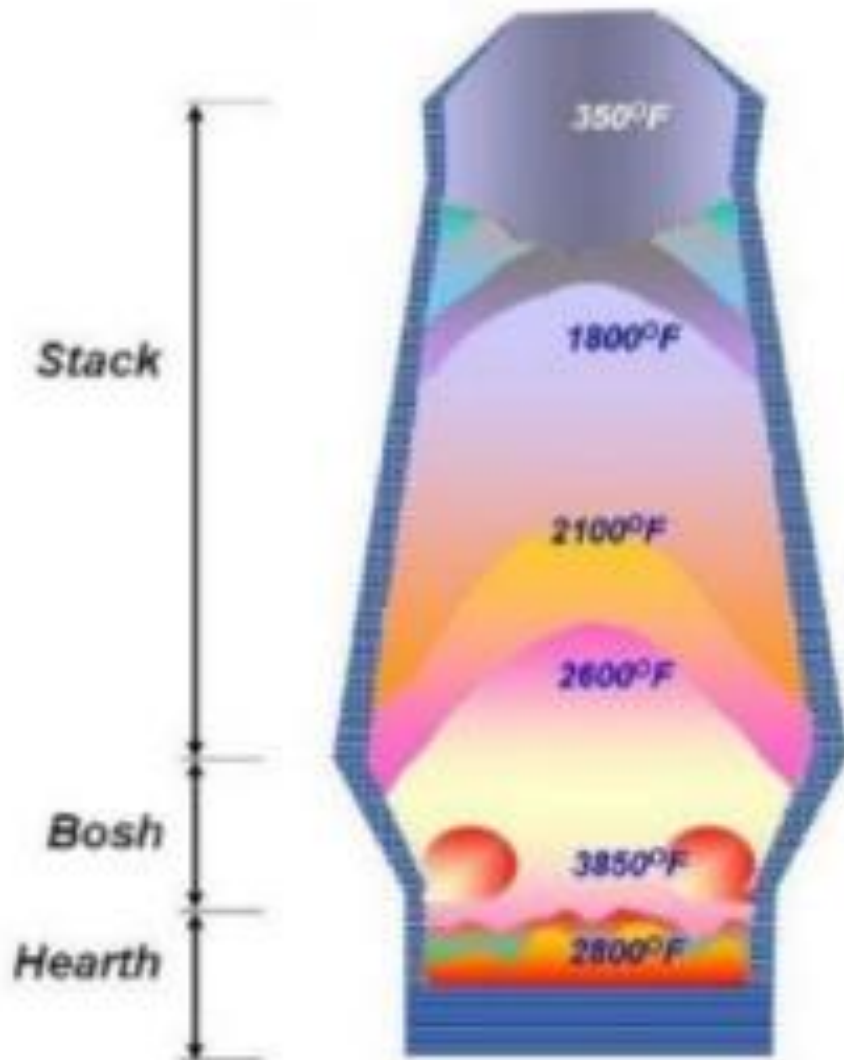


Blast Furnace Regions - Iron Making Furnace

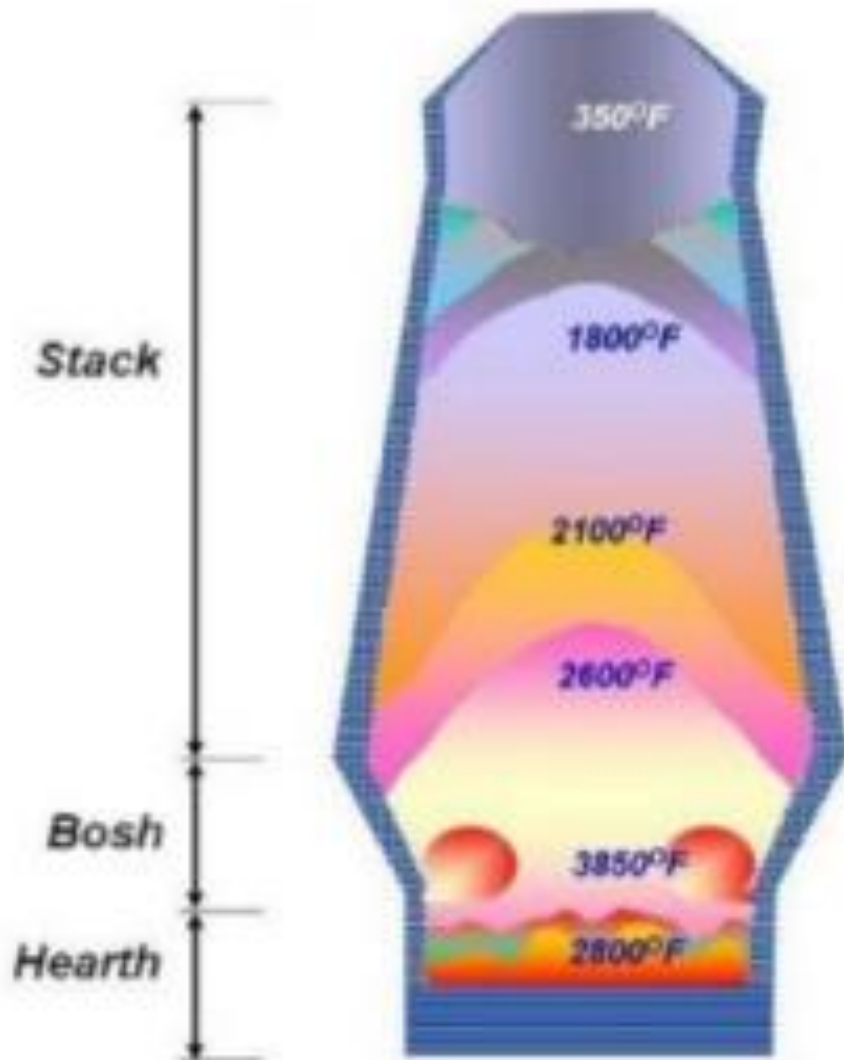


The thickness of the lining depends on the furnace size

STACK LINING

- The lining in stack should have good abrasion resistance and resistance to CO attack.
- In general, armor plates are used at the throat to withstand abrasion of the falling charge.
- The entire stack below the top few meters (2-3m) of height is lined with high duty fire bricks

Blast Furnace Regions – Iron Making Furnace

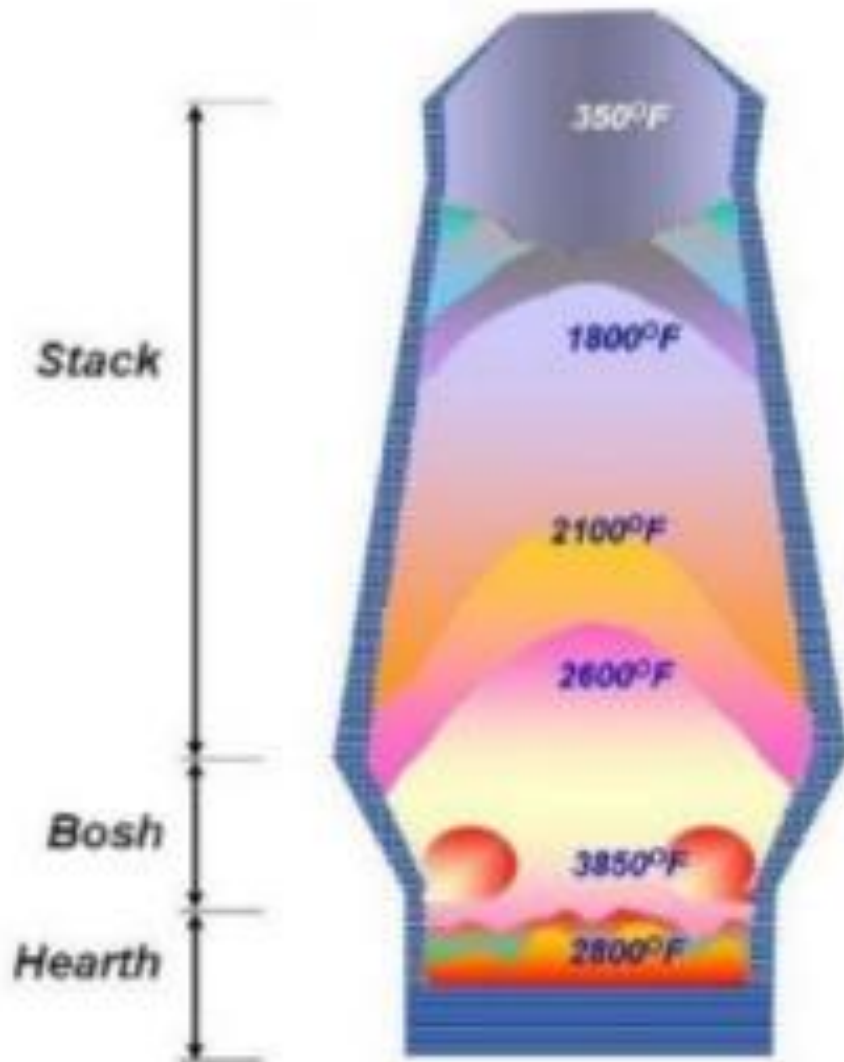


- 35-40% Al_2O_3 fire bricks are usually preferred.
- The bricks are made by machine moulding under high pressure with the absence of air.

HEARTH LINING

- The lining in hearth should prevent breakouts/leakage and have high refractoriness
- Carbon Blocks are used for lining whole wall thickness and considerable bottom thickness of the hearth. The remaining bottom thickness is made by high duty fire bricks.

Blast Furnace Regions – Iron Making Furnace

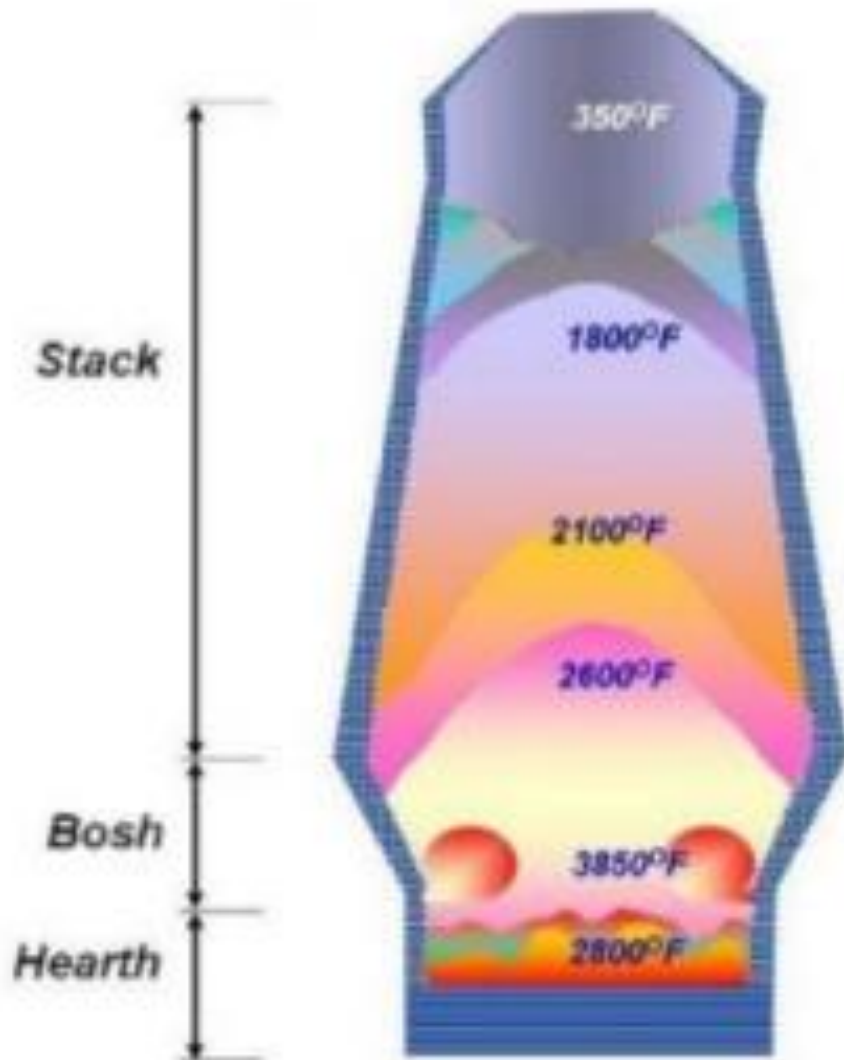


- Water cooled copper or steel plates are laid inside the walls to protect lining.
- Effective cooling of the hearth walls is improved by employing graphite as the backing layer with carbon blocks facing.

BOSH LINING

Considering the severity of T and chemical attack in the bosh region the lining should possess good refractoriness and resistance to the action of the molten metal and alkali slags.

Blast Furnace Regions - Iron Making Furnace



- High duty fire bricks with 45-60% Al_2O_3 are used for lining of bosh region with copper cooling plates.
- Carbon blocks also used for lining the bosh region since carbon refractory have better properties than conventional high duty fire bricks. Carbon lined walls can be cooled by spray coolers.

Blast Furnace Regions – Iron Making Furnace

Advantages of Carbon Lining

- Increase in overall life of the furnace
- Minimum breakouts
- Cooling design becomes more simple
- Clean surface in contact with slag and metal
- A relatively thin lining is adequate

Disadvantages of Carbon Lining

- Higher cost than conventional bricks
- Formation of steam and gases in the metal & slag tap hole region and defective coolers can damage the carbon lining.

The causes of failure of the linings are; CO attack, action of limy and alkali vapors, abrasion by solids, liquids and gases, T, action of molten metal or volatiles.

Corrosion of Refractories

Refractories are used at elevated temperatures for structural purposes and they are used in many cases to contain a high temperature corrosive environment. This corrosive environment usually contains liquid (melted) phases that participate in *chemical reactions* with the refractory at the elevated temperatures resulting in refractory consumption or wear. It is usually not immediately, but the oxidation and reduction state of the environment can participate in and influence the chemical reactions that take place. Along with chemical reactions during corrosion, *physical changes* occur that may be *accelerated by* the corrosion process.

Corrosion of refractories can be defined for the purposes of this discussion as follows:

Corrosion of Refractories – refractory wear by loss of thickness and mass from the exposed face of the refractory as a consequence of chemical attack by a corroding fluid. The refractory and the corroding fluid react approaching chemical equilibrium in the zone of contact between the refractory and the fluid.

It is an essential point that corrosion reactions proceed in a direction toward localized chemical equilibrium. This means that phase equilibrium diagrams can be used to analyze corrosion situations and to predict chemical strategies to minimize corrosion and wear rates.

First Fundamental Principal on Refractory and Slag Compatibility

The first fundamental principles is that “acid” refractories tend to resist “acid” slags better than “basic” slags and, conversely, “basic” refractories tend to resist “basic” slags better than “acid” slags. The definitions of acidity and basicity in room temperature solution chemistry and of refractory chemistry at elevated temperature have a key difference:

Definition of Acidity and Basicity in Solution Chemistry at Room Temperature –

an acid contains an excess of hydrogen ions (H^+) over hydroxyl ions (OH^-) considering a “baseline” defined as neutrality (a “pH” of 7.0). An acidic substance contributes hydrogen ions to a chemical solution to make it more acidic whereas a basic substance contributes hydroxyl ions to make it more basic.

Definition of Acidity and Basicity in Corrosion Chemistry at Elevated

Temperature – an acidic material contains an excess of silica content (SiO_2) over basic materials (usually CaO) considering a “baseline” defined as neutrality (a CaO/SiO_2 ratio of 1.0). An acidic material contributes SiO_2 in a corrosion reaction whereas a basic material contributes CaO or MgO in a corrosion reaction.

This leads to the observation that acid refractories are more “compatible” with acid slags, i.e. acid materials experience less corrosion loss against acid slags as compared to basic slags. In a like manner, basic refractories are more compatible with basic slags than with acid slags.

In a strict definition of compatibility, mineral phases will not react at elevated temperature if they are compatible. This means on a microscopic basis, they will “stand beside” one another or coexist at equilibrium without reacting to form new substances. In general usage, the term “more compatible” just means “less reactive”.

There are more complex definitions of acidity and basicity for high temperature chemistry than those given above. For example, in steel refining the term “V” ratio is used where a ratio exceeding 1.0 implies a basic chemistry (usually a basic slag chemistry) and a ratio below 1.0 implies an acid chemistry. In definitions of this sort, the “V-ratio” can be expressed in terms such as the following:

$$V = \frac{\text{CaO} + \text{MgO} + \text{FeO} + \text{MnO} + \dots}{\text{SiO}_2 + \text{P}_2\text{O}_5 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{Mn}_2\text{O}_3 + \dots}$$

In many cases, it is convenient to use three-component phase equilibrium diagrams in analyzing corrosion situations. The major refractory component can be visualized as one apex (corner) of the triangle with CaO and SiO₂ as the other components (apices). In these analyses, it is convenient to use the simple CaO/SiO₂ ratio.

Second Fundamental Principle on Porosity and Corrosion Rates

Most refractories contain void space or porosity. This porosity may be open pores that can be penetrated by a fluid media (i.e. “apparent” porosity) and/or it may be closed porosity that is not easily penetrated by fluid media. If a refractory contained no porosity (or brick joints, expansion joints, or construction joints), the corrosion reaction is limited only to the face exposed to the corrosive media (called the hot face). When porosity is present, particularly when open porosity is present, the corrosive media can penetrate the refractory causing destructive reactions behind the hot face. Most investigators have found that slag corrosion rates *increase linearly* with the percentage of apparent porosity within the refractory.

It is for this reason that attention is directed toward achieving higher densities in refractories, i.e. obtaining the lowest possible apparent porosities. Higher density refractories usually exhibit lower wear rates.

Because corrosive fluids can penetrate the refractory, such penetration usually results in disruption and even destruction of the “matrix” of the refractory. The matrix is the area of “sintered fines” that hold together “bonded” bricks and monolithic refractories. Usually, the matrix contains more impurities and more porosity than aggregate particles. Therefore, corrosion affects the “weakest” component of the refractory at a higher rate than more dense or higher purity particles. In extreme cases of matrix attack, rapid erosion of coarse refractory aggregate can occur.

The phenomena that occur during refractory corrosion are well known to anyone that has been around a furnace containing reactive process components such as slags or glasses. It is obvious that the reactive component, hereafter called the “slag”, must contact the refractory’s exposed surface or hot face at elevated temperature. It is at this interface that corrosion begins and continues throughout the life of the lining.

The situation is illustrated in considering a cross section of the slag and refractory interface (Figure 1). The refractory has a temperature gradient from the hot to cold face – meaning that the highest temperature is at the hot face and temperature declines across the refractory thickness toward its back or cold side. Slag is shown penetrating the refractory up until a “freeze plane” is reached. The freeze plane is the location in the refractory where the temperature is sufficiently low to cause the slag to solidify.

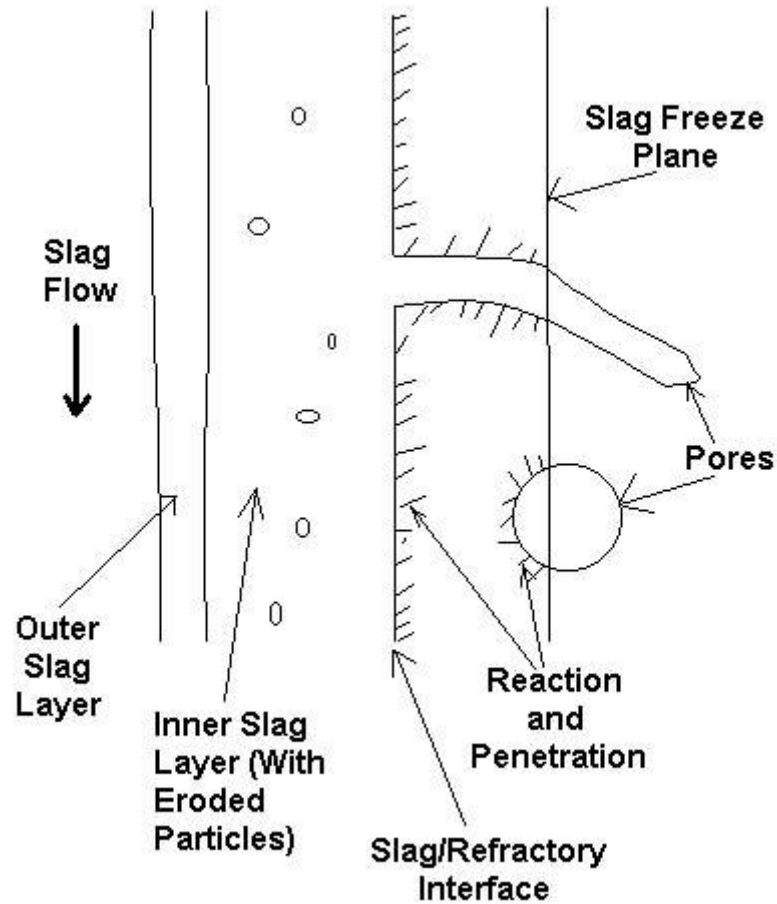


Figure 1: Cross Section of the Slag/Refractory Interfacial Area

The hot face of the refractory is coated with slag. In most metallurgical applications, this coating is relatively thin (~2-5 mm thickness). In some cases, two distinct slag layers can be observed on the outside of the refractory after a used material is sectioned. There may be a fluid “outer layer” over a “viscous appearing” inner layer with the latter directly contacting the surface of the refractory. The inner layer is typically influenced by solution of the refractory in the slag with the added components increasing the viscosity of the slag. There may be eroded particles of the refractory in the inner layer, which can be seen with the aid of a microscope. The two-layer situation is usually seen where liquid slag runs down a vertical refractory wall.

Slag reacts with the refractory forming new phases at the immediate hot face. Reaction also takes place behind the hot face where slag contacts the refractory at the pore walls. In metallurgical applications, metal can sometimes be seen penetrating the refractory along with slag.

Third Fundamental Principle on Reactions and Temperature Gradients

A key concept is that the temperature gradient affects the extent of phenomena seen in slag corrosion. In a very steep temperature gradient, very little penetration of slag is seen with corrosion reactions more or less restricted to the immediate slag and refractory interface. Mobility of fresh slag (reactant) to the slag/refractory interface may be limited, and transport of reaction products away from the slag/refractory interface may be slow. Steep gradients are seen in thin-wall refractory linings such as those used in utility boilers featuring water or steam cooling at the furnace shell.

In conventional refractory designs, the lining is at least one brick thickness (>225 mm), and the lining typically features a safety lining for a total thickness of at least 450 mm. The slag freeze plane may be located in a zone of 40-75 mm behind the hot face. In some cases, slag may penetrate up to 150 mm behind the hot face.

Thin Wall (Steep Temperature Gradient)

The corrosion situation in a thin wall refractory lining is illustrated in Figure 2. Here the refractory corrosion reactions occur primarily at the immediate hot face and there is little or no slag penetration. Microscopic examinations usually show that penetration is confined to a depth of less than 100 microns (0.1 mm) behind the exposed hot face. This situation may be called “Stage I” of slag attack where reactions occur at the immediate hot face.

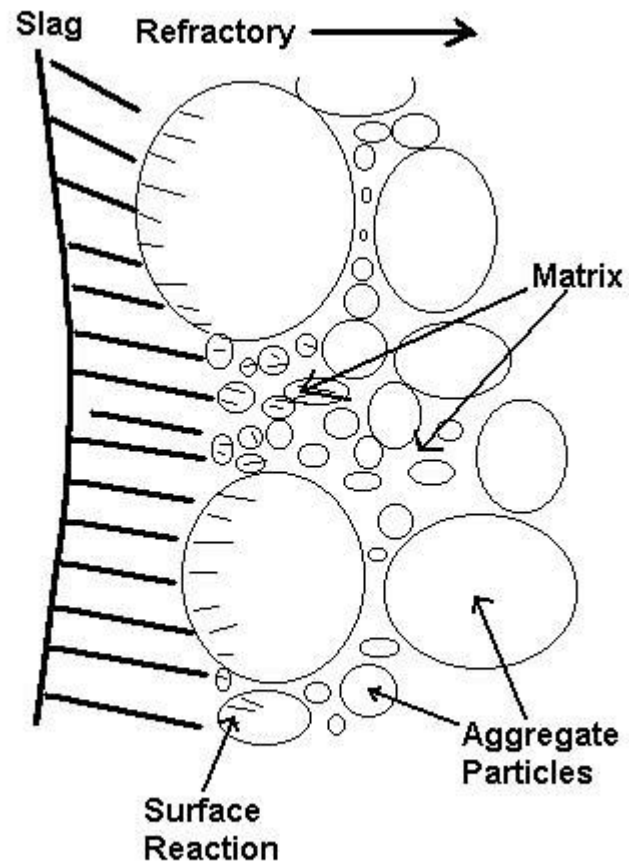


Figure 2: Stage I of Slag Attack

It is found that the hot face temperature primarily affects the rate of corrosion reactions. If the hot face temperature is held just below the point that the products of corrosion become liquid (melt), corrosion will be very slow or non-existent. Most authorities believe that if the hot face is maintained at no more than 20°C above this melting temperature (called a lowest eutectic temperature), reasonable corrosion rates will be observed. However, when the hot face temperature is more than 20°C above the eutectic, corrosion is rapid.

The reaction temperature between slag and refractory can be determined by conducting a thermal analysis test of a mixture of ground refractory and ground slag.

Thin wall refractory designs rarely exhibit more extensive corrosion phenomena than are described as “Stage I” of corrosion. Therefore, the primary process variable affecting corrosion is hot face temperature. Secondary variables influencing corrosion rates include slag velocity and slag chemistry. With respect to chemistry, the refractory will be soluble in the slag up to a certain extent (or percentage).

If the slag is “satisfied” with respect to the chemistry of the refractory, slag corrosion should be minimal. The term “satisfied” means that the slag has reached the chemical solubility limit of major refractory constituents in the slag. Usually, the slag is not satisfied, i.e. it is corrosive.

There are a few cases of thick wall designs where the refractory is so resistant to slag corrosion that corrosion reactions are restricted to the hot face region. Usually these involve fusion cast refractories employed in furnaces that remain hot during their service life.

Thick Wall (Relatively Broad Temperature Gradient)

Thick wall refractory designs begin to exhibit corrosion on their initial coating of slag at elevated temperature. The initial process is Stage I of corrosion (Figure 2). Because of the broad temperature gradient, the refractory is penetrated by slag. Penetration is aided by capillary suction as the smallest pores in the refractory (diameter <10 microns) draw the liquid slag behind the hot face.

In time, extensive corrosion of the refractory takes place so that the refractory is at “Stage II” of corrosion (Figure 3). Stage II is characterized by two phenomena: (1) full penetration of the refractory and (2) extensive disruption by corrosion of the hot face region. Stage II follows Stage I only if there is a sufficiently broad temperature gradient to allow penetration.

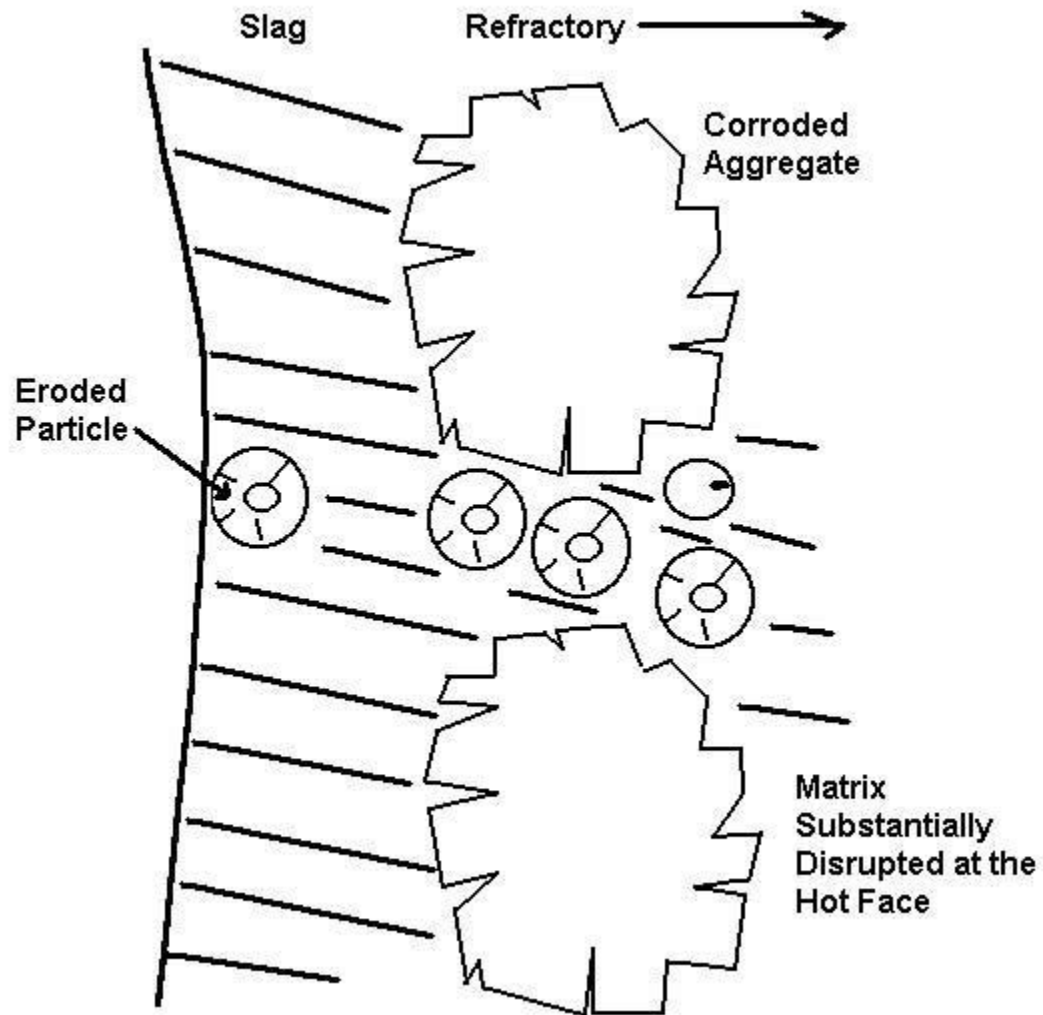


Figure 3: Stage II of the Corrosion Process

In Stage II, the coarse aggregate in a bonded refractory exhibits penetration – particularly along grain boundaries. The direct bonding between the matrix and the aggregate particles is disrupted, but this bonding still exists.

Slag penetration in Stage II can result in densification spalling (splitting). This type of spalling occurs because the thermal expansion coefficient in the slag penetrated zone is different than that in the unpenetrated cold face region. On continued thermal excursions (cooling and heating), spalling can occur at the line between penetrated and unpenetrated areas. The residual lining, after spalling, then begins the corrosion process a new progressing from Stage I to Stage II again.

Toward the end of the life of the refractory lining or in cases of relatively slow corrosion rates and where densification spalling has not taken place, the refractory hot face zone may progress to a final stage of corrosion that may be called “Stage III” (Figure 4). In this case, bonding in the hot face region and up to 2-4 mm behind the hot face is minimal. The slag itself “appears” to be the only phase holding the residual aggregate particles in place. This is probably a result of the higher viscosity of the slag in the hot face region created as a consequence of dissolution of the refractory in the slag.

Because of the influence of slag viscosity maintaining some coherence in the hot face zone in Stages II and III with thick wall designs, a key process variable affecting corrosion rate is hot face temperature. Many investigators recommend a hot face temperature not more than 20°C above the solidus temperature between the slag and the refractory. Such temperature restrictions are impractical in many thick wall refractory designs.

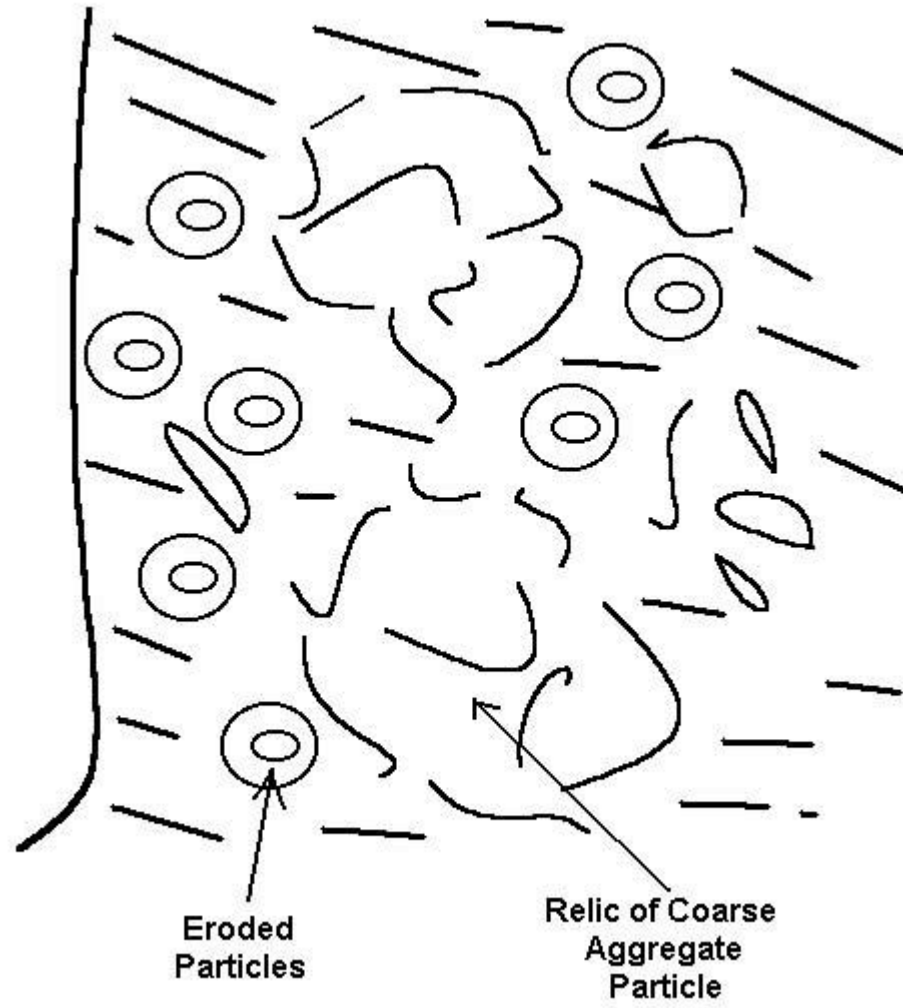


Figure 4: Stage III of the Corrosion Process

Equilibrium Considerations and Phase Diagrams

A phase diagram is a map showing equilibrium phases present as a function of composition and temperature. The phase diagram essentially shows the melting relationships in a given chemical system.

Even without a complete understanding of phase diagrams, they can be used in a “simplified method” to analyze corrosion. This method provides a “first approximation” of the corrosion potential of the system. This technique will be illustrated using the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system (Figure 5). In the chapter on Alumina-Silica Brick, two consequences of Na_2O exposure were mentioned for alumina-silica brick including “glazing” (corrosion to form melted phase) and expansions. This discussion will only consider corrosion of the refractory to form liquids during corrosion.

The *first step* is to locate the point on the diagram representing the refractory main constituents. For this discussion, we will use a 40% Al_2O_3 superduty brick in contact with a corrosive phase consisting of 20% Na_2O and 80% SiO_2 . Both of these compositions are indicated in Figure 5 with a blue dot indicating the approximate composition of the slag and a green dot indicating the approximate composition of the brick (on the Al_2O_3 - SiO_2 composition line)

The second step is to draw a line between the slag composition and the brick composition (indicated in red in Figure 5). It is *essential* to recognize that all potential reaction products between the refractory and the slag at equilibrium must be located on the red line in Figure 5.

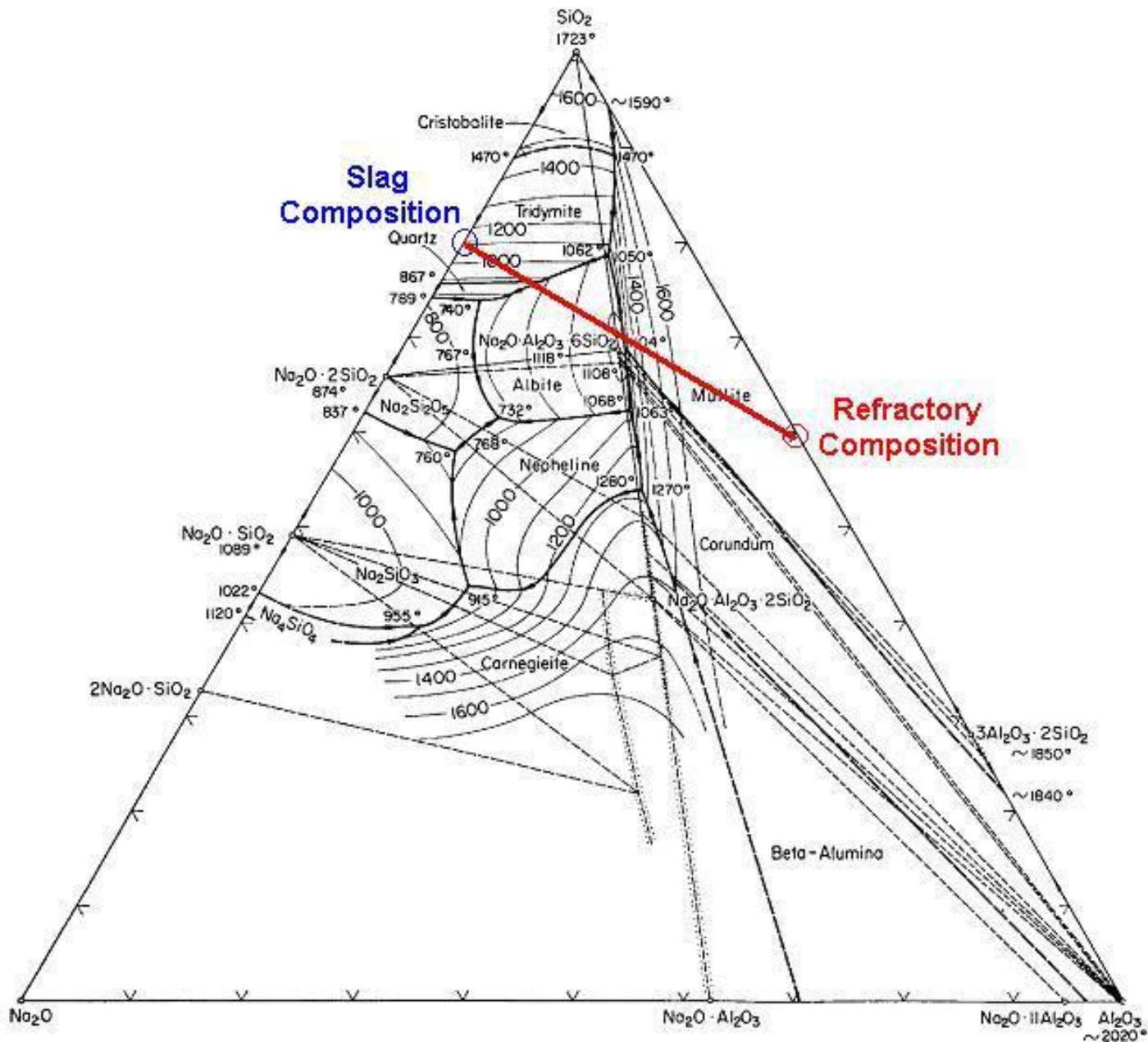


Figure 5: Na₂O-Al₂O₃-SiO₂ Phase Diagram Used in A Corrosion Example

The analysis of the corrosion potential is as follows:

1. At the slag/refractory interface, the composition must move from that of the refractory in a direction toward the composition of the slag, i.e. the local composition moves in a “northwesterly” direction.

2. The compound at equilibrium between the slag composition and the refractory composition is “albite” or $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$, melting at 1104°C .

Therefore, at equilibrium, the localized melting point of corrosion products at the hot face is 1104°C . Note that albite is contained in the “compatibility” triangle between SiO_2 , mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and albite.

The compatibility triangle establishes the phases that may be present at equilibrium. Mullite and SiO_2 (as glass or vitrified phase) are intrinsic to the refractory. Albite is formed as a consequence of corrosion reactions

3. The red line joining the refractory and the slag crosses temperatures as low as about 1000°C. This implies that non-equilibrium liquids could be formed at this low temperature during corrosion. In Stage I of corrosion, such non-equilibrium liquids are expected. Only in Stage II of corrosion will sufficient refractory be dissolved in the slag to allow observation of the equilibrium corrosion product.

4. The red line joining the refractory and the slag composition crosses the $\text{Na}_2\text{O} \cdot 2\text{SiO}_2 - \text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ compatibility triangle near the ternary (3-component) eutectic or lowest melting temperature of 740°C. This implies liquids melting as low as 740°C could be formed during non-equilibrium conditions.

Considerable qualification is needed when performing this type of analysis. One is that the refractory contains other components than Al_2O_3 and SiO_2 – notably fluxes like K_2O and Fe_2O_3 . These components can lower the melting points predicted by the diagram. Additionally, the slag may contain other components changing the melting relationships.

Selected Models for Slag Attack on Refractories

Konig's Model

Konig's analysis is appropriate for thin wall refractory with a steep temperature gradient fixed by the process (furnace) temperature and cold face temperature. Konig created a heat balance by assuming that the heat flux into the refractory surface must equal the heat flux through the furnace shell. If the heat flux into the refractory surface exceeds the heat flux out of the shell, the interface temperature (T_r) must increase causing increased corrosion rates until the heat balance is maintained once again.

Terms used in Konig's analysis are given in Table 1.

Table 1: Terms Used in Konig's Analysis

Term	Definition
Q_1	Heat flux into the refractory surface.
Q_2	Heat flux through the furnace shell.
A	Area of the exposed refractory in the furnace.
t	Time at elevated temperature.
T_i	Temperature where i =slag surface(s), refractory/slag interface(r), insulation hot face(i), or shell(sh).
x_i	Thickness of component where i =slag layer(sl), refractory working lining(r), insulation(i), or shell(sh).
k_i	Thermal conductivity where i =refractory working lining(r), insulation(i), or shell(sh).
T_c	Critical temperature at the slag/refractory interface.
f_i	A film coefficient for convective heat transfer where i = furnace environment (F) or room environment (E).

The slag/refractory interface temperature becomes T_c (critical temperature) when the heat flux into the refractory equals the heat flux out of the shell. If the actual temperature is above T_c , rapid corrosion (recession) of the refractory is expected until a dynamic equilibrium is once again achieved.

The heat flow into the refractory surface is described by the equation:

$$Q_1 = f_F A t (T_F - T_s)$$

The heat flux out of the furnace shell is:

$$Q_2 = k_{\text{eff}} A t (T_r - T_E)$$

where k_{eff} is the effective (overall) thermal conductivity through the refractory, insulation, shell, and film contribution in the room environment. From heat transfer theory, the relationship for k_{eff} is:

$$k_{\text{eff}} = \frac{1}{f_E + \frac{X_r}{k_r} + \frac{X_i}{k_i} + \frac{X_{\text{sh}}}{k_{\text{sh}}}}$$

At equilibrium, $Q_1 = Q_2$ and $T_r = T_c$, so that algebraic manipulation provides a relationship for the “equilibrium thickness” (x_r) of the working lining as:

$$x_r = k_r \left[\frac{1}{f_F} \times \frac{(T_c - T_E)}{(T_F - T_{sl})} - \left(f_E + \frac{x_i}{k_i} + \frac{x_{sh}}{k_{sh}} \right) \right]$$

Konig’s relationship for the equilibrium thickness provides the following insight:

- The equilibrium thickness x_r increases linearly as the thermal conductivity of the refractory increases.
- The equilibrium thickness x_r increases as the thermal conductivity of the insulation increases. This is why conductive ramming materials are used behind high thermal conductivity basic refractories to insure the best possible cooling effect of the shell.

- The equilibrium thickness x_r increases as the T_c of the refractory/slag system increases, i.e. as more slag resistant refractories are used. This usually means use of higher purity refractories, i.e. higher alumina content or higher MgO purity.
- The equilibrium thickness x_r changes as the heat transfer into the lining or out of the shell changes, i.e. as the film coefficients change.

The Model of Endell, Fehling, and Kley

In a classic reference, Endell, Fehling, and Kley developed an empirical relationship for slag corrosion in a thick-walled refractory lined vessel with slag flowing down a vertical refractory wall.

Table 2: Terms in the Analysis of Endell, Fehling, and Kley

Term	Definition
R	Slag attack rate, i.e. refractory recession, in cm/s.
L_0	Solubility of refractory in slag in kg of refractory/kg of slag.
T	Absolute temperature of the refractory hot face.
η	Slag viscosity in poises.
f	Fraction of ash adhering to the refractory wall – interpreted as slag impingement.
H	Heat liberated in the furnace chamber in kcal/m ³ -hr.
A	Ash content of the fuel in grams pf ash.
C	A constant for the furnace geometry.

The mathematical relationship for slag attack rate is:

$$R = CL_0 \left(\frac{T^{\frac{2}{3}}}{\eta^{\frac{2}{9}}} \right) (HA)^{1/9}$$

The empirical model of Endell, Fehling, and Kley for thick wall refractory linings provides the following information:

- There is a very *strong dependence* of refractory corrosion rates on *hot face temperature*. In fact, temperature is the most important process variable that can be considered in furnace design or process control.
- The slag attack rate *increases linearly* with the *solubility of the refractory in the slag*. While modern high Al_2O_3 or high MgO products were not included in the original research, modern practices have shown that corrosion rates can be reduced if the slag chemistry is adjusted to reduce solubility of the refractory in the slag.
- The corrosion rate is inversely proportional to slag viscosity. This is probably why refractories exhibit some coherence in Stage III of slag attack because solution of refractory in the slag has increased viscosity at the slag/refractory interface.

In their concluding remarks, Endell, Fehling, and Kley recommend maintaining a hot face temperature of no more than about 30°C above the solidus or eutectic temperature between the refractory and slag.

Case Studies of Corrosion

Alumina-Silica Brick in Ferrous Foundry Applications

Slag used in ferrous foundry applications is found to contain lime (CaO), silica (SiO₂), iron oxide (FeO), and other oxide constituents. *As a first approximation*, the slag can be assumed as a binary mixture of alumina and silica as they are usually the major components of the slag. The major components of the brick can be represented using the binary Al₂O₃-SiO₂ phase diagram, and this allows the corrosion situation to be analyzed using the three-component CaO-Al₂O₃-SiO₂ phase diagram (Figure 7).

Cases of corrosion of 70% Al_2O_3 and 90% Al_2O_3 brick are analyzed below using Figure 7. The composition of the brick is plotted on the Al_2O_3 - SiO_2 binary (2-component) side of the diagram. Then a line is drawn to the expected slag composition using the average CaO/SiO_2 ratio of the slag. For this discussion, the slag is assumed to have a CaO/SiO_2 ratio of ~ 1.0 .

A few things are very clear on looking at the lines joining the brick composition and the slag composition in Figure 7:

- Both “joins” between brick and slag pass very close to the ternary eutectic at 1265°C implying that the slag and refractory compositions will produce liquid phases, i.e. exhibit corrosion, whenever they are in intimate contact and when this temperature is reached. Other fluxing oxides typically reduce this temperature by as much as 50°C .

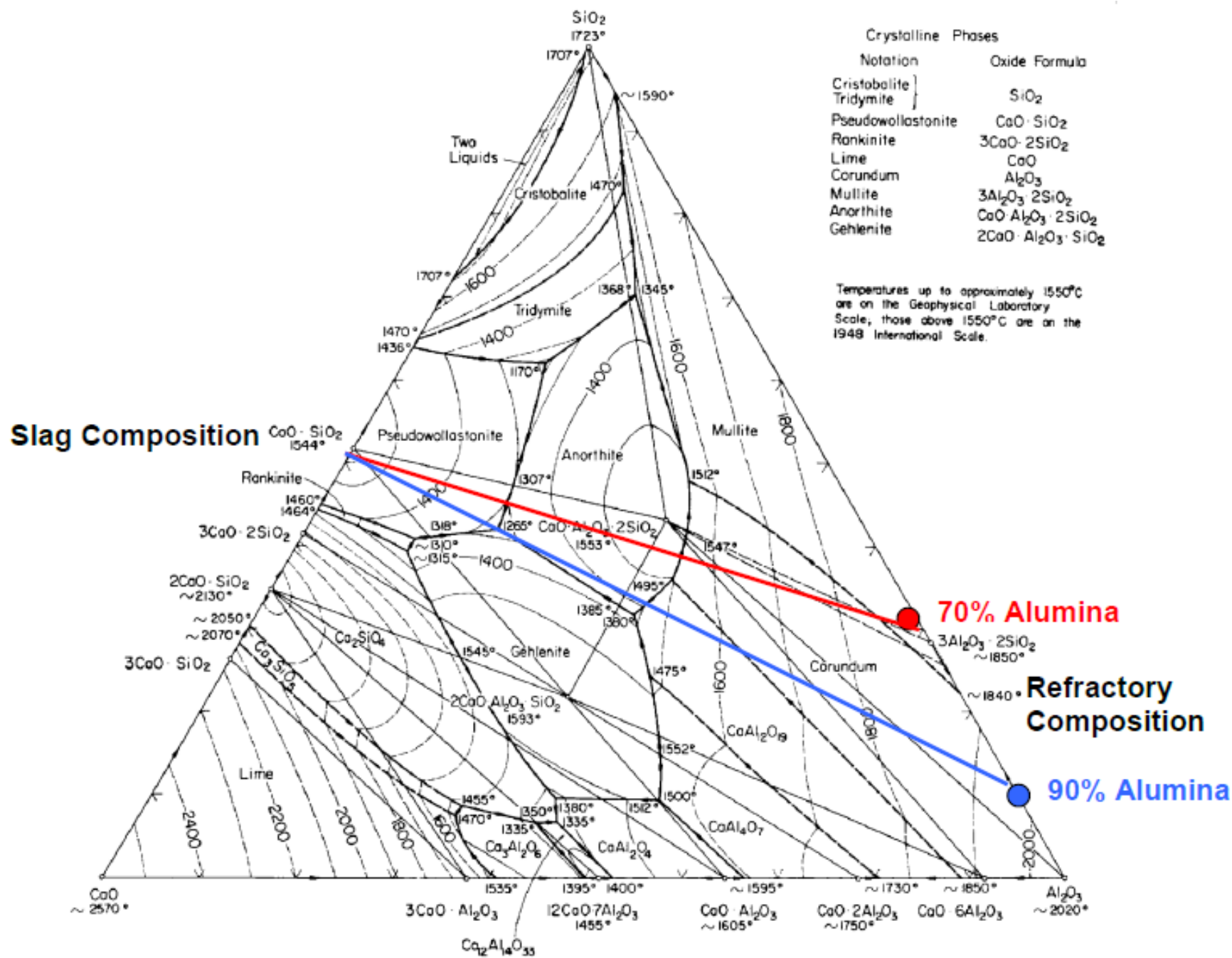


Figure 7: Representation of Corrosion of Alumina-Silica Brick In Foundry/Steel making Slag

Basic Brick in Steel Making Applications

A 90% MgO class fired, pitch impregnated brick was examined in a basic oxygen furnace producing carbon steel. The slag composition can be viewed as a high CaO/SiO₂ ratio liquid containing a substantial amount of iron oxide. Because the major component of the brick was MgO, the ternary system CaO-MgO-SiO₂ can be used to view the corrosion processes as a first approximation (Figure 15).

In the case of the 90% MgO class refractory, the brick contained 95.5% MgO, 2.7% CaO, and 1.4% SiO₂. This implies that the “native” silicate in the brick is dicalcium silicate (2CaO.SiO₂) - a very refractory second phase providing for a part of the bonding in a product where direct sintered bonds between adjacent MgO aggregate particles predominate. In service, a transient period exists in the steel refining cycle when silicon is being oxidized in the metal bath providing for temporary exposure of the refractory hot face to less basic silicates. This is also a period of enhanced iron oxide contact with the refractory.

Temperatures up to approximately 1550°C are on the Geophysical Laboratory Scale, those above 1550°C are on the 1948 International Scale.

Slag Compositions

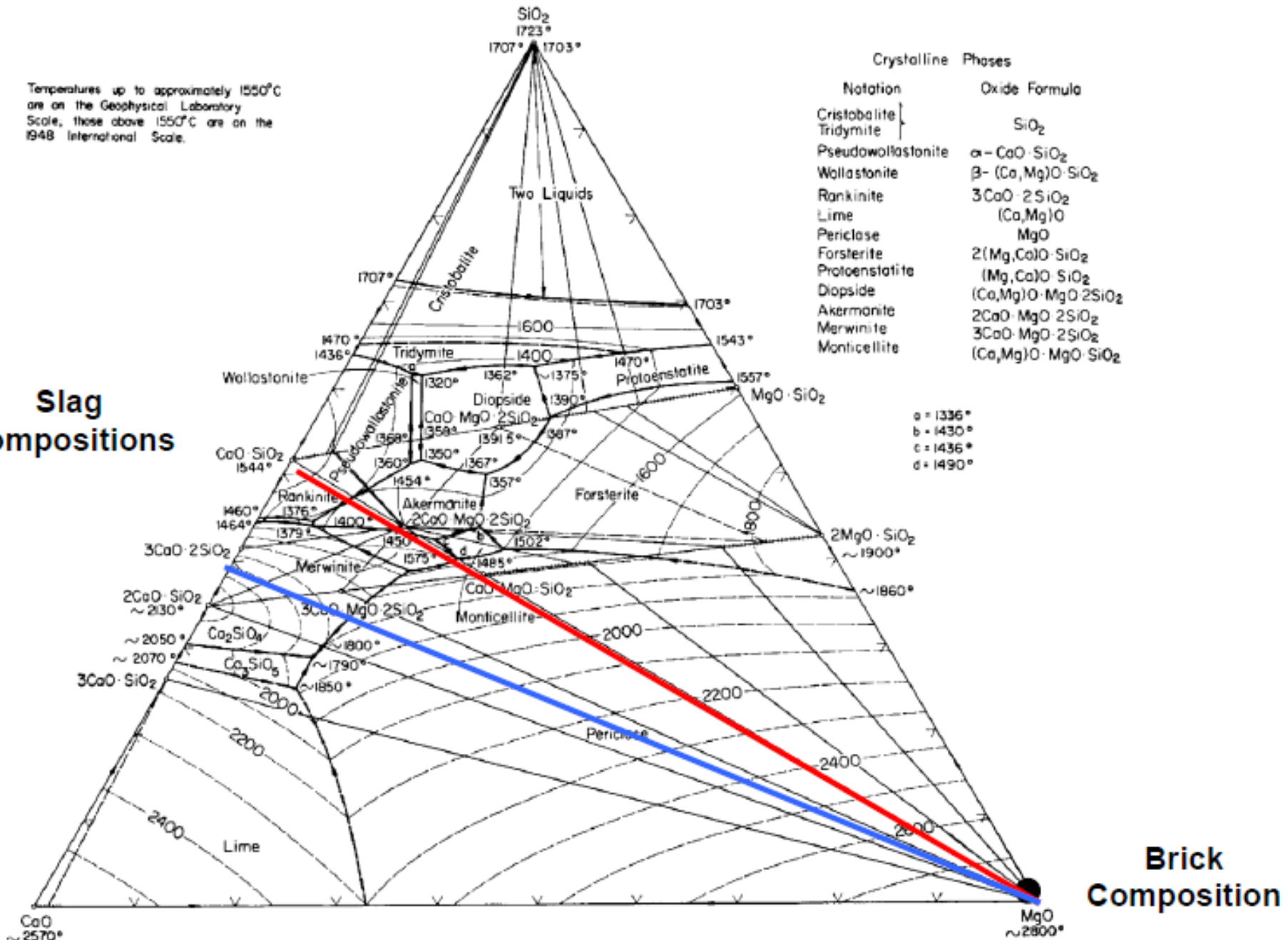


Figure 15: CaO-MgO-SiO₂ Phase Diagram

Since the refractory composition can be represented by the “MgO” apex on the phase diagram, joins can be drawn to different CaO/SiO₂ ratios illustrating the corrosion process:

- For a CaO/SiO₂ ratio of 1.0, the refractory will react with the slag forming monticellite, CaO.MgO.SiO₂, which melts at 1485°C. An iron-containing analog of monticellite called “iron monticellite” (FeO.MgO.SiO₂) has a melting point of 1230°C. Therefore, corrosion starts above about 1230°C when liquid phases are formed. Slag penetration can result in the disruption of bond phases that are native to the brick lowering the effectiveness of the “bonding silicate phase” in the immediate hot face area.

- For a CaO/SiO₂ ratio of 1.5, merwinite or 3CaO.MgO.2SiO₂ is the reaction product formed in the hot face. Merwinite melts “incongruently” at 1575°C in a process given as:



It is interesting that as the slag basicity increases (i.e. as the CaO/SiO₂ increases), corrosion reactions begin at higher temperature. This is one reason that steel makers wish to have solution of limestone slag additions as early as possible in a refining cycle to retard slag corrosion.

- For a CaO/SiO₂ ratio ≥ 2.0 , the lowest eutectic temperature is at $\sim 1790^\circ\text{C}$. Without considering the iron oxide and other components of the slag, this implies that the reaction product between the slag and the brick is above most steel making temperatures. However, the iron oxide plays an important role significantly reducing the temperature of the reaction products.

The Role of Iron Oxide in Corrosion

The role of iron oxide in corrosion in steel making slag and corrosion is to significantly reduce the melting temperatures predicted by only considering the CaO-MgO-SiO₂ phase diagram. Some of the reaction products commonly found between basic refractories and steel making slag are given in Table 3.

System CaO-MgO-Al ₂ O ₃ -SiO ₂		System FeO-MgO-Al ₂ O ₃ -SiO ₂	
Mineral	Melting Temperature, °C	Mineral	Melting Temperature, °C
2MgO·SiO ₂ (Forsterite)	1900	FeO·SiO ₂ (Fayalite)	1205
CaO·MgO·SiO ₂ (Monticellite)	1485	FeO·MgO·SiO ₂ (Iron monticellite)	1230
3CaO·MgO·2SiO ₂ (Merwinite)	1575	2CaO·(Fe ₂ O ₃ , Al ₂ O ₃)·SiO ₂ (Iron gehlenite)	1285
2CaO·SiO ₂ (Dicalcium silicate)	2130	FeO·Al ₂ O ₃ ·5SiO ₂ (Iron cordierite)	1210
3CaO·SiO ₂ (Tricalcium silicate)	2070	2CaO·Fe ₂ O ₃ (Dicalcium ferrite)	1489
CaO·Al ₂ O ₃ ·2SiO ₂ (Anorthite)	1553	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ (Brownmillerite)	1395
2CaO·Al ₂ O ₃ ·SiO ₂ (Gehlenite)	1593	6CaO·2Al ₂ O ₃ ·Fe ₂ O ₃	1365
CaO·Al ₂ O ₃ ·2SiO ₂ and 2CaO·Al ₂ O ₃ ·SiO ₂ (Melilite)	1380		

Table 3: Reaction Products Between Steel Making Slag And Basic Refractories with Melting Points for Full Melting or Partial Melting

It is immediately obvious that most of the iron containing compounds melt in the area of 1200-1350°C while most of the calcium silicate phases melt above 1485°C. It is also true that melting can typically begin below these indicated temperatures by as much as 50°C due to the effect of other impurities and due to the presence of multi-component eutectics not seen on three component diagrams.

The corrosion process between calcium-iron-silicate slag and magnesia containing refractories can depend on the mobility and concentration of reactants.

Gas Phase Reactions

The gas phase in a furnace may be the partial or even sole contributor to corrosion reactions or other deterioration in refractories. Some of the processes that have been recognized include:

1. Alkali transport to refractory surfaces resulting in surface reaction and penetration.
2. Reduction of the refractory and gas phase corrosion.
3. Alternating oxidation and reduction causing sequential dimensional changes in refractories that may enhance spalling.

The potential for alkali to cause “glazing” on the surface has been previously discussed (See Figure 5). It is less well recognized that alkali compounds can volatilize in furnace atmospheres resulting to transport of the volatile species to the surface of the refractory where vapor phase penetration may also occur.

The melting points of sodium and potassium reaction products with aluminosilicate refractories are given in Table 4. The melting points of the phases themselves are not indicative of the very low eutectic temperatures found in the system. For example, the lowest eutectic in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Figure 5) is 732°C .

Table 4: Alkali Phases Found in Used Refractories

Phase	Melting Point, °C
$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ (albite)	1100
$\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (carnegite)	1526
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ (carnegite)	1220
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ (leucite)	1686
$\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (kaliophilite)	>1700

A black slag is seen coating the fireclay brick with white salt deposits visible in this picture taken after seven years of service. Glazing is also shown on the insulating firebrick surface at the top of the kiln.

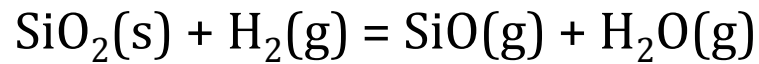


Sidewall of Sawdust Fired Tunnel Kiln After Seven Years of Service



Showing Surface Glazing and Sheet Spalling

Gas phase corrosion is also known in refractories containing SiO₂. It has long been recognized that products containing SiO₂ can be “reduced” by hydrogen or by penetration of aluminum metal. The gas phase reduction by hydrogen can be represented as:



where (s) signifies a solid phase and (g) signifies a gaseous phase.

Refractories exposed to hydrogen (or carbon monoxide) can experience gas phase removal of SiO₂ through the process of forming silicon monoxide. For example, at 1000°C a CO/CO₂ ratio of about 10⁻⁵ will be sufficient to reduce SiO₂. Mullite reduction and silica loss at temperatures exceeding 1500°C has been seen in petroleum calcining kilns.

Laboratory Slag Tests

Laboratory slag tests have been developed over the years for evaluating corrosion potential. These slag tests range from a “static” cup test to the “dynamic rotary slag test. The terms “static” and “dynamic” refer to whether the slag is stationary or whether it moves over the refractory surface respectively. Some of the test methods are summarized in Table 5.

Table 5: Laboratory Slag Tests

Test	Type	Reference or Comment
Cup	Static	The test usually consists of a ~50mm diameter hole core drilled or formed into the refractory that is packed with slag and heated to a selected test temperature for a set time. The test only reflects the isothermal reaction and penetration potential between the slag and the refractory.
Drip	Dynamic	Slag drips over a surface with evaluation of the depth of a “notch” cut in the surface by corrosion. The test is described in ASTM C768. The test reflects the isothermal reaction potential between the slag and refractory when there is a constant supply of unreacted or “fresh” slag.
Rotating Spindle	Dynamic	Refractory bars or rods ~25X25X200mm are partially immersed in a crucible containing slag while the specimen is rotating. The test reflects isothermal reaction potential of a flowing slag without a constant supply of “fresh” slag.
Rotary	Dynamic	Beveled refractory shapes (formed by saw cutting) or monolithic materials constitute a lining of a small rotary furnace that is constantly fed with slag. After the test, the specimens are examined for corrosion loss and slag penetration. This test is described in ASTM C768. The test reflects corrosion under a temperature gradient with a constant supply of “fresh” slag.