of Carbon Concentration

An iron-carbon alloy containing approximately 2.3% carbon was prepared in the open-air induction furnace. Static and dynamic runs were performed using this alloy. The alloy was held in an alumina crucible instead of a graphite crucible. The results of the runs with 'Shelrock' silica in this alloy are given in Tables 25 and 26. As can be seen from these results, the attack of the silica material in this alloy is comparable to the attack in carbon-saturated iron. Also, rotation of the specimens has no effect on the attack measured. It is therefore evident that the rate of attack
is not dependent on the carbon concentration in the composition range studied (2.3% C to carbon saturation ≈ 5.4% C at 1600°C). This effect of carbon concentration was not studied at lower concentrations.

5.8 Runs with High Silica Brick

5.8.1 Static and Dynamic Runs

Both static and dynamic runs were performed in carbon-saturated iron at 1600°C using cylindrical specimens of silica brick. The rotation runs were carried out at a constant rotation speed of 200 r.p.m. The kinetic results of both the static and dynamic runs are given in Table 28. As in the runs with 'Shelrock' silica in carbon-saturated iron, a linear relationship was found to exist between the reaction time and the weight loss, the weight loss/unit surface area, the silicon content of the melt, and the number of moles of silicon transferred to the melt/unit surface area. These results are illustrated in Figures 38 and 39. Both of these figures show that, following a short induction period, the rate of attack becomes independent of time. These curves also show a negligible difference between the results of the static and dynamic runs, indicating that the rate of attack of the brick material by carbon-saturated iron is not affected by stirring of the melt.

The reaction rates were determined from the slopes of the kinetic curves in Figures 38 and 39. These rates are given in Table 29. Unlike the runs with 'Shelrock' silica, the rate of attack of the brick material is not equivalent to the rate of silicon transfer to the melt. This is due to the fact that the high silica brick contains only 95.7% silica and therefore a certain amount of other oxides such as the alkalis, iron oxide, and to a certain extent lime and alumina, are reduced along with the silica during the reaction. It is, therefore, expected that the rate of attack of the refractory, measured in terms of the weight loss/unit surface area/hour, should be
greater than the rate of silicon transfer. Despite this difference in the measured rates, it can be seen from Table 29 that the rates for the runs with high silica brick are much larger than the rates for the runs with 'Shelrock' silica.

The surfaces of the reacted silica brick specimens were more irregular and much rougher than the 'Shelrock' silica surfaces. In particular, it was observed that the silica brick underwent a preferential type of attack by the carbon-saturated iron melt, with the glassy matrix attacked to a far greater extent than the crystalline silica grains. This preferential attack is illustrated in Figure 23, in which a silica brick specimen, which has been reacted with carbon-saturated iron, is shown along with a specimen in the as-received state and a specimen from a run in Armco iron. The increased severity of the attack in carbon-saturated iron compared to the attack in Armco iron is also illustrated by this photograph.

5.8.2 The Effect of Temperature.

Due to insufficient kinetic data, complete kinetic curves for runs with high silica brick in carbon-saturated iron at various reaction temperatures were not obtained. However, a limited number of runs were completed and an estimate of the dependence of the rate of attack on temperature was made. Measurements of the weight loss/unit surface area for one hour static runs at 1400, 1500, and 1600°C were found to be \(1.4 \times 10^{-2} \text{ gm/cm}^2\), \(3.90 \times 10^{-2} \text{ gm/cm}^2\) and \(11.19 \text{ gm/cm}^2\) respectively. From these results it can be seen that the attack exhibits a very strong dependence on temperature. When compared with the 'Shelrock' silica results under similar conditions, the attack of silica brick by carbon-saturated iron appeared to be more sensitive to temperature.
5.9 Runs with Fire-Clay Brick

The attack of cylindrical fire-clay brick specimens in carbon-saturated melts at 1600°C was studied under both static and dynamic conditions. The dynamic experiments were all done at a rotation speed of 200 r.p.m. The results of these runs are given in Table 30, and in Figure 40 the weight loss/unit area is plotted as a function of the reaction time. As can be seen from this figure, the rate of attack decreases with increasing reaction time with the rate becoming very low at the longer times. Despite the scatter of the results, it can be seen from Figure 40 that rotation of the specimens does not increase the amount of the attack above that observed in the static runs.

When examined after the runs, the brick specimens appeared to be much more porous than in the unreacted condition. This increased porosity appeared to be confined to the surface layers of the specimens. Cross-sections of the reacted specimens were analysed using an 'Acton' microprobe analyser. It was found that the surface layer of each reacted specimen was high in alumina, but the silica content was quite low. A probe trace for one of the reacted fire-clay brick cross-sections is shown in Figure 41 along with a trace of an unreacted brick.

Figure 42 shows three fire-clay brick specimens; an unreacted specimen; and specimens from 3-hour static and dynamic runs in carbon-saturated iron.

In Figure 43, the results of the static and dynamic runs in carbon-saturated iron with 'Shelrock' silica, high silica brick, and fire-clay brick are summarized. As can be seen from this diagram the attack of the high silica brick is much greater than the attack of either of the other two materials. It can also be seen that the attack, in the case of both the high silica brick and 'Shelrock' silica, remains constant with reaction time while the attack of the fire-clay brick decreases with time.
TABLE 5

DIAMETER CHANGES DUE TO DEVITRIFICATION OF TRANSLUCENT-FUSED SILICA SPECIMENS

<table>
<thead>
<tr>
<th>Length of Time Specimen Held at 1600°C</th>
<th>Diameter Change Due to Devitrification (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min.</td>
<td>.0071</td>
</tr>
<tr>
<td>10 mins.</td>
<td>.0071</td>
</tr>
<tr>
<td>.5 hrs.</td>
<td>.0071</td>
</tr>
<tr>
<td>1.0 hrs.</td>
<td>.0071</td>
</tr>
<tr>
<td>1.5 hrs.</td>
<td>.0089</td>
</tr>
<tr>
<td>2.0 hrs.</td>
<td>.0096</td>
</tr>
<tr>
<td>3.0 hrs.</td>
<td>.0109</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
</tr>
<tr>
<td>29</td>
<td>1 min.</td>
</tr>
<tr>
<td>46</td>
<td>10 mins.</td>
</tr>
<tr>
<td>30</td>
<td>.5 hrs.</td>
</tr>
<tr>
<td>1</td>
<td>1.0 hrs.</td>
</tr>
<tr>
<td>27</td>
<td>1.0 hrs.</td>
</tr>
<tr>
<td>28</td>
<td>2.0 hrs.</td>
</tr>
<tr>
<td>47</td>
<td>3.0 hrs.</td>
</tr>
<tr>
<td>48</td>
<td>3.0 hrs.</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
</tr>
<tr>
<td>39</td>
<td>1.0 hrs.</td>
</tr>
<tr>
<td>39A</td>
<td>.5 hrs.</td>
</tr>
<tr>
<td>39B</td>
<td>2.0 hrs.</td>
</tr>
<tr>
<td>39C</td>
<td>1 min.</td>
</tr>
<tr>
<td>26</td>
<td>1.0 hrs.</td>
</tr>
<tr>
<td>26A</td>
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</tr>
<tr>
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</tr>
<tr>
<td>26C</td>
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<td>40A</td>
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<tr>
<td>40B</td>
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<tr>
<td>40C</td>
<td>10 mins.</td>
</tr>
<tr>
<td>40D</td>
<td>1.5 hrs.</td>
</tr>
<tr>
<td>40E</td>
<td>1 min.</td>
</tr>
<tr>
<td>138</td>
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</tr>
<tr>
<td>138A</td>
<td>10 mins.</td>
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<tr>
<td>138B</td>
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<td>25B</td>
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</tr>
<tr>
<td>25C</td>
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<tr>
<td>25D</td>
<td>.5 hrs.</td>
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**Table 8**

**Dynamic Experiments with Fused Silica in Armco Iron at 1600°C for One Hour**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10³)</th>
<th>Weight Loss Per Unit Surface Area (Corrected for Initial Reaction) (gm/cm² x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>1 hr.</td>
<td>40</td>
<td>2.61</td>
<td>0.0964</td>
<td>15.68</td>
<td>6.15</td>
<td>3.91</td>
</tr>
<tr>
<td>26</td>
<td>1 hr.</td>
<td>110</td>
<td>7.13</td>
<td>0.1521</td>
<td>15.55</td>
<td>9.78</td>
<td>7.54</td>
</tr>
<tr>
<td>40</td>
<td>1 hr.</td>
<td>190</td>
<td>12.43</td>
<td>0.2106</td>
<td>15.71</td>
<td>13.41</td>
<td>11.17</td>
</tr>
<tr>
<td>22</td>
<td>1 hr.</td>
<td>197</td>
<td>12.87</td>
<td>0.2279</td>
<td>15.68</td>
<td>14.53</td>
<td>12.28</td>
</tr>
<tr>
<td>6</td>
<td>1 hr.</td>
<td>225</td>
<td>14.36</td>
<td>0.2396</td>
<td>15.32</td>
<td>15.65</td>
<td>13.40</td>
</tr>
<tr>
<td>138</td>
<td>1 hr.</td>
<td>270</td>
<td>17.21</td>
<td>0.2692</td>
<td>15.30</td>
<td>17.60</td>
<td>15.35</td>
</tr>
<tr>
<td>12</td>
<td>1 hr.</td>
<td>300</td>
<td>19.38</td>
<td>0.2946</td>
<td>15.51</td>
<td>19.00</td>
<td>16.75</td>
</tr>
<tr>
<td>20</td>
<td>1 hr.</td>
<td>315</td>
<td>20.68</td>
<td>0.3345</td>
<td>15.75</td>
<td>21.23</td>
<td>18.98</td>
</tr>
<tr>
<td>24</td>
<td>1 hr.</td>
<td>358</td>
<td>21.35</td>
<td>0.3079</td>
<td>14.31</td>
<td>21.51</td>
<td>19.26</td>
</tr>
<tr>
<td>14</td>
<td>1 hr.</td>
<td>360</td>
<td>23.72</td>
<td>0.3579</td>
<td>15.81</td>
<td>22.63</td>
<td>20.38</td>
</tr>
<tr>
<td>10</td>
<td>1 hr.</td>
<td>400</td>
<td>25.47</td>
<td>0.3800</td>
<td>15.28</td>
<td>24.87</td>
<td>22.61</td>
</tr>
<tr>
<td>15</td>
<td>1 hr.</td>
<td>450</td>
<td>26.75</td>
<td>0.3667</td>
<td>14.27</td>
<td>25.71</td>
<td>23.45</td>
</tr>
<tr>
<td>25</td>
<td>1 hr.</td>
<td>465</td>
<td>27.96</td>
<td>0.3749</td>
<td>14.28</td>
<td>26.26</td>
<td>24.01</td>
</tr>
<tr>
<td>9</td>
<td>1 hr.</td>
<td>550</td>
<td>35.02</td>
<td>0.4846</td>
<td>15.28</td>
<td>31.71</td>
<td>29.45</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
<td>Rotation Speed (rpm)</td>
<td>Average Peripheral Velocity (cm/sec)</td>
<td>Diameter Change**</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>----------------------</td>
<td>--------------------------------------</td>
<td>-------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1/4 From Bottom of Specimen (cm)</td>
<td>1/2 From Bottom of Specimen (cm)</td>
<td>3/4 From Bottom of Specimen (cm)</td>
<td>Average Over Whole Wetted Depth (cm)</td>
</tr>
<tr>
<td>39</td>
<td>1 hr.</td>
<td>40</td>
<td>2.61</td>
<td>.0056</td>
<td>.0058</td>
<td>.0058</td>
<td>.0056</td>
</tr>
<tr>
<td>26</td>
<td>1 hr.</td>
<td>110</td>
<td>7.13</td>
<td>.0089</td>
<td>.0089</td>
<td>.0089</td>
<td>.0089</td>
</tr>
<tr>
<td>40</td>
<td>1 hr.</td>
<td>190</td>
<td>12.43</td>
<td>.0122</td>
<td>.0122</td>
<td>.0122</td>
<td>.0122</td>
</tr>
<tr>
<td>22</td>
<td>1 hr.</td>
<td>197</td>
<td>12.87</td>
<td>.0132</td>
<td>.0132</td>
<td>.0132</td>
<td>.0132</td>
</tr>
<tr>
<td>6</td>
<td>1 hr.</td>
<td>225</td>
<td>14.36</td>
<td>.0142</td>
<td>.0145</td>
<td>.0142</td>
<td>.0142</td>
</tr>
<tr>
<td>138</td>
<td>1 hr.</td>
<td>270</td>
<td>17.21</td>
<td>.0163</td>
<td>.0157</td>
<td>.0160</td>
<td>.0160</td>
</tr>
<tr>
<td>12</td>
<td>1 hr.</td>
<td>300</td>
<td>19.38</td>
<td>.0170</td>
<td>.0175</td>
<td>.0175</td>
<td>.0173</td>
</tr>
<tr>
<td>20</td>
<td>1 hr.</td>
<td>315</td>
<td>20.68</td>
<td>.0193</td>
<td>.0196</td>
<td>.0188</td>
<td>.0193</td>
</tr>
<tr>
<td>24</td>
<td>1 hr.</td>
<td>358</td>
<td>21.35</td>
<td>.0196</td>
<td>.0198</td>
<td>.0196</td>
<td>.0196</td>
</tr>
<tr>
<td>14</td>
<td>1 hr.</td>
<td>360</td>
<td>23.72</td>
<td>.0208</td>
<td>.0203</td>
<td>.0208</td>
<td>.0206</td>
</tr>
<tr>
<td>10</td>
<td>1 hr.</td>
<td>400</td>
<td>25.47</td>
<td>.0226</td>
<td>.0226</td>
<td>.0229</td>
<td>.0226</td>
</tr>
<tr>
<td>15</td>
<td>1 hr.</td>
<td>450</td>
<td>26.75</td>
<td>.0231</td>
<td>.0234</td>
<td>.0234</td>
<td>.0234</td>
</tr>
<tr>
<td>25</td>
<td>1 hr.</td>
<td>465</td>
<td>27.66</td>
<td>.0234</td>
<td>.0246</td>
<td>.0239</td>
<td>.0239</td>
</tr>
<tr>
<td>9</td>
<td>1 hr.</td>
<td>550</td>
<td>35.02</td>
<td>.0290</td>
<td>.0287</td>
<td>.0290</td>
<td>.0288</td>
</tr>
</tbody>
</table>

** Diameter Change Corrected For Diameter Change Due to Devitrification (.0071cm)
TABLE 10

COMPARISON OF RATES OF ATTACK OF FUSED SILICA BY ARMCO IRON AT 1600°C
DETERMINED BY DYNAMIC EXPERIMENTS

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Experimental Rate From Corrected Weight Loss/Unit Surface Area vs Velocity Curve for 1 hr. Rotation Runs (gm/cm²/hr. x 10³)</th>
<th>Experimental Rate From the Slope of the Weight Loss/Unit Surface Area vs Time Curve at Constant Velocity (gm/cm²/hr. x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39 Series</td>
<td>40</td>
<td>2.61</td>
<td>3.91</td>
<td>3.97 ± .86</td>
</tr>
<tr>
<td>26 Series</td>
<td>110</td>
<td>7.13</td>
<td>7.54</td>
<td>7.53 ± .30</td>
</tr>
<tr>
<td>40 Series</td>
<td>190</td>
<td>12.43</td>
<td>11.17</td>
<td>11.22 ± .37</td>
</tr>
<tr>
<td>138 Series</td>
<td>270</td>
<td>17.24</td>
<td>15.35</td>
<td>15.22 ± .32</td>
</tr>
<tr>
<td>14 Series</td>
<td>360</td>
<td>23.70</td>
<td>20.38</td>
<td>20.50 ± .44</td>
</tr>
<tr>
<td>25 Series</td>
<td>465</td>
<td>27.96</td>
<td>24.01</td>
<td>24.56 ± .42</td>
</tr>
<tr>
<td>Run No.</td>
<td>Type of Melt</td>
<td>Length of Run</td>
<td>Rotation Speed (rpm)</td>
<td>Average Peripheral Velocity (cm/sec)</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>---------------</td>
<td>----------------------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>120</td>
<td>Electrolytic Iron</td>
<td>1 hr.</td>
<td>Static Run</td>
<td>15.58</td>
</tr>
<tr>
<td>27</td>
<td>Armco Iron</td>
<td>1 hr.</td>
<td>Static Run</td>
<td>15.53</td>
</tr>
<tr>
<td>121</td>
<td>Electrolytic Iron</td>
<td>1 hr.</td>
<td>270</td>
<td>17.29</td>
</tr>
<tr>
<td>138</td>
<td>Armco Iron</td>
<td>1 hr.</td>
<td>270</td>
<td>17.21</td>
</tr>
<tr>
<td>122</td>
<td>Electrolytic Iron</td>
<td>2 hrs.</td>
<td>270</td>
<td>17.25</td>
</tr>
<tr>
<td>138B</td>
<td>Armco Iron</td>
<td>2 hrs.</td>
<td>270</td>
<td>17.22</td>
</tr>
</tbody>
</table>

TABLE II

COMPARISON OF EXPERIMENTS IN ELECTROLYTIC IRON AND ARMCO IRON AT 1600°C WITH FUSED SILICA
### TABLE 12

EXPERIMENTS WITH FUSED SILICA IN AN IRON - 2.10% SILICON ALLOY AT 1600°C

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (gm)</th>
<th>Diameter Change Corrected for Devitrification (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>1 hr.</td>
<td>Static Run</td>
<td>12.90</td>
<td>0.0015</td>
<td>0.0002</td>
</tr>
<tr>
<td>83</td>
<td>3 hrs.</td>
<td>Static Run</td>
<td>198</td>
<td>0.0019</td>
<td>0.0005</td>
</tr>
<tr>
<td>71</td>
<td>1 hr.</td>
<td>198</td>
<td>12.90</td>
<td>+0.0010</td>
<td>0.0000</td>
</tr>
<tr>
<td>74</td>
<td>1 hr.</td>
<td>303</td>
<td>19.43</td>
<td>0.0020</td>
<td>0.0003</td>
</tr>
<tr>
<td>75</td>
<td>3 hrs.</td>
<td>465</td>
<td>27.92</td>
<td>0.0028</td>
<td>0.0004</td>
</tr>
<tr>
<td>82</td>
<td>1 hr.</td>
<td>410</td>
<td>25.62</td>
<td>+0.0012</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
### EFFECT OF ATMOSPHERE ON THE ATTACK OF FUSED-SILICA AND 'SHELROCK' SILICA BY ARMCO IRON AT 1600°C

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Experimental Conditions</th>
<th>Gas Atmosphere Used</th>
<th>Partial Pressure of Oxygen Measured by Oxygen Probe (atm)</th>
<th>Weight Loss (gm)</th>
<th>Weight Loss Per Unit Surface Area $(gm/cm^2 \times 10^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RUNS WITH FUSED SILICA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>1 hr. static run</td>
<td>Argon</td>
<td>$9.1 \times 10^{-9}$</td>
<td>0.0738</td>
<td>4.75</td>
</tr>
<tr>
<td>22</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>Argon</td>
<td>$1.11 \times 10^{-9}$</td>
<td>0.2279</td>
<td>14.53</td>
</tr>
<tr>
<td>175</td>
<td>1 hr. static run</td>
<td>52% CO$_2$, Balance CO</td>
<td>$1.78 \times 10^{-13}$</td>
<td>0.0012</td>
<td>0.08</td>
</tr>
<tr>
<td>182</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>52% CO$_2$, Balance CO</td>
<td>$1.78 \times 10^{-13}$</td>
<td>0.0018</td>
<td>0.12</td>
</tr>
<tr>
<td>178</td>
<td>1 hr. static run</td>
<td>9.94% CO$_2$, Balance CO</td>
<td>$2.31 \times 10^{-9}$</td>
<td>0.0937</td>
<td>5.97</td>
</tr>
<tr>
<td>179</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>9.94% CO$_2$, Balance CO</td>
<td>$2.31 \times 10^{-9}$</td>
<td>0.2479</td>
<td>16.01</td>
</tr>
<tr>
<td>181</td>
<td>1 hr. static run</td>
<td>13.7% CO$_2$, Balance CO</td>
<td>$4.03 \times 10^{-9}$</td>
<td>0.1317</td>
<td>8.45</td>
</tr>
<tr>
<td>183</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>13.7% CO$_2$, Balance CO</td>
<td>$4.03 \times 10^{-9}$</td>
<td>0.2897</td>
<td>18.60</td>
</tr>
<tr>
<td><strong>RUNS WITH 'SHELROCK' SILICA</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS92</td>
<td>1 hr. static run</td>
<td>Argon</td>
<td>$9.1 \times 10^{-9}$</td>
<td>0.1185</td>
<td>7.33</td>
</tr>
<tr>
<td>GS101A</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>Argon</td>
<td>$9.1 \times 10^{-9}$</td>
<td>0.3301</td>
<td>21.63</td>
</tr>
<tr>
<td>GS174</td>
<td>1 hr. static run</td>
<td>52% CO$_2$, Balance CO</td>
<td>$1.78 \times 10^{-13}$</td>
<td>0.0024</td>
<td>0.15</td>
</tr>
<tr>
<td>GS190</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>52% CO$_2$, Balance CO</td>
<td>$1.78 \times 10^{-13}$</td>
<td>0.0017</td>
<td>0.11</td>
</tr>
<tr>
<td>GS176</td>
<td>1 hr. static run</td>
<td>9.94% CO$_2$, Balance CO</td>
<td>$2.15 \times 10^{-9}$</td>
<td>0.1340</td>
<td>8.55</td>
</tr>
<tr>
<td>GS192</td>
<td>1 hr. rotation run (200 rpm)</td>
<td>9.94% CO$_2$, Balance CO</td>
<td>$2.15 \times 10^{-9}$</td>
<td>0.2774</td>
<td>17.97</td>
</tr>
<tr>
<td>Run No.</td>
<td>Weight Loss (gm)</td>
<td>Average Surface Area (cm²)</td>
<td>Weight Loss Per Unit Surface Area (gm/cm² x 10⁻³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------------</td>
<td>----------------------------</td>
<td>-----------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS104</td>
<td>0.096</td>
<td>15.32</td>
<td>5.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS 96</td>
<td>0.1194</td>
<td>15.29</td>
<td>7.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS 92</td>
<td>0.1152</td>
<td>15.27</td>
<td>7.54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS 98</td>
<td>0.1185</td>
<td>15.33</td>
<td>7.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS 94</td>
<td>0.1224</td>
<td>15.34</td>
<td>7.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GS 97</td>
<td>0.1195</td>
<td>15.21</td>
<td>7.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4**

STATIC EXPERIMENTS WITH "SHELROCK" SILICA IN ARMCO IRON AT 1600°C
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS 99</td>
<td>.5 hrs.</td>
<td>140</td>
<td>8.92</td>
<td>.1777</td>
<td>15.29</td>
<td>11.63</td>
</tr>
<tr>
<td>GS 99A</td>
<td>1 hr.</td>
<td>140</td>
<td>8.87</td>
<td>.2880</td>
<td>15.19</td>
<td>18.97</td>
</tr>
<tr>
<td>GS 99B</td>
<td>1.5 hrs.</td>
<td>140</td>
<td>8.84</td>
<td>.3746</td>
<td>15.15</td>
<td>24.73</td>
</tr>
<tr>
<td>GS 99C</td>
<td>10 mins.</td>
<td>140</td>
<td>8.94</td>
<td>.1226</td>
<td>15.34</td>
<td>7.99</td>
</tr>
<tr>
<td>GS 99D</td>
<td>2 hrs.</td>
<td>140</td>
<td>8.87</td>
<td>.4774</td>
<td>15.20</td>
<td>31.40</td>
</tr>
<tr>
<td>GS 99E</td>
<td>1 min.</td>
<td>140</td>
<td>8.93</td>
<td>.0950</td>
<td>15.36</td>
<td>6.19</td>
</tr>
<tr>
<td>GS102</td>
<td>.5 hrs.</td>
<td>265</td>
<td>16.81</td>
<td>.2373</td>
<td>15.22</td>
<td>15.59</td>
</tr>
<tr>
<td>GS102A</td>
<td>1 hr.</td>
<td>265</td>
<td>16.88</td>
<td>.3842</td>
<td>15.28</td>
<td>25.14</td>
</tr>
<tr>
<td>GS102B</td>
<td>10 mins.</td>
<td>265</td>
<td>16.89</td>
<td>.1381</td>
<td>15.30</td>
<td>9.02</td>
</tr>
<tr>
<td>GS102C</td>
<td>1 min.</td>
<td>265</td>
<td>16.91</td>
<td>.0901</td>
<td>15.24</td>
<td>5.91</td>
</tr>
<tr>
<td>GS102D</td>
<td>2 hrs.</td>
<td>265</td>
<td>16.77</td>
<td>.6756</td>
<td>15.15</td>
<td>44.59</td>
</tr>
<tr>
<td>GS105</td>
<td>.5 hrs.</td>
<td>430</td>
<td>27.24</td>
<td>.2998</td>
<td>15.20</td>
<td>19.72</td>
</tr>
<tr>
<td>GS105A</td>
<td>1 hr.</td>
<td>430</td>
<td>27.24</td>
<td>.5119</td>
<td>15.20</td>
<td>33.67</td>
</tr>
<tr>
<td>GS105B</td>
<td>10 mins.</td>
<td>428</td>
<td>27.32</td>
<td>.1457</td>
<td>15.30</td>
<td>9.53</td>
</tr>
<tr>
<td>GS105C</td>
<td>1 min.</td>
<td>430</td>
<td>27.29</td>
<td>.0980</td>
<td>15.28</td>
<td>6.42</td>
</tr>
<tr>
<td>GS105D</td>
<td>1.5 hrs.</td>
<td>432</td>
<td>27.26</td>
<td>.7053</td>
<td>15.08</td>
<td>46.78</td>
</tr>
</tbody>
</table>


**TABLE 16**

*DYNAMIC EXPERIMENTS WITH 'SHELROCK' SILICA IN ARMCO IRON AT 1600°C FOR ONE HOUR*

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10³)</th>
<th>Weight Loss Per Unit Surface Area (Corrected for Initial Reaction) (gm/cm² x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS137A</td>
<td>1 hr.</td>
<td>41</td>
<td>2.61</td>
<td>.2052</td>
<td>15.29</td>
<td>13.42</td>
<td>7.70</td>
</tr>
<tr>
<td>GS99A</td>
<td>1 hr.</td>
<td>140</td>
<td>8.87</td>
<td>.2881</td>
<td>15.19</td>
<td>18.97</td>
<td>13.25</td>
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<tr>
<td>GS101A</td>
<td>1 hr.</td>
<td>204</td>
<td>12.98</td>
<td>.3301</td>
<td>15.26</td>
<td>21.63</td>
<td>15.91</td>
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<tr>
<td>GS102A</td>
<td>1 hr.</td>
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<td>.3842</td>
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<td>25.14</td>
<td>19.42</td>
</tr>
<tr>
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<td>360</td>
<td>22.78</td>
<td>.4678</td>
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</tr>
<tr>
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<td>430</td>
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<td>.5119</td>
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<td>33.67</td>
<td>27.95</td>
</tr>
<tr>
<td>Run No.</td>
<td>Rotation Speed (rpm)</td>
<td>Average Peripheral Velocity (cm/sec)</td>
<td>Experimental Rate from the Slope of the (Weight Loss/Unit Area) vs (Velocity (cm/sec)) Curve at Constant Velocity (gm/cm²/hr. x 10³)</td>
<td>Experimental Rate from the Slope of the (Weight Loss/Unit Surface Area) vs (Time) Curve at Constant Rotation Run No. (gm/cm²/hr. x 10³)</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>--------</td>
<td>---------------------</td>
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<td>-------------------------------------------------------------------------------------------------</td>
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<tr>
<td>GS 99</td>
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<td>13.25</td>
<td>12.82 ± 0.59</td>
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<tr>
<td>Series</td>
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<tr>
<td></td>
<td>GS105</td>
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<td>27.62 ± 0.21</td>
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<tr>
<td>Run No.</td>
<td>Length of Run</td>
<td>Weight Change (gm)</td>
<td>Average Surface Area (cm²)</td>
<td>Weight Change Per Unit Surface Area (gm/cm² x 10³)</td>
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<tr>
<td>--------</td>
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<td>--------------------</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
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</tr>
<tr>
<td>II</td>
<td>1.0 hrs.</td>
<td>0.0632</td>
<td>16.54</td>
<td>3.82</td>
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<td></td>
</tr>
<tr>
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<td>1 min.</td>
<td>0.0408</td>
<td>15.47</td>
<td>2.48</td>
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</tr>
<tr>
<td>II B</td>
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<td>3.71</td>
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</tr>
<tr>
<td>II D</td>
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<td>0.0656</td>
<td>16.44</td>
<td>3.99</td>
<td></td>
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</tr>
<tr>
<td>II E</td>
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<td>16.52</td>
<td>3.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
<td>Rotation Speed (rpm)</td>
<td>Average Peripheral Velocity (cm/sec)</td>
<td>Weight Loss (gm)</td>
<td>Average Surface Area (cm$^2$)</td>
<td>Weight Loss Per Unit Surface Area (gm/cm$^2 \times 10^3$)</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>----------------------</td>
<td>-------------------------------------</td>
<td>-----------------</td>
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</tr>
<tr>
<td>16</td>
<td>1.0 hrs.</td>
<td>265</td>
<td>18.14</td>
<td>.3574</td>
<td>16.43</td>
<td>21.75</td>
<td></td>
</tr>
<tr>
<td>16A</td>
<td>2.0 hrs.</td>
<td>266</td>
<td>18.19</td>
<td>.6872</td>
<td>16.41</td>
<td>41.88</td>
<td></td>
</tr>
<tr>
<td>16B</td>
<td>1 min.</td>
<td>265/</td>
<td>18.16</td>
<td>.0378</td>
<td>16.45</td>
<td>2.30</td>
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</tr>
<tr>
<td>16D</td>
<td>.5 hrs.</td>
<td>265</td>
<td>18.18</td>
<td>.1847</td>
<td>16.42</td>
<td>11.25</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.0 hrs.</td>
<td>155</td>
<td>10.65</td>
<td>.2330</td>
<td>16.49</td>
<td>14.13</td>
<td></td>
</tr>
<tr>
<td>13A</td>
<td>2.0 hrs.</td>
<td>156</td>
<td>10.68</td>
<td>.4516</td>
<td>16.43</td>
<td>27.49</td>
<td></td>
</tr>
<tr>
<td>13B</td>
<td>1 min.</td>
<td>155</td>
<td>10.65</td>
<td>.0373</td>
<td>16.49</td>
<td>2.26</td>
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</tr>
<tr>
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<td>10.69</td>
<td>.1358</td>
<td>16.50</td>
<td>8.23</td>
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</tr>
</tbody>
</table>
### TABLE 20

**DYNAMIC EXPERIMENTS WITH HIGH SILICA BRICK IN ARMCO IRON AT 1600°C FOR ONE HOUR**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10³)</th>
<th>Weight Loss Per Unit Surface Area (Corrected for Initial Reaction) (gm/cm² x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>1 hr.</td>
<td>155</td>
<td>10.65</td>
<td>.2330</td>
<td>16.49</td>
<td>14.13</td>
<td>12.38</td>
</tr>
<tr>
<td>15</td>
<td>1 hr.</td>
<td>225</td>
<td>15.36</td>
<td>.2989</td>
<td>16.38</td>
<td>18.25</td>
<td>16.50</td>
</tr>
<tr>
<td>16</td>
<td>1 hr.</td>
<td>265</td>
<td>18.14</td>
<td>.3574</td>
<td>16.43</td>
<td>21.75</td>
<td>20.00</td>
</tr>
<tr>
<td>17</td>
<td>1 hr.</td>
<td>50</td>
<td>3.44</td>
<td>.1230</td>
<td>16.50</td>
<td>7.46</td>
<td>5.71</td>
</tr>
<tr>
<td>18</td>
<td>1 hr.</td>
<td>390</td>
<td>26.63</td>
<td>.5096</td>
<td>16.38</td>
<td>31.10</td>
<td>29.35</td>
</tr>
<tr>
<td>19</td>
<td>1 hr.</td>
<td>355</td>
<td>24.13</td>
<td>.4720</td>
<td>16.31</td>
<td>28.94</td>
<td>27.20</td>
</tr>
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</table>
### Table 21

Comparison of Rates of Attack of High Silica Brick by Armco Iron at 1600°C Determined by Dynamic Experiments

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Experimental Rate From (Corrected Weight Loss/Unit Surface Area) vs. (Velocity) Curve for 1 Hr. Rotation Runs (gm/cm²/hr. x 10³)</th>
<th>Experimental Rate From the Slope of the (Weight Loss/Unit Surface Area) vs. (Time) Curves at Constant Velocities (gm/cm²/hr. x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 Series</td>
<td>265</td>
<td>18.14</td>
<td>20.00</td>
<td>20.07 ± .17</td>
</tr>
<tr>
<td>13 Series</td>
<td>155</td>
<td>10.67</td>
<td>12.38</td>
<td>12.72 ± .22</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
<td>Weight Loss (Method 1) (gm)</td>
<td>Weight Loss (Method 2) (gm)</td>
<td>Average Surface Area (cm$^2$)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>I49</td>
<td>1 min.</td>
<td>.2850</td>
<td>.2907</td>
<td>16.35</td>
</tr>
<tr>
<td>I49A</td>
<td>.5 hrs.</td>
<td>.6542</td>
<td>.6597</td>
<td>16.47</td>
</tr>
<tr>
<td>I49B</td>
<td>1.0 hrs.</td>
<td>.6820</td>
<td>.6915</td>
<td>16.42</td>
</tr>
<tr>
<td>I49D</td>
<td>2.0 hrs.</td>
<td>.6853</td>
<td>.6948</td>
<td>16.40</td>
</tr>
<tr>
<td>I49E</td>
<td>10 mins.</td>
<td>.6033</td>
<td>.6399</td>
<td>16.43</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run</td>
<td>Rotation Speed (rpm)</td>
<td>Average Peripheral Velocity (cm/sec)</td>
<td>Weight Loss (Method 1) (gm)</td>
</tr>
<tr>
<td>---------</td>
<td>---------------</td>
<td>----------------------</td>
<td>-------------------------------------</td>
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</tr>
<tr>
<td>128</td>
<td>1 hrs.</td>
<td>303</td>
<td>20.63</td>
<td>1.6186</td>
</tr>
<tr>
<td>128A</td>
<td>1 min.</td>
<td>302</td>
<td>20.69</td>
<td>.4488</td>
</tr>
<tr>
<td>128B</td>
<td>.5 hrs.</td>
<td>303</td>
<td>20.67</td>
<td>1.0561</td>
</tr>
<tr>
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<td>303</td>
<td>20.60</td>
<td>2.2705</td>
</tr>
<tr>
<td>128E</td>
<td>10 mins</td>
<td>302</td>
<td>20.64</td>
<td>.5731</td>
</tr>
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</table>
## Table 24

**Dynamic Experiments in Armco Iron With Fire-Clay Brick for One Hour**

<table>
<thead>
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<th>Run No.</th>
<th>Rotation Speed (rpm)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Weight Loss (Method 1) (gm)</th>
<th>Weight Loss (Method 2) (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (Method 1) (gm/cm² x 10³)</th>
<th>Weight Loss Per Unit Surface Area (Method 2) (gm/cm² x 10³)</th>
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<tbody>
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<td>125</td>
<td>100</td>
<td>6.92</td>
<td>0.9379</td>
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<tr>
<td>126</td>
<td>200</td>
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<td>1.2178</td>
<td>1.2256</td>
<td>16.47</td>
<td>73.94</td>
<td>74.41</td>
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<tr>
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<td>201</td>
<td>13.72</td>
<td>1.3440</td>
<td>1.3085</td>
<td>16.46</td>
<td>81.65</td>
<td>79.50</td>
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<td>1.6186</td>
<td>1.6427</td>
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<td>99.06</td>
<td>100.53</td>
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<td>160</td>
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<td>1.1971</td>
<td>1.2072</td>
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<td>Length of Run</td>
<td>Weight Loss</td>
<td>Average Surface Area</td>
<td>Weight Loss Per Unit Surface Area</td>
<td>Weight % Silicon Analyzed</td>
<td>Gram-Moles Silicon Transferred Per Unit Surface Area</td>
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<td>---------</td>
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<td>.25</td>
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</table>

melt |


<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run (hr.)</th>
<th>Rotation Speed (r.p.m.)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10²)</th>
<th>Weight % Silicon Analyzed</th>
<th>Gram-Moles Silicon Transferred Per² Unit Surface Area (gm moles/cm² x 10²)</th>
</tr>
</thead>
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<td>2.8728</td>
<td>14.15</td>
<td>20.30</td>
<td>.77</td>
<td>33.32</td>
</tr>
<tr>
<td>GSI67C</td>
<td>1.0</td>
<td>285</td>
<td>.8887</td>
<td>14.93</td>
<td>5.94</td>
<td>.24</td>
<td>9.73</td>
</tr>
<tr>
<td>GSI84C</td>
<td>1.0</td>
<td>400</td>
<td>.8475</td>
<td>14.72</td>
<td>5.75</td>
<td>.23</td>
<td>9.46</td>
</tr>
<tr>
<td>GSI44C2 (2.3% C melt)</td>
<td>1.0</td>
<td>200</td>
<td>.8721</td>
<td>14.79</td>
<td>5.90</td>
<td>.23</td>
<td>9.39</td>
</tr>
</tbody>
</table>

**TABLE 26**

**DYNAMIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON-SATURATED IRON AT 1600°C AT A CONSTANT ROTATION SPEED OF 200 R.P.M.**
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run (hrs.)</th>
<th>Temperature</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm² x 10²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GS169C</td>
<td>1</td>
<td>1400°C</td>
<td>.1244</td>
<td>15.35</td>
<td>.810</td>
</tr>
<tr>
<td>GS164C</td>
<td>2</td>
<td>1400°C</td>
<td>.1550</td>
<td>15.15</td>
<td>1.01</td>
</tr>
<tr>
<td>GS170C</td>
<td>4</td>
<td>1400°C</td>
<td>.1877</td>
<td>15.30</td>
<td>1.23</td>
</tr>
<tr>
<td>GS165C</td>
<td>1</td>
<td>1500°C</td>
<td>.3755</td>
<td>15.09</td>
<td>2.49</td>
</tr>
<tr>
<td>GS171C</td>
<td>2</td>
<td>1500°C</td>
<td>.4449</td>
<td>15.02</td>
<td>2.96</td>
</tr>
<tr>
<td>GS185C</td>
<td>3</td>
<td>1500°C</td>
<td>.5673</td>
<td>15.05</td>
<td>3.77</td>
</tr>
<tr>
<td>GS172C</td>
<td>4</td>
<td>1500°C</td>
<td>.6312</td>
<td>15.07</td>
<td>4.19</td>
</tr>
<tr>
<td>Run No.</td>
<td>Length of Run (hr.)</td>
<td>Rotation Speed (rpm)</td>
<td>Weight Loss (gm)</td>
<td>Average Surface Area (cm²)</td>
<td>Weight Loss Per Unit Surface Area (gm/cm² x 10²)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>-----------------</td>
<td>--------------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>110C</td>
<td>.1</td>
<td>Static Run</td>
<td>.6415</td>
<td>16.14</td>
<td>3.98</td>
</tr>
<tr>
<td>111C</td>
<td>.5</td>
<td>Run</td>
<td>1.1645</td>
<td>16.35</td>
<td>7.12</td>
</tr>
<tr>
<td>112C</td>
<td>1.0</td>
<td>Run</td>
<td>1.7549</td>
<td>15.69</td>
<td>11.19</td>
</tr>
<tr>
<td>113C</td>
<td>2.0</td>
<td>Run</td>
<td>3.1691</td>
<td>15.39</td>
<td>20.60</td>
</tr>
<tr>
<td>114C</td>
<td>3.0</td>
<td>Run</td>
<td>4.1737</td>
<td>14.73</td>
<td>28.34</td>
</tr>
<tr>
<td>115C</td>
<td>4.0</td>
<td>Run</td>
<td>5.2862</td>
<td>14.17</td>
<td>37.56</td>
</tr>
<tr>
<td>116C</td>
<td>4.0</td>
<td>Run</td>
<td>5.1724</td>
<td>14.07</td>
<td>36.85</td>
</tr>
<tr>
<td>119C</td>
<td>.5</td>
<td>200</td>
<td>1.2314</td>
<td>16.23</td>
<td>7.59</td>
</tr>
<tr>
<td>120C</td>
<td>1.0</td>
<td>200</td>
<td>1.8063</td>
<td>15.88</td>
<td>11.37</td>
</tr>
<tr>
<td>121C</td>
<td>1.5</td>
<td>200</td>
<td>2.2673</td>
<td>15.94</td>
<td>14.23</td>
</tr>
<tr>
<td>122C</td>
<td>2.0</td>
<td>202</td>
<td>3.0914</td>
<td>14.90</td>
<td>20.75</td>
</tr>
<tr>
<td>123C</td>
<td>3.0</td>
<td>204</td>
<td>4.2080</td>
<td>14.85</td>
<td>28.34</td>
</tr>
<tr>
<td>124C</td>
<td>4.0</td>
<td>204</td>
<td>5.3686</td>
<td>14.10</td>
<td>38.06</td>
</tr>
</tbody>
</table>
**Table 29**

**Reaction Rates and Rate Constants for Runs with 'Shelrock' Silica and High Silica Brick in Carbon-Saturated Iron**

<table>
<thead>
<tr>
<th>Type of Refractory and Experimental Conditions</th>
<th>Temperature</th>
<th>Rate of Refractory Attack $\Delta W/A \text{ (gm/cm}^2\text{/hr x 10}^6\text{)}$</th>
<th>Reaction Rate Constant $k$ (gm/cm$^2$/hr x 10$^2$)</th>
<th>Rate of Transfer of Silicon to the Melt $n_SiO_2$ $\Delta A/\text{dt (gm-mole/cm}^2$/hr x 10$^4$)</th>
<th>Reaction Rate Constant $k_1$ (gm-mole/cm$^2$/hr x 10$^4$)</th>
<th>Reaction Rate Constant $k_1$ from Eq. (36) (gm-mole/cm$^2$/hr x 10$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Shelrock' Silica Static Runs</td>
<td>1600°C</td>
<td>3.60 ± 0.07</td>
<td>3.60 ± 0.07</td>
<td>6.22 ± 0.21</td>
<td>6.22 ± 0.21</td>
<td>5.99 ± 0.07</td>
</tr>
<tr>
<td>'Shelrock' Silica Dynamic Runs</td>
<td>1600°C</td>
<td>3.62 ± 0.06</td>
<td>3.62 ± 0.06</td>
<td>5.82 ± 0.31</td>
<td>5.82 ± 0.31</td>
<td>6.04 ± 0.06</td>
</tr>
<tr>
<td>'Shelrock' Silica Static and Dynamic Runs</td>
<td>1600°C</td>
<td>3.62 ± 0.05</td>
<td>3.62 ± 0.05</td>
<td>6.06 ± 0.20</td>
<td>6.06 ± 0.20</td>
<td>6.04 ± 0.06</td>
</tr>
<tr>
<td>'Shelrock' Silica Static Runs</td>
<td>1500°C</td>
<td>.591 ± .062</td>
<td>.591 ± .062</td>
<td>-</td>
<td>-</td>
<td>985 ± 0.062</td>
</tr>
<tr>
<td>'Shelrock' Silica Static Runs</td>
<td>1400°C</td>
<td>.136 ± .075</td>
<td>.136 ± .075</td>
<td>-</td>
<td>-</td>
<td>.227 ± .075</td>
</tr>
<tr>
<td>High Silica Brick</td>
<td>1600°C</td>
<td>8.59 ± .35</td>
<td>8.59 ± .35</td>
<td>14.34 ± .49</td>
<td>14.34 ± .49</td>
<td>14.34 ± .49</td>
</tr>
<tr>
<td>High Silica Brick</td>
<td>1600°C</td>
<td>8.78 ± .89</td>
<td>8.78 ± .89</td>
<td>14.24 ± .72</td>
<td>14.24 ± .72</td>
<td>14.24 ± .72</td>
</tr>
<tr>
<td>High Silica Brick</td>
<td>1600°C</td>
<td>8.67 ± .32</td>
<td>8.67 ± .32</td>
<td>14.30 ± .60</td>
<td>14.30 ± .60</td>
<td>14.30 ± .60</td>
</tr>
</tbody>
</table>
### TABLE 30

**STATIC AND DYNAMIC EXPERIMENTS WITH FIRE-CLAY BRICK IN CARBON-SATURATED IRON AT 1600°C**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run (hr.)</th>
<th>Rotation Speed (rpm)</th>
<th>Weight Loss (gm)</th>
<th>Average Surface Area (cm²)</th>
<th>Weight Loss Per Unit Surface Area (gm/cm²x10²)</th>
<th>Weight % Silicon Analyzed</th>
<th>Gram-Moles Silicon Transferred Per Unit Surface Area (gm.mole/cm²x10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>131C</td>
<td>0.5</td>
<td>Static Run</td>
<td>0.5927</td>
<td>16.72</td>
<td>3.54</td>
<td>0.12</td>
<td>4.34</td>
</tr>
<tr>
<td>132C</td>
<td>1.0</td>
<td>&quot;</td>
<td>1.0459</td>
<td>16.80</td>
<td>6.57</td>
<td>0.24</td>
<td>8.65</td>
</tr>
<tr>
<td>133C</td>
<td>2.0</td>
<td>&quot;</td>
<td>1.2478</td>
<td>16.48</td>
<td>9.18</td>
<td>0.37</td>
<td>13.59</td>
</tr>
<tr>
<td>134C</td>
<td>3.0</td>
<td>&quot;</td>
<td>1.7694</td>
<td>16.48</td>
<td>11.01</td>
<td>0.45</td>
<td>16.53</td>
</tr>
<tr>
<td>135C</td>
<td>4.0</td>
<td>&quot;</td>
<td>2.0932</td>
<td>16.35</td>
<td>13.84</td>
<td>0.58</td>
<td>21.47</td>
</tr>
<tr>
<td>136C</td>
<td>5.0</td>
<td>&quot;</td>
<td>2.3033</td>
<td>16.24</td>
<td>15.33</td>
<td>0.66</td>
<td>24.60</td>
</tr>
<tr>
<td>137C</td>
<td>8.0</td>
<td>&quot;</td>
<td>2.6583</td>
<td>16.42</td>
<td>16.19</td>
<td>0.74</td>
<td>27.20</td>
</tr>
<tr>
<td>138C</td>
<td>0.5</td>
<td>200</td>
<td>0.5492</td>
<td>16.60</td>
<td>3.31</td>
<td>0.10</td>
<td>3.65</td>
</tr>
<tr>
<td>139C</td>
<td>1.0</td>
<td>201</td>
<td>1.1195</td>
<td>16.46</td>
<td>7.22</td>
<td>0.25</td>
<td>9.20</td>
</tr>
<tr>
<td>140C</td>
<td>2.0</td>
<td>200</td>
<td>1.4165</td>
<td>16.55</td>
<td>8.62</td>
<td>0.35</td>
<td>12.98</td>
</tr>
<tr>
<td>141C</td>
<td>3.0</td>
<td>200</td>
<td>2.1095</td>
<td>16.85</td>
<td>12.52</td>
<td>0.57</td>
<td>20.47</td>
</tr>
<tr>
<td>142C</td>
<td>3.0</td>
<td>200</td>
<td>1.9715</td>
<td>16.59</td>
<td>11.88</td>
<td>0.47</td>
<td>17.15</td>
</tr>
<tr>
<td>143C</td>
<td>4.0</td>
<td>201</td>
<td>2.2975</td>
<td>16.32</td>
<td>14.07</td>
<td>0.57</td>
<td>21.14</td>
</tr>
<tr>
<td>144C</td>
<td>5.0</td>
<td>202</td>
<td>2.4786</td>
<td>16.34</td>
<td>15.17</td>
<td>0.64</td>
<td>23.70</td>
</tr>
<tr>
<td>145C</td>
<td>8.0</td>
<td>200</td>
<td>2.5650</td>
<td>16.39</td>
<td>15.65</td>
<td>0.71</td>
<td>26.40</td>
</tr>
</tbody>
</table>
CHAPTER 6

DISCUSSION OF THE RESULTS

6.1 Runs in Armco Iron

6.1.1 Nature of the Attack

Silica and alumino-silicate refractories were found to be chemically corroded by Armco iron at 1600°C with the formation of a liquid silicate as a corrosion product. Due to the low oxygen concentration and low flow rate of the argon reaction atmosphere, the contribution of the gas phase as a source of oxygen for the measured attack was considered negligible.

Under both static and dynamic conditions the attack proceeded with an initial fast reaction followed by a steady-state corrosion process. In the dynamic experiments the steady-state rate of attack was found to be a linear function of the peripheral velocity of the specimen.

6.1.2 The Initial Reaction

Analysis of the melt before the experiments showed the Armco iron to have a high oxygen concentration (0.078%) and low silicon concentration (<0.005%). In studying the silicon-oxygen equilibrium in liquid iron, Gokcen and Chipman (96) and Hilty and Crafts (97) found that at very low silicon concentrations and correspondingly high oxygen concentrations, solid silica was fluxed by iron oxide to form a silicate slag. At 1600°C, Gokcen and Chipman found that this reaction occurred at 0.088% oxygen and 0.003% Si. Comparable values were found by Hilty and Crafts. Since similar melt conditions existed in the present work, it is proposed that such a reaction took place when the silica or alumino-
silicate refractory was immersed in the Armco iron melt. For the relatively pure silica materials the reaction proceeded as follows:

\[ x(\text{FeO}) + y(\text{SiO}_2)_{\text{refractory}} = (\text{FeO})_x(\text{SiO}_2)_y(\text{liquid silicate}) \] (18)

A similar reaction took place with the fire-clay refractories, with the formation of an iron-aluminum-silicate containing other refractory oxides normally found in fire-clay bricks. In all the experiments these reactions proceeded quickly and a liquid silicate layer formed on the refractory surface. This initial reaction was controlled either by the diffusion of iron and dissolved oxygen to the metal/refractory interface, or by the chemical reaction at the interface. Diffusion processes in the melt would not be rate controlling until the chemical reaction has occurred to some extent, thereby establishing concentration gradients which give rise to diffusional processes. In the dynamic experiments it was observed that the initial reaction rate was independent of the rotation speed implying that a chemically-controlled rather than a transport-controlled reaction was taking place. As the reaction proceeded and the thickness of the silicate product layer increased, diffusion processes played a more important role in the reaction and the interfacial reaction was no longer the sole controlling step.

The initial reaction was observed to be fast in the systems studied. During the initial reaction period the oxygen content of the melt decreased very rapidly. This suggests that the dissolved oxygen was a reactant in the initial interfacial reaction. Expressing the oxygen content of the melt as dissolved oxygen, equation 18 becomes

\[ y(\text{SiO}_2)_{\text{refractory}} + \text{FeO}(s) + \text{O}_2 = (\text{FeO})(\text{SiO}_2)_y(\text{liquid silicate}) \] (19)

The involvement of oxygen in the initial reaction was further confirmed in runs using controlled \( \text{CO}_2/\text{CO} \) atmospheres. In these experiments a
mixture of low carbon dioxide content was used to deoxidize the melts before the introduction of the specimens. No attack or formation of a liquid silicate on the specimen surfaces was observed. On increasing the carbon dioxide content of the gas mixtures the initial reaction was observed to take place. A number of experiments were also carried out in melts previously deoxidized by the addition of a large amount of silicon (2.1% Si). The silicate phase did not form in these cases and no specimen attack was measured.

6.1.3 Steady-State Corrosion of the Refractories

After the rapid initial reaction, the rate of attack was observed to decrease until a steady-state condition was attained. In the dynamic experiments the steady state was reached very quickly. In the static experiments the rate was observed to decrease for several minutes until it dropped to a level which could not be readily measured by the experimental techniques utilized in this work.

6.1.4 Controlling Step in the Steady-State Reaction

By analyzing the melt during an experiment, it was determined that the silicon content of the melt increased in the course of the steady-state reaction. The stoichiometric equation proposed to represent the overall reaction is:

\[(\text{SiO}_2)_{\text{refractory}} + (\text{Fe})_x = \text{Si} + (\text{liquid silicate}) \]  

(20)

This equation suggests a three-phase reaction (slag, metal, and solid refractory) which is physically unrealistic since, following the initial reaction and the subsequent formation of the silicate layer on the refractory surface, such a three-phase interface does not exist in the system.
In the overall reaction it is necessary to consider a number of reactions and transport processes which take place in both the silicate/metal and refractory/silicate systems.

(a) the silicate/metal system

(1) transport of iron to the silicate/metal interface

the interfacial reactions:

(2) the discharge of silica: \( \text{Si}^{4+} + 4e = \text{Si} \), \( 2\text{O}^2- = 2\text{O} + 4e \)

(3) the oxidation of iron: \( 2\text{Fe} = 2\text{Fe}^{2+} + 4e \)

(4) the diffusion of silicon from the silicate/metal interface to the bulk metal

(5) diffusion of oxygen ions from the silicate/metal interface to the bulk metal

(6) diffusion of oxygen and iron ions to the refractory/silicate interface

(b) the refractory/silicate system

(6) diffusion of oxygen and iron ions to the refractory/silicate interface through the silicate layer

(7) reaction of iron and oxygen ions with the refractory at the refractory/silicate interface to form additional liquid silicate

(8) removal of the liquid silicate product

In order to determine the controlling step, each of the preceding processes must be examined individually. The experimentally observed dependence of the rate of attack on the peripheral velocity of the specimen eliminates steps 2, 3 and 7 as possible rate-limiting steps. If these interfacial chemical reactions were rate-controlling rather than the transport processes, no velocity dependence of the rate would be observed. Step (1) is not considered rate limiting since the supply of iron at the
interface is more than adequate to maintain the reaction.

In view of the strong dependence of the rate of attack on the rotation speed, the rate controlling step is either the diffusion of silicon in the metal phase (step 4), the diffusion of oxygen ions in the metal phase (step 5), or the diffusion of iron and oxygen ions through the liquid silicate to the refractory/silicate interface (step 6). Rotation enhances the convective mass transfer in steps 4 and 5 and reduces the thickness of the silicate layer thus decreasing the diffusion distance in step (6). The fact that the rate failed to decrease with increasing time despite the increasing silicon content in the melt is sufficient to rule out step (4) as the controlling step. Similarly step (5) is eliminated since after the initial reaction had taken place, the reaction rate was independent of the oxygen content of the melt.

An essential feature of a diffusion-controlled process is the existence of a concentration gradient of the diffusing species across the diffusion layer. Analysis of cross-sections of reacted refractory specimens, using a micro-probe analyser, showed steep iron gradients across the slag layers. A series of representative probe traces are shown in Figure 44. Step (6) is therefore the most likely rate-controlling step.

The removal of the reaction product (step 8) must also be considered. In the static and dynamic experiments the removal of the silicate reaction product will take place at the silicate/metal interface since the slag wets the refractory and the liquid slag is less dense than the metal.

In the static system the product layer will increase in thickness until the liquid density differences and the distance to the adhering refractory/slag interface result in the removal of a quantity of the silicate. The slow reaction rates observed in the static experiments, after the initial reaction, indicate a slow rate of product removal. This will allow the product layer to build up with the consequent decrease in the diffusion rates of iron and oxygen ions through the layer.

In the dynamic experiments, the removal of the reaction product
is aided by the shearing forces due to rotation of the specimen. The constant rotation speed produces a product layer of constant thickness. Hence the rate of removal of silicate is controlled by the chemical reaction producing the silicate at the refractory/silicate interface. It should be noted that, in identifying the controlling step of the overall reaction under dynamic conditions, the thickness of the silicate layer is determined by an independent parameter, the rotation speed. Therefore, once the rotation speed of the specimen is fixed the connection between step (8) and the other steps is severed so that it should not be considered as the possible rate-controlling step in the overall reaction.

Based on the above argument it is expected that the diffusion layer thickness should be a function of the rotation speed or peripheral velocity of the specimen. Experimentally it was found that the steady-state rate of attack was directly proportional to the peripheral velocity. It therefore follows that the product layer thickness is inversely proportional to the peripheral velocity.

6.1.5 The Steady-State Rate of Attack

In the last section it was proposed that the steady-state rate of attack of silica, silica brick, and fire-clay brick in Armco iron, was controlled by the diffusion of iron and oxygen ions across the liquid silicate layer. In the overall reaction, both oxygen and iron ions are created at the silicate/metal interface and consumed at the refractory/silicate interface. These species are transported through the silicate layer by ionic diffusion. According to Lu and Jin (93), the diffusional fluxes of oxygen and iron ions are coupled by the electroneutrality condition, and are, therefore, equal-molar and concurrent. Hence one flux equation is sufficient to represent the diffusion of these ions, and it can be written in terms of iron oxide diffusion in the silicate.

Assuming a fixed composition of the silicate slag, the rate of corrosion
of the refractory, $J$, can be expressed by a modified form of the Nernst equation for a diffusion-controlled reaction:

$$J = \frac{D}{\delta} A \delta (C_{FeO}^{I} - C_{FeO}^{II}) \quad (21)$$

where $\delta = \text{rate of refractory attack (gm/hr.)}$
$D = \text{diffusion coefficient for iron oxide in the liquid silicate (cm}^2/\text{hr.})$
$\delta = \text{product layer thickness (cm)}$
$C_{FeO}^{I} = \text{concentration of iron oxide at the silicate/metal interface (weight fraction)}$
$C_{FeO}^{II} = \text{concentration of iron oxide at the refractory/silicate interface (weight fraction)}$
$A = \text{interfacial surface area (cm}^2)\,$
$\delta = \text{density of liquid silicate (gm/cm}^3)\,$

The interfacial area is assumed to be constant. (The measured change in the area during the experiment was usually less than 1% and this change in geometric area will be compensated for by surface roughening of the refractory during the reaction.) If the diffusion coefficient, $D$, is assumed constant at constant temperature and over a small range of composition, and the diffusion layer thickness, $\delta$, remains constant due to the particular hydrodynamics of the system, the concentration difference of iron oxide across the liquid silicate, $(C_{FeO}^{I} - C_{FeO}^{II})$, must also be constant to give rise to a steady-state rate of attack. As can be seen by the probe analysis of the silicate layer (Figure 44) the concentration of iron oxide at the refractory/silicate interface, $C_{FeO}^{II}$, is small and comparable to the concentration of iron oxide in the refractory material. For the purposes of this discussion it will be considered negligible.

Rewriting equation (21) the following expression is obtained:

$$\frac{J}{A} = \frac{D}{\delta} \delta (C_{FeO}^{I}) \quad (22)$$
The experimentally observed steady-state rate of attack implies that the concentration of iron oxide at the silicate/metal interface, $C_{\text{FeO}}^I$, is constant.

6.1.6 The Iron Oxide Concentration at the Silicate/Metal Interface

The exact value of the iron oxide concentration at the silicate/metal interface, $C_{\text{FeO}}^I$, could not be determined from the experimental results since the value of the diffusivity of iron oxide in the silicate ($D$), the density of the silicate ($\rho$), and the product layer thickness ($h$) were not known. It is believed, however, that the concentration of iron oxide at the interface is not the thermodynamic equilibrium value associated with the reaction at the silicate/metal interface:

$$
(SiO_2)_\text{silicate} + 2 Fe(\beta) = 2(FeO)_\text{silicate} + Si
$$

(23)

The above reaction takes place without the oxygen in the melt taking part. If the concentration, $C_{\text{FeO}}^I$, is the thermodynamic equilibrium value, then as equilibrium is approached (as the silicon content increases), the reaction rate should decrease due to the lowering of the iron oxide concentration, $C_{\text{FeO}}^I$. It is proposed that it is impossible for the preceding reaction to reach equilibrium in the presence of the refractory, connected by a slag layer to the melt. This condition arises because of the continuous removal of one of the reaction products, i.e. iron oxide, to a sink of acid refractory of infinite size.

Under steady-state conditions the rate of diffusion of iron oxide to the refractory/silicate interface must be equal to the rate of the chemical reaction at that interface. Under these conditions, the value of the concentration of iron oxide at the silicate/metal interface, $C_{\text{FeO}}^I$, is adjusted kinetically by the rates of diffusion and chemical reaction, and is independent of time. If any fluctuations in $C_{\text{FeO}}^I$ occur, the system will adjust the rates of diffusion and chemical reaction, and restore the concen-
tration of iron oxide to its original value.

6.1.7 Effect of Atmosphere on the Reaction of Silica and Alumino-Silicate Refractories in Armco Iron

As has been previously stated, deoxidation experiments with CO₂/CO mixtures of very low carbon dioxide contents resulted in no attack being measured or slag formed on the refractory surface. Similar results were obtained when the melt was deoxidized with silicon prior to immersion of the specimen. Both these cases illustrated the necessity of the presence of the slag phase in order to produce a measurable amount of attack of the specimens. Without the existence of the slag phase, an equilibrium reaction between the refractory and the melt will take place:

\[(\text{SiO}_2)_{\text{refractory}} + 2 \text{Fe} = (\text{FeO}) + \text{Si}\]  

or as more commonly written

\[(\text{SiO}_2)_{\text{refractory}} = \text{Si} + 2 \text{O}\]  

This equilibrium reaction proceeds at a very slow rate as shown in this and other work. This reaction takes place with the iron oxide going into solution in the melt, rather than forming a silicate slag, due to its low activity in the metal phase. As the concentration of oxygen in the melt increases, the conditions for silicate formation become more favourable. This was demonstrated experimentally by using CO₂/CO mixtures of 9.94 and 13.7% carbon dioxide. Under these conditions the atmosphere acted as a source of oxygen and the silicate was formed. In these runs the rates of attack measured were greater than runs in argon under the same conditions. This was due to the higher concentrations of iron oxide available for the initial reaction and the continuation of this reaction mechanism (Eq. 19) because of the steady supply of oxygen from the atmosphere. A parallel
reaction (Eq. 20) also takes place under these conditions.

6.1.7. Comparison of Rates of Attack of Refractories in Armco Iron

As can be seen from the phase diagram of the iron oxide-silica system (Figure 2), the addition of a small amount of iron oxide to a relatively pure silica refractory results in the formation of a significant amount of high silica liquid silicate. Such a liquid has a high viscosity which will decrease as the amount of iron oxide in the liquid silicate increases. The results of the static and dynamic runs in Armco iron with fused silica, 'Shelrock' silica, high silica brick, and fire-clay brick are summarized in Figures 28 and 29. The magnitude of the attack measured for each of the silica refractories, under the same experimental conditions, was the same. The similarity in the rates of attack of the various refractories despite the difference in their physical properties, reflects the nature of the rate-controlling step which has been proposed. Since the materials were composed of relatively pure silica (even the high silica brick contained > 96% silica), the physical properties of the liquid silicates formed should have been alike. In effect, the viscosities and densities of these liquids, and the diffusivities of iron and oxygen ions in these silicates should all be comparable, and therefore the rates of attack similar.

The attack of fire-clay brick in Armco iron was much greater than the attack of the silica refractories. This was due to the greater fluxing power of iron oxide (FeO) for the fire-clay brick, and in particular for the alumino-silicate based glassy phase which also contains Na₂O and K₂O. The quantity of liquid silicate formed on addition of a small amount of iron oxide to a fire clay brick is therefore considerably larger. The lowering of the viscosity will increase the diffusion rates through the product layer with a resultant increase in the rates of attack.

In the experiments with high purity alumina and magnesia specimens
in Armco iron, no attack was observed under any of the conditions investigated. This is due mainly to the ability of alumina and magnesia to absorb iron oxide in large quantities and still develop little or no liquid phase at steelmaking temperatures.

6.2 Rates of Attack of Silica and Alumino-Silicate Refractories in Carbon-Saturated Iron

6.2.1 Possible Reaction Mechanisms

In the absence of any slag formation, the refractory attack was most likely due to the reduction of silica by carbon dissolved in the melt, according to the stoichiometric equation:

\[
(SiO_2)_{\text{refractory}} + 2\, C = Si + 2\, CO(g)
\]  

The reaction as written requires the coexistence of three phases: solid, liquid, and gas. A three-phase reaction as suggested by the above equation can only take place at a three-phase interface, i.e., along a line, and therefore the equation does not represent the actual reaction mechanism which took place. However, this overall reaction can be broken down to a few elementary steps:

1. dissociation of silica at the refractory/metal interface to form silicon and oxygen in the melt as follows:

\[
SiO_2 (\text{refractory}) = Si + 2\, O
\]  

2. diffusion of silicon from the refractory/metal interface to the bulk metal
(3) diffusion of oxygen from the refractory/metal interface to a gas bubble/metal interface

(4) diffusion of carbon in the bulk metal to a gas bubble/metal and a refractory/metal interface

(5) reaction of carbon and oxygen at a gas bubble/metal interface to form carbon monoxide according to the reaction:

\[ C + O = CO(g) \]  \( \text{(28)} \)

Steps (1) and (5) are chemical reactions whereas steps (2), (3) and (4) are transport processes. Each of the steps must be examined in turn in order to determine which is the slow, rate-controlling step for the overall reaction. The negligible effect of rotation on the measured corrosion rate would tend to rule out all transport processes between the bulk metal phase and the solid refractory surface as the possible rate-controlling steps. This conclusion is supported by additional experimental evidence. It was found that the overall reaction rate was independent of the silicon concentration in the bulk metal for periods of time of up to five hours, thus supporting the elimination of step (2) as a rate-limiting step. Since the metal was maintained at a high carbon concentration by using a graphite crucible and there was sufficient turbulence in the system to avoid any significant concentration gradients of carbon, step (4) may be considered as non-limiting. The fact that experiments with melts containing 2.3% C produced similar reaction rates to those with carbon-saturated iron, is further evidence that carbon diffusion is not controlling.

It was also observed that reaction (28) took place at the refractory/metal interface with the surface of the refractory providing sites for the nucleation of the carbon monoxide bubbles. It is possible that this reaction is not rate controlling in view of the roughness of the interface and the
observations of Darken and Gurry\textsuperscript{100} to the effect that equilibrium is attained quite rapidly in this reaction once the gas bubble/metal interface has been established. Therefore step (5) may be eliminated as the possible rate-controlling step.

Step (1) remains as a possible rate-limiting step along with step (3) which has not been definitely eliminated. As discussed in section 2.9, extensive work has been done to study the overall reaction (26), and the opinions are sharply divided as to which of the aforementioned steps is rate-controlling. It is obvious from the literature that the controlling mechanism depends not only on the physical state of the system but also on the configuration of the apparatus and the experimental procedure.

6.2.2 Proposed Reaction Mechanism

In this investigation, the nucleation and growth of carbon monoxide bubbles was observed to take place at the surfaces of the refractory specimens. For the porous materials, there is gas in the small open pores so that nucleation of the gas phase was unnecessary. Due to the formation of the gas phase at the specimen surface, the diffusion of oxygen, which is available at the refractory/metal interface, to the gas/metal interface (step 3) would take place over a very short diffusion distance and, therefore, is not likely to be rate-controlling. If this is the rate-controlling step, a very strong dependence of the rate on the rotation of the specimens should have been observed.

The rate-controlling step is, therefore, most likely to be step (1) which is the dissociation of the silica at the refractory/metal interface according to the reaction:

\[
\text{SiO}_2 \text{ (refractory)} \xrightleftharpoons{\frac{k}{T}} \text{Si} + 2 \text{O}
\]  (29)
For this simple step it is certainly reasonable to apply the mass action law in terms of activities to obtain a kinetic expression. This expression can then be applied to the experimental data to give values of the kinetic parameters. This rate equation may be written as follows:

\[ n_{Si} = k_1 A a_{SiO_2} - k_2 A a_{Si}^2 a_{O} \]  

(30)

where

\[ \frac{d n_{Si}}{dt} \text{ moles silicon transferred to the melt per unit time} \]

\[ k_1 = \text{forward reaction rate constant (moles silicon/cm}^2/\text{hr.)} \]

\[ k_2 = \text{reverse reaction rate constant (moles silicon/cm}^2/\text{hr.)} \]

\[ A = \text{silica/metal interfacial area (cm}^2) \]

\[ a_{SiO_2} = \text{activity of silica at the silica/metal interface} \]

\[ a_{Si} = \text{activity of silicon in the metal phase at the silica/metal interface} \]

\[ a_{O} = \text{activity of oxygen in the metal phase at the silica/metal interface} \]

In all the experiments, the concentration of both oxygen and silicon in the melt was very low so that the reverse reaction is relatively insignificant. Therefore, the rate equation becomes:

\[ n_{Si} = k_1 A a_{SiO_2} \]  

(31)

In the present investigation, since pure silica or high silica refractories were used, the activity of silica can be taken as unity. Rewriting equation (31), the rate of transfer of silicon to the melt is given by:

\[ n_{Si} = A k_1 \quad \text{(or)} \quad \frac{n_{Si}}{A} = k_1 \]  

(32)
Integrating this equation with the area taken as a constant, the following expression is obtained:

\[
\frac{n_{\text{Si}}}{A} = k_1 t
\]  

(33)

6.2.3 Determination of Reaction Rates and Rate Constants

It was observed that the geometric area of each cylindrical specimen decreased during the course of the experiment. In the case of the long time runs, these area changes were as much as 15%. Despite this area change the weight losses measured and the silicon contents of the melts remained linear functions of time. This would be contradictory if the geometric area is the right quantity to convert the observed total change to the specific rate. Realizing that the external geometric area was not the area of the refractory/metal interface, microscopic examination of the specimen surfaces was carried out. Figures (45) and (46) show the surfaces of specimens of 'Shelrock' silica and silica brick which have been immersed in carbon-saturated melts for various lengths of time. As can be seen from these photographs, the surfaces of the specimens became rougher as the reaction proceeded. It would thus seem that while the geometric area of each specimen was decreasing with time, the actual refractory/metal interfacial area remained approximately constant due to the surface roughening of the specimen. Since measurement of the effective area of each specimen was not possible, a mean value of the initial and final geometric areas, \( \bar{A} \), was used as the value of 'A' in equation (33) in order to analyse the experimental data.

Using the mean value of the surface area for each run, the weight loss measured was expressed in terms of the weight loss per unit area, \( \Delta W/\bar{A} \) (gm/cm\(^2\)). The slopes of the weight loss per unit area vs time curves for the various refractories gave the rates of attack for those refractories in carbon-saturated iron. Since \( n_{\text{Si}} = n_{\text{SiO}_2} \), where \( n_{\text{SiO}_2} \)
is the number of moles of silica reduced, the rate equation (33) can be written:

\[
\frac{n_{\text{SiO}_2}}{A} = k_1 t \quad (34)
\]

In terms of the weight loss, the equation becomes:

\[
\frac{\Delta W}{A} = k t \quad (35)
\]

where \( k \) = rate constant (gms/cm\(^2\)/hr.)

For pure silica refractories these two rate constants, \( k_1 \) and \( k \), are related through the conservation of mass relationship:

\[
k = k_1 M_{\text{SiO}_2} \quad (36)
\]

where \( M_{\text{SiO}_2} \) is the molecular weight of silica. For impure silica brick it follows that \( k > k_1 M_{\text{SiO}_2} \). From a plot of \( \Delta W/A \) vs \( t \), the value of \( k \) can be obtained directly from the value of the slope and in the case of pure silica refractories the value of \( k_1 \) can also be obtained from the slope.

The rate constants were also obtained by measurement of the concentration change of silicon in the melt. The number of moles of silicon transferred per unit area was obtained from the measured silicon concentration as follows:

\[
\frac{n_{\text{Si}}}{A} = \frac{C_{\text{Si}} \times W}{100 \times M_{\text{Si}} \times \bar{A}} \quad (37)
\]

where \( C_{\text{Si}} \) = the concentration of silicon (analysed) in the melt (wt. %)

\( W \) = the weight of the melt

\( M_{\text{Si}} \) = the atomic weight of silicon
Once the concentration measurements were treated in this manner, the reaction rate constant, $k_1$, for each reaction was obtained directly from the slope of the $\frac{n_{Si}}{A}$ vs time plot.

6.2.4 Comparison of the Experimental Reaction Rates of the Various Refractories

In Table 29 the reaction rates for runs with 'Shelrock' silica and silica brick in carbon-saturated iron are listed. For the relatively pure 'Shelrock' silica the rate of attack expressed in gms/cm$^2$/hr. is equivalent to the rate of silicon transfer expressed in gm-moles/cm$^2$/hr. Values of the reaction rate constants, $k$ and $k_1$, for this material are also shown in Table 29. In the case of the runs with silica brick the two rates are not equivalent. This is evident, since the brick material has a silica content of approximately 96% and thus a portion of the attack, measured in terms of the weight change, was due to the loss of the other mineralogical components making up the brick. In Table 29, the values of the two rates are given together with the reaction rate constants $k$ and $k_1$, the latter being determined from the rate of silicon transfer.

Figure 43 shows the kinetic curves for the attack of 'Shelrock' silica, silica brick, and fire-clay brick in carbon-saturated iron. As can be seen from this figure and the results in Table 29, the attack of silica brick is much greater than the attack of 'Shelrock' silica. This behaviour was due to the composition and structure of the phases present in these refractory materials. The silica brick, as received, is a mixture of crystalline silica and a siliceous glassy matrix. During the reaction with carbon-saturated iron it was observed that the glassy matrix was preferentially attacked with the result that the matrix was attacked to a greater degree than the crystalline phase. This was due to the fact that the glassy phase was "liquid" at the reaction temperatures. The 'Shelrock' silica, on the other hand, is composed entirely of a crystalline phase which accounts for the lower rate of attack. This type of behaviour was observed by
Wojcieć (84) in the reactions between quartz and pyrex tubes with carbon-saturated iron. He found that the rate of attack of the pyrex tubes was much greater than the attack of the quartz tubes. This is consistent with the results of the present investigation.

The attack of fire-clay brick was not a linear function of time and decreased with time as can be seen in Figure 43. Some insight into this behaviour can be obtained from a knowledge of both the unreacted and reacted structures of the fire-clay brick. The brick, as received, is composed of a mixture of alumina, mullite, cristobalite, and a siliceous glassy phase. In view of the behaviour of the silica brick in carbon-saturated iron, it is reasonable to assume that during the reaction the silica of the glassy phase was reduced first. Subsequently the cristobalite and the silica from the mullite phase were also reduced leaving a portion of the brick which was composed almost entirely of alumina. Microprobe analysis of a reacted fire-clay brick specimen (Figure 41) showed that the portion of the brick near the surface was almost entirely alumina. Maas and Abratis (90) studied the reaction of fire-clay bricks with iron-carbon melts (0.5 to 2.0% C) at temperatures from 1500 to 1650°C by measuring the change in silicon concentration of the melt as a function of time. They also observed the formation of the alumina layer at the surface of each of their specimens. Due to the non-linearity of their kinetic curves they eliminated a chemical control mechanism and suggested that the reaction was diffusion-controlled with the diffusion of silicon monoxide and carbon dioxide (formed as intermediate compounds) in the pores of the alumina layer, the rate-controlling step. Though similar kinetic behaviour was observed in the present study, the possibility that the attack by carbon-saturated iron was chemical reaction-controlled rather than diffusion-controlled has not been rejected. It is believed that the rate of attack initially was controlled by the chemical reaction as was shown to be the case with the other refractories tested. However, as the surface layer of the brick became depleted of silica, other factors could have played an important role in the observed behaviour. Due to the loss of silica, the
effective silica/metal surface area decreased with time and could have accounted in part, for the observed decrease in the rate of attack. Since alumina is wetted less by carbon-saturated iron than silica, the alumina skeleton in the surface layer could have inhibited metal phase penetration of the specimen preventing reaction at unreacted areas of brick in the specimen interior. This effect could also have caused the rate to decrease with increasing time as was observed. The decrease in the rate with time, as a result of the possible separation of liquid metal and silica by carbon monoxide gas in the porous alumina layer, is certainly consistent with the fact that the rate was independent of the rotation speed of the specimen.

6.2.5 The Effect of Temperature on the Reaction Rates

Experimentally it was observed that the rates of attack were strongly dependent upon the temperature. The rate constant, \( k_1 \), may be expressed in the form of the Arrhenius equation as follows:

\[
  k_1 = B \exp\left(-\frac{Q}{RT}\right)
\]  

(38)

where \( Q \) = the activation energy (cal/mole)
\( R \) = the universal gas constant and is equal to 1.987 cal/mole/°K
\( B \) = a constant for the particular system.

For the runs with 'Shelrock' silica at 1400 and 1500°C, values of the rate constant '\( k \) were used to calculate values of \( k_1 \) using equation 36, because of the uncertainty in the silicon analysis at the low silicon levels encountered. A plot of \( \ln k_1 \) vs \( 1/T \) is shown in Figure 47.

The value of the apparent activation energy was determined from the slope of this line and was found to be 102 ± 16 Kcal. Although the activation energy of the reactions in the runs with silica brick was not obtained, it was observed that the attack of this material was also strongly dependent on temperature.
6.2.6 The Formation of Silicon Monoxide

In various studies the formation of silicon monoxide has been suggested as a side reaction occurring during the reduction of silica by carbon-saturated iron. In the present work, there was no evidence to indicate that the formation of silicon monoxide had taken place. A mass balance between the analysed silicon concentrations and the weight loss measurements showed that the contribution of the side reaction forming silicon monoxide to the overall measured attack was negligible (Figure 48).

Grimble (82), Aurini (95), and Turkdogan et al (81) used graphite crucibles to contain silica saturated slags and carbon-saturated iron alloys. In their systems, the slag was in contact with carbon in the melt and the crucible wall. In both these cases the carbon had unit activity. In Turkdogan et al's experiments, pure carbon monoxide, having a very high carbon activity, was impinged directly on the slag/metal interface. The difference in properties of the various interfaces present in these systems would favour different types of reactions. The liquid metal, for instance, can act as a solvent for the products resulting from an interfacial chemical reaction whereas solid graphite cannot. The possible reduction of silica to its lower oxidation states (silicon monoxide and silicon) must be considered at each interface. At the gas/slagger and graphite/slagger interfaces, silica can not be reduced to silicon because the lack of solvent available locally would set the silicon activity equal to unity, which makes this reaction thermodynamically impossible. However, silicon monoxide can be formed as observed by a few authors (82, 95, 81). At the slag/metal interface, silica can be reduced to both silicon and silicon monoxide. However, it is known that when the metal has a high carbon and low silicon content, silicon monoxide will be reduced by carbon to form silicon and carbon monoxide (103).

It is obvious from the preceding discussion that conditions in the system used in this work were not favourable for the formation of silicon monoxide. This was confirmed by the experimental results.
6.3 The Physical Erosion of Refractories in Iron and Carbon-Saturated Iron Melts

The possibility exists that part of the attack measured was due to the physical removal of solid portions of the refractory by the liquid metal. Such attack is classified as erosion and is most likely in dynamic systems because of the associated shearing forces. When only erosion takes place in a metal/refractory system, the attack should be independent of the chemical state of the phases involved; for example, the concentration of the melt or the composition of the gas phase. In the runs with silica and fire-clay refractories in both Armco iron and carbon-saturated iron, it was found that the rate of attack depended strongly on the chemical state of the system. Even in systems in which chemical corrosion of the refractories was non-existent, no evidence of pure erosion of the refractories was found; for example, the runs with alumina and porous magnesia specimens in Armco iron.

Erosion processes can be facilitated by the chemical corrosion of the refractory bond. Metallographic examination of refractory surfaces reacted with Armco iron (Figures 49 and 50) showed that they were relatively smooth and free of sharp fracture surfaces which are a feature of a physical erosion process. In these runs the formation of the silicate product layer may have protected the specimens from erosion by the liquid metal. Similarly, no evidence of erosion was apparent in the runs with carbon-saturated iron. In particular, the surfaces of silica and fire-clay brick specimens (Figures 45 and 46) showed no signs of erosion despite considerable chemical corrosion of the glassy bond in each brick.
CHAPTER 7

CONCLUSIONS

In the investigation of the corrosion of silica and alumino-
silicate refractories in Armco iron it was found that:

1. The initial rate of corrosion was controlled by chemical reaction
   rather than by diffusion. The reaction was between iron, oxygen
dissolved in the iron, and the silica of the refractory. The reaction
was found to be strongly dependent on the oxygen concentration
of the melt.

2. After the initial reaction period, the rate became diffusion-controlled
giving rise to a constant corrosion rate. This rate was found
to be a linear function of the peripheral velocity of the refractory
specimen.

3. In the steady-state corrosion process the rate-controlling step was
determined to be the diffusion of iron and oxygen ions from the
silicate/metal interface to the refractory/silicate interface.

4. The steady-state rate of corrosion was found to be independent of
the oxygen content of the melt and was sustained by the reduc-
tion of silica in the slag by the iron melt and the subsequent
reaction of the iron oxide formed with the refractory.

5. The rates of corrosion of the silica refractories were similar in
magnitude whereas the corrosion of the fire-clay refractories
took place at a much faster rate.

6. Pure alumina and magnesia refractories were not corroded by the
Armco iron melt.
A study of the corrosion of silica and alumino-silicate refractories in carbon-saturated iron melts showed that:

1. The corrosion of silica and alumino-silicate refractories was due to the reduction of silica by carbon in the melt.

2. The rate of corrosion of the refractories was independent of the silicon concentration in the melt and the carbon concentration, in the range 2.3%C to saturation. The rate was also independent of the rotation of the specimens.

3. The reaction rate was strongly dependent on the temperature of the system and as expected increased with increasing temperature. The activation energy for the reaction of 'Shelrock' silica with carbon-saturated iron was found to be approximately 102 Kcal/mol.

4. The silica refractories exhibited linear reaction kinetics while the kinetics for the alumino-silicate refractories were non-linear due to the formation of an alumina layer in the refractory.

5. Contrary to previous studies, no evidence was found for the side reaction producing silicon monoxide.

6. In both the runs with carbon-saturated iron and Armco iron, the attack is entirely attributed to chemical corrosion with a negligible contribution from pure physical erosion.
APPENDIX I

THE OXYGEN PROBE

In order to measure the partial pressure of oxygen in the reaction atmosphere, $P_{O_2}$, an oxygen probe was used. The probe was the same type used in the work of Kontopoulos \(^\text{(102)}\) and Vahed \(^\text{(103)}\), and had a stabilized zirconia electrolyte and a Cr$_2$O$_3$ mixture as a reference electrode. The cell was made up as follows:

$$Pt/\text{Cr-Cr}_2\text{O}_3/\text{Lime-Stabilized Zirconia}/\text{Reaction Atmosphere}/Pt$$  

($P_{O_2}$)

The zirconia electrolytes, 3 mm diameter x 6 mm in length, were supplied presealed into 1" long x 6 mm O.D. vycor tubes. Each vycor tube was extended to a 24" length with a silica tube of the same diameter. The tube was then packed with a powdered mixture of Cr/Cr$_2$O$_3$ (90/10 by weight). Contact was made with a Pt wire and the tube was sealed under vacuum.

The value of $P_{O_2}$ in the Reaction Atmosphere:

The free energy change for the cell reaction,

$$O_2 + \frac{4}{3} \text{Cr} = \frac{2}{3} \text{Cr}_2\text{O}_3$$  

(39)

is expressed by:

$$\Delta G_{\text{cell}} = \Delta G_{\text{cell}}^0 + RT \ln K_{\text{cell}}$$  

(40)

or

$$\Delta G_{\text{cell}} = \Delta G_{\text{cell}}^0 - 4.575 T \log P_{O_2}$$  

(41)

The free energy change for the cell reaction, $\Delta G_{\text{cell}}^0$, is given by,

$$\Delta G_{\text{cell}} = -n E F$$  

(42)
where \( n = \) number of electrons involved in the electrode reactions
\[ E = \text{measured emf (volts)} \]
\[ F = \text{Faraday's Constant (23,066 cal/volt-equivalent)} \]

It therefore follows that:

\[ \log P_{O_2} = \frac{nEF}{4.575T} + \frac{\Delta G^o_{\text{cell}}}{4.575T} \] (43)

In the runs using \( CO_2/CO \) mixtures the values of the partial pressure of oxygen \( (P_{O_2}) \), which were measured with the probe, were found to be consistent with the values calculated from the equilibrium expression:

\[ CO(g) + \frac{1}{2} O_2(g) = CO_2(g) \quad \Delta G^o = -66,630 + 20.22T^{(104)} \] (44)

Examples of the results obtained with the probe compared with the calculated value of \( P_{O_2} \) are shown below:

13.7% \( CO_2/\)Balance \( CO \) mixture
E. M. F. measured = .345 volts
measured \( P_{O_2} = 4.03 \times 10^{-9} \) atm

Temperature 1600\(^\circ\)C

9.94% \( CO_2/\)Balance \( CO \) mixture
E. M. F. measured = .322 volts
measured \( P_{O_2} = 2.15 \times 10^{-9} \) atm.

Temperature 1600\(^\circ\)C

...
APPENDIX 2

MEASUREMENT OF DIAMETER CHANGES AND WEIGHT LOSSES

All measurements of specimen diameters were made using a micrometer with an accuracy of ± .0010 cm. Specimen diameters were measured in two ways. First, positions were marked on the specimen 1/4", 1/2", and 3/4" from the bottom of the specimen. At each of these heights, the average of thirty diameter measurements was determined. The other method of diameter measurement consisted of taking the average of one hundred diameters over a fixed length of refractory. Diameter measurements before and after the experiments were made using these two methods.

Each specimen was weighed before and after each run using a Sauter microbalance with an accuracy of ± .0005 gm. The surfaces of the specimens reacted with Armco iron were usually free of any metal. However, in the runs with carbon-saturated iron a small amount of metal was occasionally found to adhere to the specimen. In each of these runs, the metal did not adhere strongly to the specimen and could be removed by gentle brushing.

In the runs with fire-clay brick in Armco iron, special methods had to be used to measure weight losses and diameter changes, due to the large quantity of slag which adhered to each specimen. A major portion of this slag solidified at the melt line. In order to measure weight losses two methods were used. In the first method, a diamond saw was used to cut off the specimen below the melt line. This portion of the specimen was then weighed and the length determined with a set of calipers. Knowing the original bulk density of the fire-clay brick, an estimate of the weight of an equal length of unreacted brick was made, from which the weight loss for the experiment was determined.
In the second method the same cut-off portion of refractory was used as in the first method. The specimen was cut once again into 1/4" cross-sections. The sections were then mounted and photographed. The area of each cross-section was then measured from the photographs with a planimeter. Knowing this area and the length of the reacted portion of the refractory, an estimate of the volume of the reacted portion of the refractory was made. Having measured the diameter of the specimen prior to the experiment, the unreacted volume of the length of refractory was also determined. The volume change due to the reaction was obtained and using the bulk density of the unreacted refractory an estimate of the weight loss during the reaction was made.
APPENDIX 3

THE LEAST SQUARES LINE AND EXPERIMENTAL ERRORS

The method\(^{(105)}\) of fitting a set of N points \((X_1, Y_1), (X_2, Y_2), \ldots, (X_N, Y_N)\) to a line of the form:

\[ Y_e = a + bX \]

in such a way that \[\Sigma(Y - Y_e)^2\] is a minimum, is called the method of least squares where:

- \(Y_e\) = the value of \(Y_e\) obtained from the line
- \(Y\) = actual measured value of \(Y\)
- \(a\) = intercept of the line at \(X = 0\)
- \(b\) = slope of the line

The constants \(a\) and \(b\) are obtained by solution of the equations:

\[ \Sigma Y = aN + bX \]
\[ \Sigma XY = a\Sigma X + b\Sigma X^2 \]

to give:

\[ a = \frac{(\Sigma Y)(\Sigma X^2) - (\Sigma X)(\Sigma XY)}{N\Sigma X^2 - (\Sigma X)^2} \]
\[ b = \frac{N\Sigma XY - (\Sigma X)(\Sigma Y)}{N\Sigma X^2 - (\Sigma X)^2} \]

The line obtained in this manner is called the line of regression of \(Y\) on \(X\).

The scatter in the vertical \((Y)\) direction of the observed points about the regression line is measured by the standard error of estimate.
$S_{YX}$ and is given by:

$$S_{YX} = \sqrt{\frac{\sum (Y - Y_e)^2}{N-2}} = \sqrt{\frac{\Sigma Y^2 - a \Sigma Y - b \Sigma XY}{N-2}}$$

The standard error in the slope, $b$, can be estimated for the sample by:

$$S_b = \frac{S_{YX}}{S_X \sqrt{N-2}}$$

where:

$$S_X = \sqrt{\frac{\sum (X - X)^2}{N}}$$

The 95% confidence interval for the slope, $b$, is:

$$b \pm t_{0.975,N-2} S_b$$

**Experimental Errors**

**Systematic Errors**

The error associated with the rate of attack of a refractory in a melt was obtained by estimating the errors associated with the measured parameters.

The rate of attack of a fused silica specimen in Armco iron is given by:

$$\text{rate} = \frac{d(\Delta W/\Delta)}{dt} \quad (1)$$
\[ \approx \frac{\Delta W/A}{\Delta t} \quad \text{(ii)} \]

where \( \Delta W \) is the weight change in the time interval \( \Delta t \) and \( A \) is the average surface area. The relative error in the rate is then given by the sum of the relative errors in \( \Delta W \), \( A \) and \( \Delta t \).

The systematic errors in \( \Delta W \), \( A \) and \( \Delta t \) were estimated for a typical experimental run (e.g., fused silica rod in Armco iron with rotation for one hour). These estimates were found to be:

\[
\begin{align*}
\Delta W &= 0.2106 \text{ (gms)} \pm 0.25\% \\
A &= 15.71 \text{ (cm}^2\text{)} \pm 1.50\% \\
\Delta t &= 1 \text{ (hr.)} \pm 0.25\%
\end{align*}
\]

Thus the total (\%) error in the rate is given by:

\[
\text{error in rate} = (\text{error in } \Delta W) + (\text{error in } A) + (\text{error in } \Delta t)
\]

\[
= \pm 0.25\% + 1.50\% + 0.25\% \\
= \pm 2.0\%
\]

For the same experimental run the least squares analysis gave a standard deviation of \( 1.9 \times 10^{-4} \) and a rate of \( 11.19 \times 10^{-3} \text{ (gm/cm}^2\text{-hr)} \). A reasonable estimate of the relative probable error in the rate is given by:

\[
\text{relative error} = \frac{2 \times \text{standard deviation}}{\text{value of rate}} \times 100\%
\]

\[
= \frac{2 \times 1.9 \times 10^{-4}}{11.19 \times 10^{-3}} \times 100\% \\
= 4\%
\]
Thus we see that the systematic error is less than the relative inherent error as estimated above, so that the calculated bounds on the rates (as given in the experimental section) provide a sufficient estimate of the experimental errors.
APPENDIX 4

SILICON AND OXYGEN ANALYSES

In the runs carried out in Armco iron, it was found that the silicon
and oxygen analyses of the melts were not reproducible. Quite a large
variation existed between analyses of the metal taken from the same
suction sample. No explanation for this behaviour was found. To
illustrate this discrepancy in the analytical results, the analyses of the
melts of runs with fused silica in Armco iron are summarised in the
following table.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Length of Run</th>
<th>Rotation Speed (r.p.m.)</th>
<th>Average Peripheral Velocity (cm/sec)</th>
<th>Silicon Analyses (wt.%</th>
<th>Oxygen Analyses (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>1 hr.</td>
<td>40</td>
<td>2.61</td>
<td>.005, .010, .005</td>
<td>.038, .045, .055</td>
</tr>
<tr>
<td>26</td>
<td>1 hr.</td>
<td>110</td>
<td>7.13</td>
<td>.010, .014, .005</td>
<td>.054, .045, .030</td>
</tr>
<tr>
<td>40</td>
<td>1 hr.</td>
<td>190</td>
<td>12.43</td>
<td>.010, .020, .010</td>
<td>.041, .025, .047</td>
</tr>
<tr>
<td>22</td>
<td>1 hr.</td>
<td>197</td>
<td>12.87</td>
<td>.020, .005, .015</td>
<td>.027, .040, .021</td>
</tr>
<tr>
<td>6</td>
<td>1 hr.</td>
<td>225</td>
<td>14.36</td>
<td>.013, .014, .024</td>
<td>.024, .027, .021</td>
</tr>
<tr>
<td>138</td>
<td>1 hr.</td>
<td>270</td>
<td>17.21</td>
<td>.012, .017, .022</td>
<td>.020, .010, .025</td>
</tr>
<tr>
<td>12</td>
<td>1 hr.</td>
<td>300</td>
<td>19.38</td>
<td>.014, .021, .025</td>
<td>.017, .006, .010</td>
</tr>
<tr>
<td>20</td>
<td>1 hr.</td>
<td>315</td>
<td>20.68</td>
<td>.009, .019, .024</td>
<td>.024, .011, .021</td>
</tr>
<tr>
<td>24</td>
<td>1 hr.</td>
<td>358</td>
<td>21.35</td>
<td>.012, .024, .032</td>
<td>.012, .017, .025</td>
</tr>
<tr>
<td>14</td>
<td>1 hr.</td>
<td>360</td>
<td>23.72</td>
<td>.020, .028, .029</td>
<td>.031, .011, .019</td>
</tr>
<tr>
<td>10</td>
<td>1 hr.</td>
<td>400</td>
<td>25.47</td>
<td>.037, .010, .025</td>
<td>.010, .024, .015</td>
</tr>
<tr>
<td>15</td>
<td>1 hr.</td>
<td>450</td>
<td>26.75</td>
<td>.045, .029, .037</td>
<td>.005, .015, .021</td>
</tr>
<tr>
<td>25</td>
<td>1 hr.</td>
<td>465</td>
<td>27.96</td>
<td>.035, .024, .042</td>
<td>.009, .019, .025</td>
</tr>
<tr>
<td>9</td>
<td>1 hr.</td>
<td>550</td>
<td>35.02</td>
<td>.046, .047, .039</td>
<td>.017, .014, .019</td>
</tr>
</tbody>
</table>
APPENDIX 5

THERMODYNAMICS OF REFRACTORY/METAL REACTIONS

In an iron melt, in which oxygen is the major impurity, the reaction between the melt and a silica refractory can be represented by the following equation:

\[ \text{SiO}_2(s) + 2\text{Fe}(l) + 20\% (1 \text{ wt. } \%) = 2\text{FeO} \cdot \text{SiO}_2(l) \]  

(45)

This reaction can be written as consisting of the two reactions:

\[ 2\text{Fe}(l) + 20\% (1 \text{ wt. } \%) = 2\text{FeO}(l) \quad \Delta G^o_{46} = -57,800 + 25.02 \text{ Tcal/mol*} \]  

(46)

\[ \text{SiO}_2(s) + 2\text{FeO}(l) = 2\text{FeO} \cdot \text{SiO}_2(l) \quad \Delta G^o_{47} = 3450 - 4.58 \text{ Tcal/mol} \]  

(47)

It follows that:

\[ \Delta G^o_{45} = \Delta G^o_{46} + \Delta G^o_{47} = -54,350 + 20.44\text{Tcal/mol} \]  

(48)

The equilibrium constant for reaction (45) can be written as:

---

* All thermodynamic data used is that given by Elliott, Gleiser and Ramakrishna.
\[ \log K_{45} = \log \frac{a_{2FeO, SiO_2}}{a_{SiO_2} a_{Fe(h_0)}^2} = \frac{11.880}{T} - 4.47 \]  

(49)

In Figure 51, the relationship between % Si and % O for the Fe-O-Si system is shown. At very low silicon and correspondingly high oxygen concentrations the formation of a liquid silicate will take place according to equation (45). At 1600°C, the formation of this slag phase takes place at approximately 0.005% Si and 0.080% O. Under the conditions of this investigation, the silicon and oxygen contents of the Armco iron were 0.005% and 0.078% respectively and were such that the formation of the liquid silicate was favoured.

At lower oxygen and higher silicon concentrations, the formation of the silicate phase is not expected. Under these conditions the following reaction takes place:

\[ \text{SiO}_2(s) = \frac{Si}{(1 \text{wt. %})} + \frac{2O}{(1 \text{wt. %})} \]  

(50)

\[ \Delta G^0_{50} = 142,000 - 55.0 \ T \text{ cal/mol} \]  

(51)

\[ \log K_{50} = \log \frac{(h_{Si}) (h_{O})^2}{a_{SiO_2}^2} = \log \frac{a_{Si} (a_{O})^2}{a_{SiO_2}} = \frac{-31.005}{T} + 12.1 \]  

(52)

Assuming that \( a_{SiO_2} = 1 \) and the product \( a_{Si} \times a_O^2 \) is approximately unity, equation (52) becomes:

\[ \log K_{50} = (\% \text{ Si})(\% \text{ O})^2 = -\frac{31.005}{T} + 12.1 \]  

(53)
This equation is valid except at high oxygen and low silicon concentrations, under which conditions a silicate slag is formed. The addition of silicon to the Armco iron melt prior to the introduction of the refractory resulted in the deoxidation of the melt to an oxygen well below that needed for the formation of the silicate. In these experiments no silicate was formed and reaction (50) took place. This reaction was observed to proceed at a very slow rate.

In many industrial processes, reactions take place between the melt, refractory, and the atmosphere. This reaction can be written as:

$$\text{SiO}_2(s) + 2\text{Fe}(l) + \text{O}_2(g) = 2\text{FeO}.\text{SiO}_2(1)$$  \hspace{1cm} (54)

This reaction can be written as consisting of three reactions:

$$\text{O}_2(g) = 2\text{O}(1 \text{ wt. \%}) \quad \Delta G^0_{56} = -56,000 - 1.38T \text{ cal/mol}$$  \hspace{1cm} (55)

$$2\text{Fe}(1) + 2\text{O}(1 \text{ wt. \%}) = 2\text{FeO}(1) \quad \Delta G^0_{56} = -57,800 + 25.02T \text{ cal/mol}$$  \hspace{1cm} (56)

$$2\text{FeO}(1) + \text{SiO}_2(s) = 2\text{FeO}.\text{SiO}_2(1) \quad \Delta G^0_{57} = 3450 - 4.58T \text{ cal/mol}$$  \hspace{1cm} (57)

$$\Delta G^0_{54} = \Delta G^0_{55} + \Delta G^0_{56} + \Delta G^0_{57} = -110,350 + 19.06T \text{ cal/mol}$$  \hspace{1cm} (58)

$$\log K_{54} = \log \frac{a_{2\text{FeO}.\text{SiO}_2}}{(a_{\text{SiO}_2})^2(a_{\text{Fe}})^2(P_{\text{O}_2})^2} = \frac{24,120}{T} - 4.17$$  \hspace{1cm} (59)

If it is assumed that $a_{2\text{FeO}.\text{SiO}_2} = a_{\text{SiO}_2} = a_{\text{Fe}} = 1$, it follows from equation (59) that at $1600^\circ\text{C}$, $P_{\text{O}_2} = 1.95 \times 10^{-9}$ atm. Figure 52 shows the stability of the phases for the iron-silica system at various oxidation levels. At $1600^\circ\text{C}$ under oxidising conditions the stable phases are liquid silicate, silica, and
Figure 52. Iron Oxide-Silica Phases vs. Oxidation Level.
molten iron. This was demonstrated by the experiments using controlled CO₂/CO gas atmospheres. With the 9.94% and 13.7% CO₂ mixtures with measured oxygen partial pressures of 2.31 x 10⁻⁹ atm and 4.03 x 10⁻⁹ atm respectively, the formation of the silicate was thermodynamically favoured and was observed to take place. Under highly reducing conditions the liquid silicate is not formed and the stable phases are silica and iron. This was shown to be the case in the experiments using a 0.52% CO₂/balance CO gas mixture for which the partial pressure of oxygen was found to be 1.78 x 10⁻¹³ atm.

**Reactions in Carbon-Saturated Iron**

The reaction between a silica refractory and carbon-saturated iron can be written as:

\[
\text{SiO}_2(s) + 2\text{C} \text{(graphite)} = \frac{\text{Si}}{(1 \text{ wt. %})} + 2\text{CO}_2(g)
\]

(60)

This reaction can be written as consisting of the following reactions:

\[
\text{SiO}_2(s) = \text{Si}_1 + \text{O}_2(g) \quad \Delta G_{61}^0 = 226,500 - 47.50T \text{ cal/mol}
\]

(61)

\[
2\text{C} \text{(graphite)} + \text{O}_2(g) = 2\text{CO}_2(g) \quad \Delta G_{62}^0 = -56,400 - 40.32T \text{ cal/mol}
\]

(62)

\[
\frac{\text{Si}}{(1 \text{ wt. %})} = \frac{\text{Si}}{(1 \text{ wt. %})} \quad \Delta G_{63}^0 = -28,500 + 4.09 T \text{ cal/mol}
\]

(63)

\[
\Delta G_{60}^0 = \Delta G_{61}^0 + \Delta G_{62}^0 + \Delta G_{63}^0 = 141,600 - 93.91T \text{ cal/mol}
\]

(64)

\[
\log K_{60} = \log \frac{(h_{\text{Si}})(P_{\text{CO}})^2}{(a_{\text{SiO}_2})(a_{\text{C}})^2} = -30.950 + 20.52
\]

(65)
Assuming that \( \frac{a_{\text{SiO}_2}}{a_{\text{C}}} = 1 \) and \( P_{\text{CO}} = 1 \) atm, the equilibrium silicon concentration at 1600°C is found to be approximately 6% Si. In the experiments carried out with carbon-saturated iron, the silicon contents of the melts were well below this equilibrium value and therefore the reaction rates measured in these experiments were independent of the silicon concentration of the melts.

In a number of studies, the formation of silicon monoxide, \( \text{SiO} \), has been suggested as a side reaction occurring during the reduction of silica by carbon-saturated iron.

\[
\text{SiO}_2(a) + C(\text{graphite}) = \text{SiO}(g) + \text{CO}(g)
\]  

(66)

This reaction can be written as consisting of the reactions:

\[
\text{SiO}_2(a) = \text{Si}(l) + \text{O}_2(g) \quad \Delta G^0_{67} = 226,500 - 47.50T \text{ cal/mol}
\]  

(67)

\[
\text{Si}(l) + \frac{1}{2} \text{O}_2(g) = \text{SiO}(g) \quad \Delta G^0_{68} = -36,000 - 11.70T \text{ cal/mol}
\]  

(68)

\[
C(\text{graphite}) + \frac{1}{2} \text{O}_2(g) = \text{CO}(g) \quad \Delta G^0_{69} = -28,200 - 20.16T \text{ cal/mol}
\]  

(69)

\[
\Delta G^0_{66} = \Delta G^0_{67} + \Delta G^0_{68} + \Delta G^0_{69} = 162,300 - 79.36T \text{ cal/mol}
\]  

(70)

\[
\log K_{66} = \log \left( \frac{P_{\text{SiO}}(P_{\text{CO}})}{a_{\text{SiO}_2}a_{\text{C}}} \right) = \frac{-35,475}{T} + 17.35
\]  

(71)

Assuming that \( a_{\text{SiO}_2} = a_{\text{C}} = 1 \) and \( P_{\text{CO}} = 1 \) atm, it follows that at 1600°C, \( P_{\text{SiO}} = 2.57 \times 10^{-3} \) atm and therefore it is expected that SiO may form to a small extent only. In the present investigation, no evidence was found to indicate that the formation of SiO had taken place and had contributed to the measured refractory attack.
REFERENCES


FIGURE 12: STATIC EXPERIMENTS WITH FUSED SILICA IN ARMCO IRON AT 1600°C.
FIGURE 13. EXPERIMENTS AT CONSTANT ROTATION SPEEDS WITH FUSED SILICA IN ARMCO IRON AT 1600°C.
Figure 14. Dynamic experiments with fused silica in ARMCO iron at 1600°C. for 1 hour.
FIGURE 15. FUSED SILICA SPECIMENS: (A) AS RECEIVED,
(B) HEATED AT 1600 °C. FOR 1 HOUR, (C) 1 HOUR ROTATION
RUN IN ARMCO IRON AT 225 R.P.M.
FIGURE 16. STATIC EXPERIMENTS WITH 'SHELROCK' SILICA IN ARMCO IRON AT 1600 °C.
FIGURE 17. EXPERIMENTS AT CONSTANT ROTATION SPEEDS WITH 'SHELROCK' SILICA IN ARMCO IRON AT 1600°C.
FIGURE 18. DYNAMIC EXPERIMENTS WITH 'SHELROCK' SILICA IN ARMCO IRON AT 1600°C FOR 1 HOUR.
FIGURE 19. 'SHELROCK' SILICA SPECIMENS: (A) AS RECEIVED.

(B) 1 HOUR ROTATION RUN IN ARMCO IRON AT 265 R.P.M.
FIGURE 20. STATIC EXPERIMENTS WITH HIGH SILICA BRICK
IN ARMCO IRON AT 1600 °C.
Figure 21. Experiments at constant rotation speeds with high silica brick in Armco iron at 1600°C.
FIGURE 22. DYNAMIC EXPERIMENTS WITH HIGH SILICA BRICK IN ARMCO IRON AT 1600°C FOR ONE HOUR.
FIG. 23. Silica Brick Specimens: (A) As received; (B) 1 hr. rotation run in Armco iron; (C) 1 hr. static run in carbon-saturated iron.
FIG. 24. FIRE-CLAY BRICK (a) unreacted specimen, (b) cylindrical specimen rotated in Armco iron, (c) rectangular specimen rotated in Armco iron.
FIGURE 25. STATIC EXPERIMENTS WITH FIRE-CLAY BRICK IN ARMCO IRON AT 1600°C.
FIGURE 26. EXPERIMENTS AT CONSTANT ROTATION SPEED WITH
FIRE-CLAY BRICK IN ARMCO IRON AT 1600°C.
FIGURE 27. DYNAMIC EXPERIMENTS WITH FIRE-CLAY BRICK IN ARMCO IRON AT 1600 °C. FOR 1 HOUR.

- METHOD 1.
- METHOD 2.
- EXPERIMENTAL RATES.
- CORRECTED FOR INITIAL REACTION.
FIGURE 28. STATIC EXPERIMENTS IN ARMCO IRON AT 1600 °C.

(1) HIGH SILICA BRICK
(2) FUSED SILICA
(3) 'SHELROCK' SILICA
(4) FIRE-CLAY BRICK
Figure 29. Dynamic experiments in Armco iron at 1600 °C.

(1) FUSED SILICA
(2) 'SHELROCK' SILICA
(3) HIGH SILICA BRICK
(4) FIRE-CLAY BRICK

WEIGHT LOSS/UNIT SURFACE AREA/HOUR (g/m²/hr x 10²)

PERIPHERAL VELOCITY (cm/sec)
FIGURE 30: WEIGHT LOSS vs TIME FOR STATIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON-SATURATED IRON AT 1600°C.
FIGURE 31. WEIGHT LOSS / UNIT SURFACE AREA vs TIME FOR STATIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON-SATURATED IRON AT 1600°C.
Figure 32. Silicon content vs time for static experiments with 'Shelrock' silica in carbon-saturated iron at 1600°C.
FIGURE 33. MOLES SILICON TRANSFERRED/UNIT SURFACE AREA vs TIME FOR STATIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON-SATURATED IRON AT 1600 °C.
FIGURE 34. DYNAMIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON-SATURATED IRON AT 1600°C.
FIGURE 35. STATIC AND DYNAMIC EXPERIMENTS WITH 'SHELROCK'
SILICA IN CARBON-SATURATED IRON AT 1600 °C.
FIG. 36. Shelleck Silica Specimens: (A) As received; (B) 1 hr. static run in carbon-saturated iron; (C) 3 hr. static run in carbon-saturated iron.
FIGURE 37. STATIC EXPERIMENTS WITH 'SHELROCK' SILICA IN CARBON SATURATED IRON AT 1400, 1500, 1600 °C.
FIGURE 38. STATIC AND DYNAMIC EXPERIMENTS WITH HIGH SILICA BRICK IN CARBON–SATURATED IRON AT 1600 °C.
FIGURE 39. STATIC AND DYNAMIC EXPERIMENTS WITH HIGH SILICA BRICK IN CARBON-SATURATED IRON AT 1600°C.
FIGURE 40: STATIC AND DYNAMIC EXPERIMENTS FOR FIRE-CLAY BRICK IN CARBON SATURATED IRON AT 1600 °C.
FIGURE 41. MICRO-PROBE TRACES FOR FIRE-CLAY BRICK.

(a) AS RECEIVED SPECIMEN. (b) ROD IN CARBON-SATURATED IRON.
FIG. 42. FIRE-CLAY BRICK (a) unreacted specimen, (b) 3 hr. static run in carbon-saturated iron, (c) 3 hr. rotation run in carbon-saturated iron.
(1) HIGH SILICA BRICK
(2) 'SHELROCK' SILICA
(3) FIRE-CLAY BRICK

Figure 43. Static and dynamic experiments with 'shelrock' silica, high silica brick, and fire-clay brick in carbon-saturated iron at 1600 °C.
FIGURE 44. MICRO-PROBE TRACES ACROSS SILICATE LAYERS.
(a) FIRE-CLAY BRICK IN ARMCO IRON (b) HIGH SILICA BRICK IN ARMCO.
(a) AS RECEIVED
(b) 6 MINUTE ROTATION RUN
(c) 1 HOUR ROTATION RUN
(d) 3 HOUR ROTATION RUN

FIGURE 45. 'SHELROCK' SILICA RODS FROM ROTATION RUNS IN CARBON-SATURATED IRON (20X).
(a) AS RECEIVED

(b) 6 MINUTE ROTATION RUN

(c) 1/2 HOUR ROTATION RUN

(d) 2 HOUR ROTATION RUN

FIGURE 46. HIGH SILICA BRICK SPECIMENS FROM ROTATION RUNS IN CARBON SATURATED IRON (20 X)
Figure 47. Reaction rate constant $k_t$ as a function of temperature for runs with 'SHELROCK' silica in carbon-saturated iron.
FIGURE 48. MASS BALANCE FOR SILICON IN RUNS WITH 'SHELROCK' SILICA IN CARBON SATURATED IRON AT 1600°C.
(a) DEVITRIFIED

(b) 1 HOUR ROTATION RUN IN ARMCO IRON.

FIGURE 49. FUSED SILICA SURFACES UNDER SCANNING ELECTRON MICROSCOPE (250 X)
(a) AS RECEIVED. (b) 1 HOUR STATIC RUN.

(c) 2 HOUR ROTATION RUN.

FIGURE 50. 'SHELROCK' SILICA SURFACES UNDER SCANNING ELECTRON MICROSCOPE (250 X).