Chapter 1
1.0 Safety

Safety at any industrial facility is paramount and in the case of making steel is absolutely critical. The operation deals with molten liquids over 1600°C in close proximity to people and therefore requires a high amount of diligence. In refractory design, everything we do from a design point of view takes safety into account.

For this discussion, the safety component will be broken into the following key areas:

1. Containment of the process
2. Ladle fumes
3. Ceramic fibres
4. Silica

Containment of the Process

First and foremost, the main goal is zero breakouts, which means that molten liquid (liquid iron or steel) does not go out of the vessels in an uncontrolled manner. Injuries to people and/or damage to equipment are a major risk. Figures 1.1 and 1.2 show a ladle bottom breakout and give a sense of the impact that breakouts have.

![Fig. 1.1: A ladle bottom breakout](image1)

![Fig. 1.2: Damage after the ladle breakout](image2)

All areas lined with refractory in the shop (most notably, Basic Oxygen Furnace (BOF), Electric Arc Furnace, (EAF), hot metal ladle, steel ladle, tundish, etc.) have this inherent risk, and prevention must be included in the design. Risk increases with increases in liquid steel temperature and processing intensity. In my experience, breakout rates in the industry are approximately as follows for each vessel:

**Steel Ladles**

- Highest ~ 2-3/year for the vessel proper (slagline, barrel, bottom, Ar plugs) and ~3-6/year gate breakouts (mainly minor in nature but can be catastrophic).
A steel ladle is made up of four key sections as shown in figure 1.3.

![Fig. 1.3: Steel Ladle Design](image)

As an example, ladle breakout frequency and type is shown in Figure 1.4.

![Fig. 1.4: Steel ladle breakout example](image)
From the example, there are some key points to be made (more detail will be provided in the steel ladle section itself).

- The slagline area (typically at bath level) of the ladle is the highest risk area because the processing of steel is at its most intense here (high temperature, superheated slag).
- For steel ladles, the different designs and process routes will lead to different results.

Steel ladles also have a high risk of breakout around slide gate systems, as shown in Figure 1.5 as an example only.

![Ladle Gate Breakouts per Year](image)

**Fig. 1.5: Steel ladle gate breakout example**

Again, from the graph shown, there are some key points to be made (more detail will be provided in the steel ladle section itself).

- For steel ladle gates, the design of the gate and the product mix of steel going through the system lead to different results.
- Changes to systems and/or personnel can have a detrimental effect on this metric, not just refractory changes.
Hot Metal Ladle (Figure 1.6)

- This vessel has the lowest risk of a breakout. It is used as a transport vessel only, and breakouts are rare due to the low freeze point of the liquid iron (1535°C). It freezes fairly quickly and is therefore “self-sealing”.
- For cases in which the hot metal ladle is used for desulphurizing, the risk increases with stirring intensity and amount of sulphur to remove. This creates a slagline type area with associated higher wear.

Basic Oxygen Furnace (BOF) (Figure 1.7)

- Medium risk ~One every second year, depending on how well the vessel is managed (higher risk with vessels with bottom tuyeres and/or removable bottoms).
- The bottom tuyeres are high risk, especially in an oxygen blowing bottom design due to the large size of the tuyeres (~25 mm diameter), and the risk of any loss of blowing pressure during processing can and will lead to breakouts through the piping itself.
- Removeable bottoms are especially tricky around the joint area between the wall and the bottom as the joint mix needs to have high integrity, otherwise a failure can occur with an associated breakout.
- Breakouts through the walls are rarer but can occur if the vessel lining is allowed to become thin.
Electric Arc Furnace (EAF) (Figure 1.8)
- Medium risk ~one every year ~ main risk is the “hot spots” in the slagline of the furnace due to high temperatures from the furnace electrodes and the entire slagline area.
- Typical breakout locations are underneath burners / injectors or near the back tap pad (when a furnace tilts to tap a heat, the bath level rises on the back tap pad).
- The hearth has some risk, especially if a door lance is used, because the angle of high flow oxygen can quickly wear a hole in the bottom of the vessel.
- Breakouts can also occur near the gunned splitline (interface of the top course of brick and the water-cooled sidewall) when the heel becomes too large.

![EAF layout](image)

**Fig. 1.8: EAF layout**

Tundishes (Figure 1.9)
- Low and rare due to being more of a containment vessel than a processing vessel, although temperatures are still high.
- Note that this does not include tundish gate breakouts or submerged entry nozzle (SEN) failures at the caster.
- Breakouts can occur in the nozzle area due to poor ramming between the bottom and the well block near the casting taphole.
- Breakouts have also occurred in the wall area near the ladle shroud. This is because the design of furniture may cause steel to “flow back” into the sidewall of the tundish. This creates a high wear zone and steel flows out the back of the tundish.

![Tundish layout](image)

**Fig. 1.9: Tundish layout**

Summary
The first and foremost goal of steelmaking is zero breakouts, which means that molten liquid (liquid iron or steel) does not go out of the vessels in an uncontrolled manner. All other goals are subsidiary to this, and design must be prioritized but never compromised.
Ladle Fumes

The second key issue for the health and safety of employees is fuming from process vessel initial heat ups / dryouts of any material that contains tar, pitch, or is resin bonded.

Formaldehyde is classified by IARC (International Agency for Research on Cancer) as a “probable human carcinogen” (Class 2A) and can cause irritation of the eyes and throat in high concentrations. The Ministry of Labour (MOL) of Ontario, Canada. time weighted average exposure value (TWAEV) for formaldehyde is one part per million (ppm). Chronic overexposure to phenols can cause harmful effects on the liver and kidneys, eye irritation and dermatitis. The (MOL) of Ontario, Canada. (TWAEV) for phenol is 5 ppm.

Steel plants have had employee complaints of headaches, nausea and eye and throat irritation due to poor air quality. These symptoms may be due to the components released in the fumes from resin bonded bricks. They are producing well below the tolerance level; however, the problem is that the workers’ sense of smell picks it up at a much lower tolerance level. (e.g., Fig. 1.10)

This is a normal material found in MgO-C brick, alumina - magnesia - carbon (AMC or MAC) brick or other types that are not kiln fired but carbon bonded. Another area is the joint mix for the BOF that also contains these materials and can be found in some BOF patching materials.

In the normal state of the BOF and EAF these are not a major issue because the off gas systems remove the fumes during burn in / dryout and do not cause problems for employees due to limited actual exposure.

For steel and hot metal ladles, however, they can be problematic and you need to ensure that the materials are “low fume” and meet applicable standards.

From an internal point of view, the key point is to ensure the ladle preheaters work properly. In the case of shops that preheat, they have an incinerator to post-combust fumes due to the proximity of employees to the area, and it being the only solution for preventing the employee health and safety concerns.

With this alternative there is no impact on refractory costs or masonry resources. The only continuing costs are system maintenance and increased natural gas consumption. In principle, post-combustion works by "re-burning" gases to products of complete combustion, which do not contain any harmful components in high concentrations. Existing ladle dryer, burner and dryout programs are retained. An enclosure is erected around the ladle stand to capture all fumes. Controlled ambient air inlets are used to provide combustion air and regulate waster gas temperature. An incinerator chamber with a burner is installed, designed to provide adequate time and temperature to neutralize the emissions into products of complete combustion. Ducting and an exhaust fan are used to direct the captured gasses through the incinerator and expel the "cleaned" waste gasses into the building, as shown in Figure 1.11.
The other control mechanism for incoming brick has been to utilize a third party test that measures the fuming of the brick. One possible special test from Penn State University is described as follows:

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) analyses were performed on each sample. The instrument used was a Hewlett Packard 5890 Series II GC fitted with a 5971A MSD and a CDS Analytical Pyroprobe 1000. Each sample was separately pyrolyzed at three different temperatures: 300, 480 and 700°C, and chromatographically separated using a Restek Rtx-5ms column (30 m x 0.25 mm) with a temperature program beginning at 60°C then ramped immediately to 150°C at 6°C/min followed by a ramp at 12°C to 220°C with a final ramp at 25°C to 320°C. The final hold time was 10 minutes. This technique is not quantitative and the mass of each pyrolyzed sample was not the same. However, the analyst endeavored to maintain an equivalent mass for each sample, and so the quantities of the species evolved during pyrolysis can be compared to assess the differences between each sample.

TMAH (tetramethylammonium hydroxide) thermochromolysis experiments were performed to examine the distribution of polar species that might not be amenable to GC chromatography. TMAH facilitates methylation of acidic functional groups while simultaneously cleaving groups attached by ester and ether linkages. The reaction occurs in the injector port of the gas chromatograph. Approximately three times more TMAH than sample is added to the quartz pyrolysis boat.

The contact for this test is:

Contact: Penn State University
> Refractory brick testing for low fume brick
> Ask for Qualitative Chemical Analysis of the Pyrolyzed Samples-Py-GC/MS analyses
Ceramic Fibres

What Are Synthetic Vitreous Fibres?
Synthetic vitreous fibres (SVFs) are a group of fibrous inorganic materials that are made from rock, slag, clay or glass. SVFs differ from natural mineral fibres such as asbestos because they do not have a crystalline molecular structure and do not persist in the body for long periods of time. SVFs are finding increasing use as a substitute material for asbestos. They are primarily used for heat and sound insulation, reinforcement of other materials and filtration.

There are two broad categories of SVFs: filaments and wools. Filaments consist of continuous glass filaments, while wools are subdivided into glass wool, rock wool, slag wool and refractory ceramic fibres (RCFs).

Routes of Exposure
SVFs most commonly enter the body through inhalation. Some fibres can be deposited in the nasal and oral passages and on the surfaces that line the lungs. Most fibres deposited in the nasal and upper lung airways are easily removed from the body by a layer of mucous and carried away to the stomach to be excreted. Fibres deposited in the deepest parts of the lungs where gas exchange occurs require more time to be removed from the body. Fibres can also penetrate the outer layer of the skin.

Health Effects

. Continuous Glass Filament, Glass Wool, Rock Wool, Slag Wool
Application, maintenance or removal of continuous glass filaments, glass wool, rock wool or slag wool has been associated with acute skin irritation, eye irritation and symptoms of the upper respiratory tract, such as sore throat, nasal congestion, laryngeal pain and cough.
Because of inadequate evidence of carcinogenicity in humans and relatively low persistence in the body, continuous glass filaments, glass wool, rock wool and slag wool are not classifiable as to their carcinogenicity in humans by the IARC.

. Refractory Ceramic Fibres
Application or removal of refractory ceramic fibres (RCFs) has been associated with acute skin irritation, eye irritation and symptoms of the upper respiratory tract, such as sore throat, nasal congestion, laryngeal pain and cough.

RCFs inhaled deep into the lung persist for longer periods of time compared with their SVF counterparts. Concern has been raised surrounding the carcinogenic properties of RCFs. The principal target organs of concern for cancer are the lungs and the pleura. Animal studies have detected elevated incidences of lung tumors and the formation of mesotheliomas following exposure to RCFs. However, there is insufficient evidence in humans as to the carcinogenicity of RCFs. As a result, the IARC has classified RCFs as possibly carcinogenic to humans.

There is also a concern that some RCF material could be converted into a form of free crystalline silica (cristobalite) at temperatures above 1800°F (982°C). Exposure to elevated levels of cristobalite over extended periods of time can cause irreversible lung disease. Free crystalline silica is also suspected of causing lung cancer.
There are two types of RCFs. One is regular and the other is bio-soluble. Table 1.1 presents a comparison of the two.

<table>
<thead>
<tr>
<th>Regular</th>
<th>Bio-Soluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3 - \text{SiO}_2$</td>
<td>$\text{MgO} - \text{Ca} - \text{SiO}_2$</td>
</tr>
<tr>
<td>Possible Carcinogen</td>
<td>Non-carcinogen</td>
</tr>
<tr>
<td>Remain in lungs for 10 yrs</td>
<td>Remain in lungs for 2 weeks</td>
</tr>
<tr>
<td>Aspect ratio = $D/L$</td>
<td>Dissolves in water</td>
</tr>
</tbody>
</table>

- **Bio-soluble Wools**
  These new wools are a SVF designed to replace refractory ceramic fibres. Results from well-designed, long-term inhalation studies in animals have not shown any significant increase in the incidence of lung tumors or any mesotheliomas.

**Exposure Limits**

The exposure limits for SVFs shown in Table 1.2 are based on Ontario MOL Regulation respecting Control of Exposure to Biological or Chemical Agents (O. Reg. 833) and the American Conference of Governmental Industrial Hygienists (ACGIH).

<table>
<thead>
<tr>
<th>Type of SVF</th>
<th>8-hour Exposure Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>(fibres/cubic centimeter)</td>
<td>2002 IARC Evaluation</td>
</tr>
<tr>
<td>Glass Wool Fibres</td>
<td>1</td>
</tr>
<tr>
<td>Rock Wool Fibres</td>
<td>1</td>
</tr>
<tr>
<td>Slag Wool Fibres</td>
<td>1</td>
</tr>
<tr>
<td>Refractory Ceramic Fibres</td>
<td>0.2</td>
</tr>
</tbody>
</table>

All exposure limits represent respirable fibres (length greater than 5 microns, aspect ratio greater than or equal to 3:1).
In recent years, as employers investigate avenues to increase efficiency and lower cost, the emphasis on health and safety has intensified. Many companies have begun rolling out a “control strategy” regarding the use of RCFs to those departments utilizing these materials. RCFs are a component of the SVFs widely used to provide effective, low cost, high temperature insulation. RCFs are composed of a mixture of silica and alumina and were originally developed as a substitute for asbestos. The IARC classifies RCFs as “possible human carcinogens”. The need for an improved control strategy stemmed from the fact that in 2000 the ACGIH included SVFs on their “Notice of Intended Change” list, indicating that the TWAEV would be reduced to lower levels.

Controls
Employers have implemented a series of activities aimed at quantifying and controlling employee exposure to RCFs. Employee education programs have been undertaken whereby employees were exposed to literature and information on the suspected health effects of RCFs. The use of specialized handling procedures and personal protective equipment was a large component of this training.

Given that some employee exposure test results indicated exposures approaching the future proposed TWAEVs, employers have developed suitable reaction plans. Employers can identify and systematically evaluate/rationalize each RCF application individually. The aim is to eliminate the RCF material, substitute an alternate material or at least mitigate employee exposure to RCFs for each application, as seen in Table 1.3.

<table>
<thead>
<tr>
<th>RCF Application</th>
<th>Strategy</th>
<th>Old Material</th>
<th>New Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle Lip Gasket</td>
<td>Eliminate</td>
<td>1” RCF blanket</td>
<td>Nil</td>
</tr>
<tr>
<td>SEN Insulation</td>
<td>Substitute</td>
<td>RCF paper</td>
<td>Thermal spray coating</td>
</tr>
<tr>
<td>Ladle Preheaters</td>
<td>Substitute</td>
<td>RCF modules</td>
<td>Castable</td>
</tr>
<tr>
<td>TCD Insulation</td>
<td>Mitigate</td>
<td>1” RCF blanket</td>
<td>High temp. clay wrap</td>
</tr>
<tr>
<td>Tundish Preheat Covers</td>
<td>Substitute</td>
<td>RCF Modules</td>
<td>Castable</td>
</tr>
<tr>
<td>SEN Preheat Wrap</td>
<td>Substitute</td>
<td>1” RCF blanket</td>
<td>Mortar rope</td>
</tr>
<tr>
<td>Packing Hairpin/Hood of BOF</td>
<td>Substitute</td>
<td>1” RCF blanket</td>
<td>Stainless steel wool</td>
</tr>
<tr>
<td>BOF Tapping Doors</td>
<td>Substitute</td>
<td>1” RCF blanket</td>
<td>MgO sand</td>
</tr>
<tr>
<td>Rayonet Gasket at CC</td>
<td>Mitigate</td>
<td>1” RCF blanket</td>
<td>Pre-cut gaskets</td>
</tr>
<tr>
<td>Tundish Lid Seals</td>
<td>Substitute</td>
<td>1” RCF blanket</td>
<td>Mortar rope</td>
</tr>
<tr>
<td>LMF Packing Roof/Beehive</td>
<td>Eliminate</td>
<td>1” RCF blanket</td>
<td>Roof design change</td>
</tr>
</tbody>
</table>
Employers have taken the approach of minimizing use of fibres and/or moving to bio-soluble in as many applications as possible, (e.g., Figures 1.12 and 1.13).

Silica

What Is Silica?
Silica or silicon dioxide (SiO₂) is a naturally occurring compound (e.g., beach sand). Silica may be present in an amorphous form, a crystalline form or bound as a silicate. The crystalline form of silica or free crystalline silica (FCS) (e.g., quartz, cristobalite and tridymite) is of greatest concern in terms of health effects.

Health Effects
Silica (FCS) may produce disease only if it is inhaled into the lungs. A silica hazard exists if silica is airborne or has the potential to become airborne in very fine sizing. Exposure to excessive airborne levels of FCS over a period of many years can cause a fibrotic disease in the lungs known as silicosis. This disease causes the person to lose the elasticity of their lungs. Early symptoms are shortness of breath during physical work and a dry cough. Silicosis is a disease that will cause new scar tissue even after the person is no longer exposed to FCS. The IARC has concluded that inhalation of quartz or cristobalite is carcinogenic to humans. Cristobalite and tridymite are more hazardous because they cause new scar tissue to grow faster. Avoiding exposure is the only way to prevent silicosis as there is no treatment that exists for this occupational disease.

Acceptable Exposure Limit

Legal Requirement
The ACGIH TWA-TLV for respirable crystalline silica is 0.05 milligrams per cubic meter (mg/m³) averaged over a workday or a work week. When silica levels are high, a program to control silica exposure should be implemented.

There are two key factors for lowering the risk that refractory designers can help with:

1. Material with 60% Al₂O₃ or more reduces the risk (the more alumina which means the less free silica, the better).
2. Low free silica (the more free silica, the higher the risk). For example, raw materials that are mullite based (Al₂O₃- SiO₂) contain no free silica, which is good. In the tundish area, olivine ties up the free silica, which is also good.

**Note that the risk to employee health is only at demolition when dust is airborne. This can be mitigated with respirators.**
1.1 Goal of Availability

At the end of the day, the refractory lining is a protective layer for the process vessel and allows the process, any process (e.g., steelmaking, petrochemical, lime kiln, etc.) to run and make product for a given industry. The goal of the lining therefore is threefold for any refractory from a productivity point of view:

- Be transparent to the process
- Meet targeted life of vessel
- Meet targeted wear rates

Transparent to the Process

- Refractories have been called the “Achilles heel” of steelmaking and even a “necessary evil” due to their effect on the processing of steel if things go wrong
- If the steelmaking process runs smoothly and the refractory design matches perfectly, then the issue of refractories may never be brought up (though cost will always be an issue)
- Being transparent or invisible to the process is more difficult in a bottleneck operation because it means perfection isn’t achievable. Therefore, target lives can be set to minimize the impact.

- Matching the life of the refractories to the major maintenance cycles of the process for bottleneck processes is a key target. In any major process streams there are regular maintenance patterns that are required for process equipment. These need to be known and utilized.
  - Example #1 – The BOF stream has BOF gas cleaning and Continuous Caster (CC) segment lives that dictate shutdowns every 8 weeks and major work every 6 months. Therefore the BOF bottom life is set for 8 weeks and the furnace reline to every 6 months to minimize the impact to the steelmaking production results.
  - Example #2 – The EAF stream has mould life at CC as the key production outage – e.g., 1000 heats. Therefore the EAF furnace bottom life is targeted at 1000 heats to match. As the bottleneck process life increases with the mould moving to 1200 heats, the furnace life must match or an additional production outage would be required and there would be a loss of capacity.

- Minimize repair rate on bottleneck processes
  - Production time lost at the BOF or castor mould is critical time and forever lost. The production losses will normally be 5-10X the cost of the refractory itself in a bottleneck operation.
  - Therefore design of bottleneck working lining can be “over specified” in order to minimize repairs and therefore increase production capacity.
  - In non-bottleneck operations, lower lining quality and/or higher repairs may be tolerated (e.g., a shop with multiple BOFs or more BOFs may chose to use a cheap lining and rotate to a new furnace when the old one is worn).
  - Non-bottleneck operating refractories are still designed for the lowest total cost of ownership (TCO), however more flexibility exists.

- Predictability in design is favoured in all cases:
  - When refractory life is highly variable (high standard deviation) then it becomes extremely difficult for operations/maintenance to plan for shutdowns, etc. leading to higher costs.
  - BOF bottom life ranges from 400 to 1000 heats with no predictability. This leads to difficulty in planning BOF and Blast Furnace (BF) shutdowns and thereby higher maintenance costs with less workforce sharing, more contracting, more premium time, etc. Life of 1300 +/- 100 heats leads to very predictable life and minimum maintenance costs.
  - Steel ladle life – early shutdowns lead to fewer ladles in service and at some point slows the steelmaking process down to match the pace of ladles – delays that are unwanted. This can also lead to adding more ladles in service, which seems good but leads to higher wear rates due to more thermal cycling, more oxidation and less predictability, as shown in Figure 1.14. Optimal design in the only solution.
Note that the maintenance process dictates target wear rates:

The Maintenance Process

\[ \downarrow \]

(dictates)

Refractory

Life

\[ \downarrow \]

(dictates) Target

Wear Rate

Target Wear Rate = \(\frac{\text{original thickness} - \text{final aim thickness}}{\text{target life}}\)

For example – a BOF trunnion brick - \((765-300) / 1200\) - 0.38 mm/ht.

* The target wear rate is NOT dictated by refractory but by the process owner.*

The target wear rate also assumes risk tolerance – thickness aim can be based on risk aversion to breakouts and/or thermal loading on the vessel shell.

At the end of the day, the refractory lining is a protective layer for the process vessel and allows the process, any process (e.g., steelmaking, petrochemical, lime kiln, etc.), to run and make product for a given industry. The goal of the lining therefore is threefold for any refractory from a productivity point of view:

- Be transparent to the process
- Meet targeted life of vessel
- Meet targeted wear rates
1.2 Total Cost of Ownership (TCO)

Total cost of ownership (TCO) is an analysis methodology that tries to capture all of the costs associated with a refractory in use from purchase to disposal including the impact to the process itself. From a basic point of view, it starts with what is the total cost/tonne of refractory including all costs (refractory, process, etc.) and divided by the total tonnage produced. An example of a TCO for the BOF furnace that will be used to demonstrate how these calculations are done and what the actual impact is as follows.

There are six major areas:

1. Actual main refractory purchase
2. Logistical costs
3. Installation and demolition costs
4. Refractory maintenance costs
5. Refractory energy costs
6. Operational impact

Refractory Material Purchase

The first and most obvious cost and the one that draws the most attention is the purchase cost itself. This can represent “sticker shock” in some cases whereby a BOF lining can be over $1M in a one time purchase. Therefore it will always draw attention of those in the purchasing process as an area of opportunity to drive down costs.

This purchase cost is then broken down by the following equation:

$$\text{Total price of the refractories (}) = \text{wt. of material needed (kg)} \times \text{price of the material ($/kg)}$$

The weight of the material needed is a function of the design of the vessel, and the only way to change this is to make the lining thinner in areas in which it has low wear – without risking undermining other areas, as presented in Figure 1.15.

![Fig. 1.15: Localized wear due to varying material thickness](image-url)
The price of the material is the other variable, and this is influenced by the material selected (e.g., fused grain, material purity, supplier, etc.). Note that the materials must always be chosen first to match the Thermal Mechanical and Chemical (TMC) design analysis (to be discussed in a later chapter) and not to have a lower price per kg for low price purposes only! This will always be a key pressure point with people who purchase the refractories with a mindset of it being a commodity rather than an engineered material. (Which of course we know it is not!)

* There is always a trade-off between performance and cost. See Figure 1.16 as an example. As the purity increases, the price per kg rises exponentially. This is true for most components, i.e., MgO, graphite, etc.

![Price vs Material Purity Graph](image)

**Fig. 1.16: Effect of material purity on price**

The final part of this equation is of course the cost/tonne of refractories following the equation:

\[
\text{Cost/tonne} = \frac{\text{Cost of the refractories (\$)}}{\text{Tonnes of steel produced through the campaign. The tonnes of steel produced - # of heats made X average heat size}}
\]
Therefore, in order to reduce the cost/tonne, there are only three options:

1. Reduce the cost of the refractories (as presented previously)
2. Increase the campaign life or # of heats on the production unit (longer life) - (less downtime)
3. Increase the average heat size (usually restricted by design of vessel or cranes)

In the case of design all three options have been and continue to be utilized:

1. Example – redesigning the materials in a BOF in low wear areas or in the ladle slagline (lower purity MgO, lower purity graphite, etc.), which maintains heat life and heat size but lowers the initial cost.
2. Example – redesigning an EAF bottom to go from 500 heats to 1200 heats through a change in construction with the same brick sizing and costs but longer life leading to a lower cost/tonne.
3. Example – redesigning a ladle to increase average heat size – thinner safety linings, higher ladle shell-same life of the ladle, same refractory cost – but lower cost/tonne.

All options are available, although some are more restricted based on steel plant design itself.

Logistical Costs

Logistical costs are those associated with transport, storage and administration.

1. Transport costs – these are the costs associated with getting the product from Japan, Europe, China or Canada to a plant. It would naturally be assumed that the closer the manufacturing plant, the lower the costs – but that is not always true. For instance, there was an example in which brick brought up from the southern USA by truck to Canada was more expensive than brick brought from Europe by boat! When you are sending out a quotation it is good to ask for the delivered price (FOB steel plant) rather than the price at the supplier’s warehouse (FOB point of manufacture).

2. Administration costs – these are the costs associated with paperwork, administration, etc. If you are dealing with a small supplier with unsophisticated systems – more paperwork, etc., you will have more costs associated with the order. Another good example is if you put the material on a $/t program or consignment. The supplier is then responsible for it and you don’t have to count it, leading to less people in a logistics group and possible savings.

3. Storage costs – these are costs associated with having a large inventory stored anywhere, carrying costs of financing the warehousing. A lot of suppliers store material at a local warehouse and must pay a fee for this, which is built into the price. Ideally you can store at a steel plant, but this costs money as you usually pay when the material arrives on site. Also too much storage leads to safety issues when there is not enough room – poor housekeeping. The ideal state is for the manufacturer to make it, ship it and install immediately – no stock anywhere in the system. This allows for lower prices, as the cost is eliminated, but it also increases risk that if there is no inventory and there is a manufacturing problem or a transportation issue, a major problem with shortage can result. A good example is that a brick for the BOF which comes from China to the US, could get stuck in Seattle during a dock strike causing a major panic that would have to extend the BOF life with gunning until the brick arrived.

Installation and Demolition Costs

Installation and demolition costs are costs associated with the installation of the initial lining by the masonry group (whether internal or contractor) and the costs to demolish and dispose of the final end product of the campaign.

1. Installation costs – these are the costs associated with bricking the furnace itself with a basic formula as below:

\[
\text{Installation cost} = \# \text{ of people to install} \times \# \text{ of hours/person} \times \$/\text{hour}
\]

In order to reduce this cost, you can only (in reference to the three options) make the job simpler and faster in order to decrease the number of people or the time it takes or you can use people who charge a lower labour rate.
From a design point of view, a furnace can be designed with a varying amount of brick types and panels in order to either achieve optimal wear patterns or to speed up the bricking time. Some areas may be over-specified as an over-designed multiple panel lining could make bricking time much longer. The number of panels used usually depends on whether the furnace is a bottleneck operation or not.

Another example of an installation cost is the ladle bottom, which is a two piece precast bottom (as opposed to per piece bricking) used to minimize bricking time and to help in ergonomic safety (balance of safety, cost and speed).

2. Demolition costs – these are the costs associated with tearing out the used refractory. The basic cost formula is described as follows:

\[
\text{Demolition cost} = \# \text{ of hrs. to demolish} \times \text{X$\,\text{hour}} + \text{Disposed tonnes} \times \$\,\text{tonne}
\]

To reduce this cost you can only make the job simpler and faster in order to decrease the time it takes. This is normally a minimal cost in the big picture so it is not looked at too closely.

Also associated with this is the cost of disposal of the material. Many refractories can be recycled or externally sold (MgO-C brick sold as a recyclable product) or landfill (if there is no demand for recycled product, it is paid to be landfill based on a price / tonne). However, it can be a significant cost. An example is magnesia chrome brick in which the chrome oxide in the brick changes valency during steelmaking and then may become a danger to the environment as it may leach into the water if stored in a regular landfill. The material must be disposed of as a hazardous waste, which is very expensive. Therefore, this material can be designed out of the system to eliminate this cost as well as providing an environmental positive.

**Refractory Maintenance Costs**

Operations can be very volatile and refractory wear will follow suit based on process parameters. Refractory maintenance / patching is applied to working linings when they experience higher than expected wear rates. Patching is applied to help the working lining achieve desired targets.

This section includes gunning and patching materials.

1) Cost to Install Material

   A) Equipment
      - A company has the choice to own gunning and shotcreting equipment, however, unless you have the expertise internally, one may move away from this because the maintenance is complicated and expensive.
      - You also have the option to rent / lease the machines from suppliers with a full service contract where they service the equipment and guarantee availability.
B) People - there are three options for who can do gunning and/or shotcreting and/or patching:
   1. Internal – Upside is skill level of team but downside is additional people that are required who do not have ownership of the process.
   2. Operators – Downside is the need to gain the skills but upside is to prevent downtime.
      The operators can take ownership of the furnace. It is actually a motivation to maintain a stable process to keep their own workload down. Otherwise they could take a break while the furnace is being gunned by internal personnel or contractors. There is also a cost savings because operators are being paid to be there anyway.
   3. Contractor – Some plants have the contractors do all of the gunning.
      This ends up being more expensive than having your workforce complete the work in some cases. Also, the same logic as masonry completing the work applies: operators will take ownership if they have to gun the furnace themselves.

2) Cost of Material

Refer to the same Equation from Part A), outlined as follows:

This purchase cost is then broken down by the following equation:

\[
\text{Cost of the refractories (\$) = wt. of material needed (kg) X price of the material (\$/kg)}
\]

Weight of Material
- There is balance between taking care of the furnace and minimizing the time until it’s in service again.
- The operators used to judge by eye to determine where the patching material would go. Normally, operators would gun the furnace in multiples of the number of bags regardless of what the furnace actually required.
- Today, the laser is the operator’s greatest tool. It highlights the thinnest areas of the lining and the operators gun on the target areas.

Price of the Material (\$/kg)
- The price of the material is the other variable and this is influenced by the material selected (e.g., fused grain, material purity, supplier, etc.). Note that the materials must always be chosen first to match the TMC design analysis (to be discussed in chapter 2), and not to have a lower price per kg for low price purposes only!
- Suppliers may try to change the gunning material and then add a cost each time they change materials to increase their profit margins. Controlled trials must be done to justify extra expenses in order to lower the actual \$/tonne.
- The only way to justify the price increase is if we design to the TMC or increase the expected life.

**Refractory Energy Costs**

Heat Up / Dry Out
- Any new lining must be heated up in order to remove moisture, impurities and resins and to get the lining up to process temperature.

\[
\text{Total Cost of Energy (\$) = Total number of hours of dry out X Energy usage per hour X Cost per unit energy}
\]

**Example 1: BOF Ladle Dry Out**

Total Cost of Energy (\$) = 40 hours of dry out X 1000 btu / hr X $ 2 / btu = $80,000 ($80,000 is not the true number)

However, it’s a small amount in the big picture.

**Example 2: BOF Burn In**

**Example 3: EAF Green Furnace Practice.**
Refractory Operational Impact

**Ref**er to Section 1.1 Goal of Availability, to see the instances of when the process is down and the associated impacts.

Note that operational impact costs usually dwarf actual refractory costs. Table 1.4 gives an example of the type of operational impacts one may see but is not all-inclusive, and each operator will have to calculate this for their own furnace.

<table>
<thead>
<tr>
<th>Repair</th>
<th>Frequency</th>
<th>Total Mins</th>
</tr>
</thead>
<tbody>
<tr>
<td>(per year)</td>
<td>Mins/repair per year</td>
<td></td>
</tr>
<tr>
<td>Furnace Relines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom Changes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tuyere Meas./Torque</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laser Readings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taphole - Inserts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tap Pad</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taphole - Pipes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taphole - Faces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taphole - Blocks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mouth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trunnions/etadium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bottom Maintenance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charge Pad - maintenance</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.4: Example of the type of operational impacts on the furnace operation

<table>
<thead>
<tr>
<th></th>
<th>mins per year</th>
<th>mins per month</th>
<th>mins per week</th>
<th>mins per day</th>
<th>mins per hour</th>
<th>$/min Delay cost (validated by Financial Accounting)</th>
<th>Hrs</th>
<th>Hoists per year</th>
<th>Total production delay cost for refractories</th>
</tr>
</thead>
</table>


1.3 Energy and Heat Flow Overview

One of the key goals of refractories is to hold in heat, whether it is a BOF or a boiler. Energy is expensive and once you put it into the process you don’t want to lose it.

There are two key goals for heat:
- Retention for the process
- Protection of the furnace shells from warping/cracking/etc.

It is a fundamental of refractories that these goals must be met, and an understanding of heat flow through a lining is critical.

We should begin with some key definitions:

Thermal conductivity (K) – ability to conduct heat through a material
Heat capacity (C) – the ability of a material to retain heat
Thermal diffusivity (δ) – the ability to diffuse heat through the material
Density (ρ) – Density of a material

\[ \delta = \frac{K}{C \cdot \rho} \]

An example of high conductivity materials versus low is shown in figure 1.17. The faster that you can diffuse heat out of the system, the lower the temperature gradient from the front to the back of the brick, the lower the stress generated for cracking.

A good home example would be the difference between an aluminum frying pan and a cast iron frying pan. The aluminum heats up faster and cools faster – high diffusivity; versus the cast iron, which has a high heat capacity and holds heat, taking longer to heat up and cool down, but retains a steady temperature better.

It should also be noted that there are three ways of moving heat through a system:

1. Conduction

\[ Q = \frac{a \cdot x \cdot (t_1 - t_2)}{K} \]

Q = heat flow
a = surface area
x = distance travelled (thickness)
t = time
K = conductivity constant of the material

Therefore, in the simplest terms, the amount of heat flow through a wall (assuming the wall size doesn’t change) is mainly determined by the thickness of the material and the conductive ability through the material. Note also that the conductivity of a product is a function of two key elements – the raw material used and the percent porosity (which is an insulator).
Insulating materials have low thermal conductivities, while some other refractories (e.g., MgO-C) have high thermal conductivities. See chart in Figure 1.18.

Fig. 1.18: Thermal conductivity of various refractory bricks (after Rub and Spotts McDowel)

It should be noted that conductivity in relation to heat loss is a direct correlation with temperature (T).

2. Convection

Convection is the second mode of heat movement and involves movement of a fluid over the outside surface to take away the heat more or less quickly.

Convection may be natural (a steel ladle in the air) or may be forced (water sprays on the outside shell of a blast furnace).

For natural convection the regular equation used is:

\[ Q = 0.7 \left( \frac{1}{T_{\text{air}}} \right)^{0.15} (T_{\text{outside shell}} - T_{\text{air}})^{1.27} \]

The greater the difference between the shell temperature and the ambient, the faster it will naturally cool. This makes sense as ladles cool faster in winter than the summer by approximately 50%.

Forced convection has a higher cooling factor as the cooler air / water is forced across the shell to remove heat quickly. The equations and factors become much more complex and will not be discussed here, except to say that the relationship between convection and temperature is closer to \( T^{1.5} \) ... better than conduction but lower than radiation.
3. Radiation

Radiation is actually the fastest method of heat removal and is governed by the equation:

\[ Q = (5.67 \times 10^{-8}) \ v (T_{\text{outside shell}}^4 - T_{\text{air}}^4) \]

\( v \) - emissivity of surface

What is important to note here is that the relationship between radiation and temperature is \( T^4 \), which is much higher than either conduction or convection.

A good example where this is applicable is steel ladles. With energy prices continuing to increase, steelmakers are constantly trying to preserve the temperature added into the ladle. Many times the focus is first on the safety lining of the ladle to increase its insulation factor; however, since it is only related to temperature directly, it would be more effective to focus on keeping the ladle covered at all non-processing steps as radiation losses are to the exponent of four!

**Thermal Modeling**

It should be noted here that heat flow calculations can be done “old school” (by hand), or by spreadsheet (see example in Table 1.5) or even by computer models.

<table>
<thead>
<tr>
<th>Table 1.5: Example of computer heat flow analysis – Ladle thermal analysis in three layer refractory lining</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>DATA</strong></td>
</tr>
<tr>
<td>Ladle Radius (Inside Steel Shell)</td>
</tr>
<tr>
<td>Working lining thickness (in)</td>
</tr>
<tr>
<td>Safety lining thickness (in)</td>
</tr>
<tr>
<td>Permanent lining thickness (in)</td>
</tr>
<tr>
<td>Height of Slagline (in)</td>
</tr>
<tr>
<td>Safety lining conductivity (W/mK)</td>
</tr>
<tr>
<td>Permanent lining conductivity (W/mK)</td>
</tr>
<tr>
<td>Steel shell conductivity (W/mK)</td>
</tr>
<tr>
<td>Steel temperature (deg. C)</td>
</tr>
<tr>
<td>Outside Air temperature (deg. C)</td>
</tr>
<tr>
<td>Film coefficient (cold face/slab)</td>
</tr>
<tr>
<td>Film coefficient (cold face/shell)</td>
</tr>
<tr>
<td>Film coefficient (outside shell)</td>
</tr>
</tbody>
</table>

**CALCULATIONS**

| **Total resistance (R)** | 0.00805 | 0.00847 | 0.00859 | 0.008595 | 0.008595 | 0.008595 |
| **Resistance in hot face** | 0.001664 | 0.00192 | 0.00192 | 0.00192 | 0.00192 | 0.00192 |
| **Resistance in layer 1** | 0.00105 | 0.00105 | 0.00105 | 0.00105 | 0.00105 | 0.00105 |
| **Resistance in layer 2** | 0.001569 | 0.001569 | 0.001569 | 0.001569 | 0.001569 | 0.001569 |
| **Resistance between shell** | 0.000674 | 0.000674 | 0.000674 | 0.000674 | 0.000674 | 0.000674 |
| **Resistance in layer 3** | 0.000604 | 0.000604 | 0.000604 | 0.000604 | 0.000604 | 0.000604 |
| **Resistance in outside shell** | 0.000628 | 0.000628 | 0.000628 | 0.000628 | 0.000628 | 0.000628 |
| **Total Heat Flow (W)** | 200629 | 215597 | 231372 | 396793 | 410966 | 438895 |
| **Steel temperature (deg. C)** | 1630 | 1630 | 1630 | 1630 | 1630 | 1630 |
| **Temperature at W/S/L interface (deg. C)** | 1205 | 1286 | 1402 | 1159 | 1259 | 1372 |
| **Temperature at S/S/L interface (deg. C)** | 888 | 926 | 1032 | 520 | 564 | 614 |
| **Temperature at S/L/L interface (deg. C)** | 472 | 537 | 547 | 520 | 564 | 614 |
| **Temperature at S/S interface (deg. C)** | 337 | 352 | 389 | 371 | 402 | 437 |
| **Temperature at outside shell (deg. C)** | 330 | 354 | 381 | 383 | 393 | 427 |
Some key notes are:

- One dimensional models are basic and can only give a “gut feel” for actual thermal flow results.
- Two dimensional models are the ones usually done and give a good approach to the problem. For cylindrical vessels like ladles, the cylindrical equations should be used as shown previously, which yields a better result.
- One of the key assumptions in all modeling is the film coefficient for convection – these are best back-calculated off of actual thermal scans that give the outside shell temperature as they are not readily available and accurate. In other words, use these as the variable to fine-tune your model.
- Most models will always give steady state results, however, in real life steelmaking, since it is a batch process, steady state is rarely reached! Always take this into account so that you don’t over design the insulation required.

**Design of Linings for Thermal Implications**

Lining design is a balance (as is everything in refractories) between three key areas – heat flow (shell protection, thermal losses), insulation material strength (lining integrity) and chemical wear (higher corrosion).

Table 1.6 gives the pros and cons for different insulation types, although many are used in combination.

<table>
<thead>
<tr>
<th>Material</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
</table>
| Brick    | - High strength stable lining  
           - Properties well determined as installation variability removed  
           - Can have the refractoriness to run the process on if designed that way | - Thicker than boards or blankets, which may take up vessel capacity  
           - Brick joints can be sources for metal penetration in liquid carrying vessels  
           - Required skilled tradespeople to install |
| Monolithic | - High strength stable lining, properties can be compromised with installation variability  
            - If installed properly, there are no joints for metal penetration | - Thicker than boards or blankets which may take up vessel capacity  
            - Required skilled tradespeople to install |
| Board    | - Medium strength, better than blanket  
           - Can be made thin in order to gain vessel capacity  
           - Easy to install | - Strength may not be high enough depending on process temperatures leading to material degradation and loss of insulation and lining support  
           - Little refractory value and joints, possible metal penetration |
| Blanket  | - Can be made thin in order to gain vessel capacity  
           - Easy to install | - Little strength, which may lead to material degradation and loss of insulation and lining support  
           - Little refractory value, possible metal penetration |
| Micro-board | - Can be made very thin in order to gain vessel capacity  
             - Easy to install | - Little strength, which may lead to material degradation and loss of insulation and lining support  
             - Little refractory value and joints, possible metal penetration |
One final issue to discuss is the balance between shell temperatures and chemical corrosion.

- As you increase the amount of insulation, you will increase the temperature of the lining and therefore the wear increases exponentially.
- However, as you increase the amount of insulation the shell temperature will decrease.

Therefore, as stated before, designing refractories is always a balance, as shown in Figure 1.19.

![Figure 1.19: Balance of insulation on a lining](image)
1.4 Quality - Inert to the Steel Process

End User Demands

The demand from final customers (automotive, packaging, etc.) for thinner, lighter high strength steels will continue. This translates into a need for “cleaner steel” production, which in turn dictates the need for a decrease in the size and quantity of inclusions in the steel. From a refractory point of view, the need for refractories to be inert to the steel is the minimum. In the future the ability of the lining to clean the steel of impurities will become imperative. Key demands are:

1. No pickup of undesired chemical elements (e.g., C for E-ULC products <30ppm).
2. No re-oxidation of the refractory into the steel (e.g., silica).
3. Minimize inclusion size of de-oxidation products (e.g., alumina).
4. No formation of liquid oxides that could become detrimentally solid in the final steel product.
5. Active cleansing of the oxidation products (lime based refractories that can absorb alumina inclusions).
6. Refractory systems that prevent air entrainment and/or nitrogen pickup.
7. Minimize inclusion size in the final product (D&I cans, ball bearings) must be <20 microns (and possibly 10 um) in the future which is encroaching on the technological minimum. Figure 1.20 shows an example of the decreasing weight and therefore thickness of D&I tin cans over the past 30 years.

From the previous notes, chemical/physical interactions with the refractories themselves should not lead to any pickup of undesirable elements (e.g., carbon for ULCs or oxides from the lining leading to inclusions).

Refractory producers must be active in helping the steel companies manufacture products that meet their customers’ stringent demands.

Carbon Pickup

There is much debate about this topic in literature vs. reality, as seen in Figure 1.21.
Steel Ladle Brick – Carbon Pickup

Theory #1
Magnesia carbon brick has 15% C + 3% resin binder. The C from the brick will be absorbed by the steel in a ULC product as it is so low that it will immediately grab any C available to it.

Theory #2
The surface of the ladle brick is exposed to air ~75% of the time the ladle is in service. During this period of time a 5 mm deoxidized layer (approx.) is formed on the surface. Since there is no C available on the surface that touches the actual steel, then 0% C pickup is actually experienced.

Fig. 1.21: Theories about C pickup from ladle MgO-C bricks into steel

1. The diagram in Figure 1.21 shows the two current theories on C pickup from steel during processing.

2. In order to have C pickup it is necessary to have:
   • free C available on the surface in contact with the liquid steel
   • very low levels of C in the steel to promote absorption (driving force)
   • reducing atmosphere so C isn’t oxidized first

3. The reality is that each plant/steel grade combination will be different and you must test actual samples yourself.

Inclusion Formation from Dislodging of Refractories
   It is possible for pieces of refractory to be dislodged from the linings – usually due to spalling of either small or large chunks.
   However it is extremely rare that these pieces ever end up in the steel itself, even if dislodged from the SEN due to Stokes law. Stokes law states that the velocity of an ascending spherical inclusion is

\[ v = \frac{2gr^2(p_r - p_i)}{9\eta} \]

Where:
- \( r \) is the radius of the sphere,
- \( p_r \) is the density of the steel,
- \( p_i \) is the density of the inclusion, and \( \eta \) is the coefficient of viscosity for the steel.
- Since the density of most refractories is around 2.5g/cm³ and steel is 7.0g/cm³, velocity is very high for floating.
- The factor after this is the radius of the sphere, which is a squared phenomenon, so as spalled pieces are bigger and bigger they will float out extremely quickly. Table 1.7 shows work to correlate defect size/type and its effect on final customer products.
- From the literature it is known that inclusions in the steel are rare to find at >500 microns in size (or 0.5 mm); therefore spalled pieces of refractory at 25 mm or more will have flotation time in the range of seconds and will rarely be seen.

### Table 1.7: Correlation between defect size/type of inclusions and the effect on the final product

<table>
<thead>
<tr>
<th>Type of Inclusion</th>
<th>Size of inclusion (microns)</th>
<th># of inclusions in one heat</th>
<th>Potential Product Impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle Sand</td>
<td>&gt;100</td>
<td>Rare</td>
<td>All products</td>
</tr>
<tr>
<td>Clogging in Tundish/</td>
<td>50-100</td>
<td>&gt;100</td>
<td>Most products</td>
</tr>
<tr>
<td>Mould powder</td>
<td>50-100</td>
<td>&gt;100</td>
<td>Most products</td>
</tr>
<tr>
<td>Tundish slag</td>
<td>20-50</td>
<td>&gt;100</td>
<td>Mainly for bearing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>grades or Drawn and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron cans</td>
</tr>
<tr>
<td>Reoxidation in Mould</td>
<td>20-50</td>
<td>&gt;100</td>
<td>Mainly for bearing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>grades or Drawn and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron cans</td>
</tr>
<tr>
<td>Deoxidation in Ladle</td>
<td>&lt;10</td>
<td>&gt;1000</td>
<td>Mainly for bearing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>grades or Drawn and</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron cans</td>
</tr>
</tbody>
</table>

### Inclusion Formation from Reaction with Refractories
- Inclusions can be formed by interaction of the refractory and the steel itself.
- The first type is one that happens naturally and not by design.
- This is mainly influenced by Gibbs free energy (Figure 1.22): the issue is that the refractory must be designed not to break down in service – that is, that the oxide does not break down releasing free oxygen into the system, which combines with Al in the steel, forming alumina that is detrimental to the final product.

![Fig. 1.22: Free energies of formation of simple oxides vs T, per equivalent (Ref.23)](image-url)
- From the diagram we can see that at steelmaking temperatures (1600-1700°C), oxides that are unstable and have Gibbs free energy between 0 and 150 kJ/eq are silica, chromic oxide and iron oxide.
- There are many studies that show that in the early days of Steelmaking and as late as the 1980s, ladles that had higher free silica (clay based ladles between 50-70% silica) would have lower steel cleanliness.
- Based on this work, steelmakers have always aimed for all barrel refractories to have greater than 70% Al2O3 and to minimize free silica.
- For shops making very clean steels, they will specify only basic lining materials (MgO and CaO based) due to this phenomena.
- The move to AMC/MAC brick in the industry continues to move us in the direction of non-reactive refractories.
- This is also critical in the tundish spray lining that touches the steel. Currently many linings contain 30% silica, however, the linings are olivine based so the silica is not free and does not devolve at steelmaking temperatures.
- Work has been done on tundish powders with basic fluxes that actually will clean up the steel by absorbing alumina from the bath. Work done by P. Rasmussen (Fig. 1.23) shows that free oxygen in the steel can be lowered from 23 to 20 ppm by the use of basic fluxes.
- The second type of interaction is one that is on purpose and materials that are designed to interact with the steel (e.g., “slippery” SENs).

- Inclusions can be formed by interaction of the refractory and the steel itself and in some cases this is promoted.
- An example is as previous with the tundish powder.
- Another example is “slippery SENs” or “slippery nozzles”. In these cases, the refractory is set up to have free lime (CaO) in the mix in order to promote a reaction between the alumina in the steel and the free lime according to the phase diagram presented in Figure 1.24.

![Phase Diagram](image)

**Fig. 1.24:** Binary phase diagram CaO-Al₂O₃

*Fig. 12715-System CaO-Al₂O₃. (A)-(B) Calculated phase diagrams.*


By permission of The American Ceramic Society
It is well known that lime and alumina have low melting points, so solid alumina can be reacted to become liquid calcium aluminate and then prevents clogging in the bore of the nozzle or SEN at the caster.

Though this reaction is good for clogging it may not be good for the final product. Where does this calcium aluminate go? Based on Stoke’s law, if cast speed is not too fast, it may float out into the mould powder and it is positive. If it doesn’t have time to float out there may be a defect in the steel, depending on the final customer product. This is part of what is now called “inclusion engineering” for steel shops!

Therefore, you can use refractories to clean up steel, but it must be in a very controlled manner!

### Inclusion Formation from Air Ingress with Refractories

Another key area of control that is not particularly refractory related – but is system related is that of air ingress.

Once steel is clean and everything floated out, the last thing you want is to have the steel exposed to air and picking up both oxygen (turning into alumina) and nitrogen. This is a key function of the ladle gate system and the tundish flow control system.

Key areas are presented in Table 1.8.

<table>
<thead>
<tr>
<th>Area</th>
<th>Issue</th>
<th>Control mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ladle slidegate system</td>
<td>Air ingress between the ladle slidegate plates</td>
<td>- High face pressure to limit any gaps</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Control of steel fins in the plates and removal so that fins do not form</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wedges to open up the system to air</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Argon gas put into the gate to shroud it so that air cannot get in</td>
</tr>
<tr>
<td></td>
<td>Air ingress between the plates and the upper nozzles</td>
<td>- Good long life refractory (clay based) gasket with C to give tight seal and</td>
</tr>
<tr>
<td></td>
<td></td>
<td>prevent any steel breakout through this joint</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Argon gas put into the gate to shroud it so that air cannot get into steel</td>
</tr>
<tr>
<td></td>
<td>Air ingress between the lower nozzle and ladle shroud</td>
<td>- Lots of work done in this area – key areas to look at are:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Geometry of nozzle, shroud connection to match seal</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Material for the seal</td>
</tr>
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<td></td>
<td></td>
<td>- Oxygen cleanout between heats</td>
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<tr>
<td>Tundish flow control system</td>
<td>Air ingress through the stopper rod</td>
<td>- The stopper rod, though it looks solid, may have a hole down through the</td>
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<tr>
<td></td>
<td></td>
<td>center for the hook up mechanism and for Ar supply into the steel stream</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Key points are around the sealing design at the top connection point to prevent</td>
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<tr>
<td></td>
<td></td>
<td>any air ingress</td>
</tr>
<tr>
<td></td>
<td>Air ingress through the gates system</td>
<td>- There are two joints in the gate mechanism – the first between the nozzle</td>
</tr>
<tr>
<td></td>
<td></td>
<td>and the plate and this is filled with mortar</td>
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<td></td>
<td></td>
<td>- The upper plate itself can have air ingress if the plate cracks and the vacuum</td>
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<tr>
<td></td>
<td></td>
<td>formed by the high speed of casting will suck air into through the crack</td>
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<td></td>
<td></td>
<td>- The plate also has a notched groove for argon if there is a crack to protect</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ingress</td>
</tr>
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<td></td>
<td>Air ingress after SEN changes</td>
<td>- The second joint in the system between the plate and the SEN itself</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- High face pressure on this joint will limit any gaps for air</td>
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<td></td>
<td></td>
<td>- After SEN changes, this gap is more susceptible to air infiltration and argon is</td>
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<tr>
<td></td>
<td></td>
<td>shrouded into this area to prevent reoxidation of the steel</td>
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</tbody>
</table>
Fig. 1.25: Inclusion control for ladle slidegate and tundish flow control system
1.5 Environment

Chrome Ore

Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Exposure may occur from natural or industrial sources of chromium. Chromium (III) is much less toxic than chromium (VI). Chromium (VI) in soils may pose a risk for dermatitis and a cancer risk from the inhalation of respirable particles. However, naturally occurring particles, such as abraded crystal materials, are unlikely to have a MMAD (mass median aerodynamic diameter) of less than 10 mm, and therefore are far too large to penetrate deeply into the lung. Further, chromium (VI) may well be in water-soluble form, which is either entirely non-carcinogenic or only very slightly carcinogenic.

Chromium (VI) contaminated soils are also thought to pose a risk of dermatitis as it can be absorbed by the skin. The absorption of chromium (VI), from aqueous solutions, by skin is documented in a number of studies. However, unlike aqueous solutions of chromium, soil-bound chromium is not immediately available to be absorbed by the skin; it must first be leached from the soil. As reported in the literature, only a small percentage of the chromium bound in soil is expected to be extractable either as total chromium or as chromium (VI). Therefore, in the case of skin exposure to contaminated soils, the degree of chromium (VI) absorption will depend on how much chromium (VI) can leach from soil.

Chrome ore is found most commonly in MgO chrome brick (MgO – Cr₂O₃) used in R-HOB degassers snorkel materials and other areas in the steel industry.

When brought in from the refractory company, they are harmless, however, when they are heated through the steelmaking process – the Cr valence may change in the presence of alkalis from Cr³⁺ to Cr⁶⁺, which is the bad form from the viewpoint of health. It is used because of its high melting point of 2100°C and also because it contains no carbon. From a metallurgical point of view, steel producers who manufacture ultra low carbon (ULC) steel prefer using refractory lining with MgO-Cr₂O₃ because it does not contain carbon. However, MgO-Cr₂O₃ usually has a higher wear rate than MgO-C brick so it is cost prohibitive depending on the application.

Most plants that have an Ruhrstahl Heraeus Oxygen Blowing (R-HOB) type degrosse with much more surface contact with the brick. Figure 1.26 presents an R-HOB that recirculates the steel from the ladle, up one snorkel, removes the carbon, and then sends the reduced steel back down the other snorkel.
This higher contact with the surface area would be prone to carbon pickup, so this is why they utilize MgO Cr2O3 in order to lower interaction with the final steel product. Work is continuing in the industry to minimize usage of chrome ore.

Radioactivity

NORM is an acronym for naturally occurring radioactive material, which potentially includes all radioactive elements found in the environment. However, the term is used more specifically for all naturally occurring radioactive materials where human activities have increased the potential for exposure compared with the unaltered situation.

Over 95% of the market for zirconium requires it in the form of zircon (zirconium silicate). This mineral occurs naturally and is mined, requiring little processing. It is used chiefly in foundries, refractories manufacture and the ceramics industry. Zircons typically have activities of up to 10,000 Bq/kg of U-238 and Th-232. No attempt is usually made to remove radio-nuclides from the zircon as this is not economical. Because zircon is used directly in the manufacture of refractory materials and glazes, the products will contain similar amounts of radioactivity. Higher concentrations may be found in zirconia (zirconium oxide), which is produced by high temperature fusion of zircon to separate the silica.

Almost all refractories contain low levels of radiation naturally (radioactive elements are in dirt, refractories are just formed dirt). The refractories with higher levels of radiation will set off radiation detectors at the gates of steel plants but are not health hazardous; they are zirconia based (ZrO2 SiO2). The products in which these are found are SENs, EAF deltas, ladle well sand, some brick and some nozzles.

This is more of an awareness issue rather than a health and/or environmental issue.