# Chapter 3

# Steel Plant Refractories

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## 3.1 Classification of Refractories

Refractories are the primary materials used by the steel industry in the internal linings of furnaces for making iron and steel, in vessels for holding and transporting metal and slag, in furnaces for heating steel before further processing, and in the flues or stacks through which hot gases are conducted. At the risk of oversimplification, they may, therefore, be said to be materials of construction that are able to withstand temperatures from 260–1850°C (500–3400°F).

As seen in Fig. 3.l, the melting point of refractory materials in the pure state varies from 1815–3315°C (3300°–6000°F). Refractories in service can tolerate only small amounts of melting
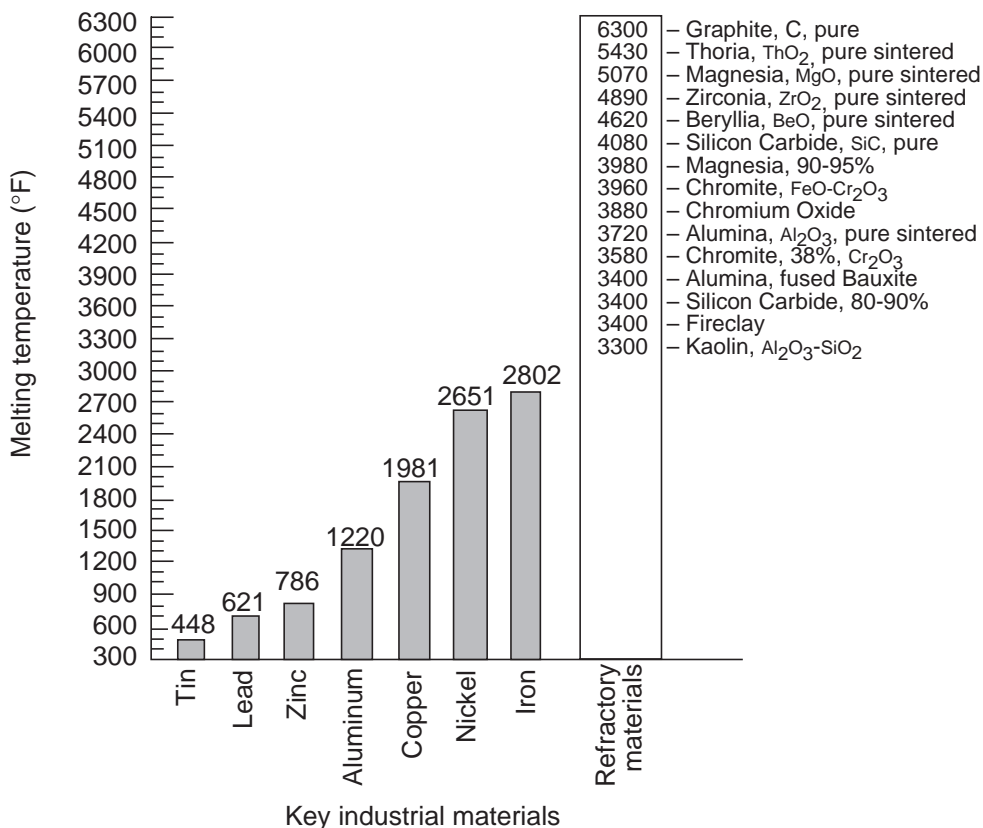


Fig. 3.1 Refractory and industrial materials melting point chart.

(1–5%) without loss of their important structural characteristics. Subsequent discussion will show, however, that the use of many such materials is limited by factors such as cost or instability in certain atmospheres. Also, fluxes present in the initial impure refractory and/or encountered in service can seriously reduce these melting points.

Refractories are expensive, and any failure in the refractories results in a great loss of production time, equipment, and sometimes the product itself. The type of refractories also will influence energy consumption and product quality. Therefore, the problem of obtaining refractories best suited to each application is of supreme importance. Economics greatly influence these problems, and the refractory best suited for an application is not necessarily the one that lasts the longest, but rather the one which provides the best balance between initial installed cost and service performance. This balance is never fixed, but is constantly shifting as a result of the introduction of new processes or new types of refractories. History reveals that refractory developments have occurred largely as the result of the pressure for improvement caused by the persistent search for superior metallurgical processes. The rapidity with which these ever recurring refractory problems have been solved has been a large factor in the rate of advancement of the iron and steel industry. To discuss the many factors involved in these problems and to provide information helpful to their solution are the objectives of this chapter.

Refractories are also vital in the safe operation of the processes and must not expose personnel to hazardous conditions during their manufacture, installation, use or during disposal following their use.

Refractories may be classified in a number of ways. From the chemical standpoint, refractory substances, in common with matter in general, are of three classes; namely, acid, basic, and neutral. Theoretically, acid refractories should not be used in contact with basic slags, gases or fumes whereas basic refractories can be best used in contact with a basic chemical environment. Actually, for various reasons, these rules are often violated. Hence, the time honored chemical classification is largely academic, and of little value as a guide to actual application. Also, the existence of a truly neutral refractory may be doubted. Classifications by use, such as blast furnace refractories or refractories for oxygen steelmaking, are generally too broad and are constantly subject to revision.

For our purposes, refractories will be classified with reference to the raw materials used in their preparation and to the minerals predominating after processing for use. This classification is believed to offer the best possibility for a clear understanding of the origin and nature of steel plant refractories.

## 3.1.1 Magnesia or Magnesia–Lime Group

This group includes all refractories made from synthetic magnesites and dolomite. These constitute the most important group of refractories for the basic steelmaking processes. All these materials are used primarily as a source of magnesia (MgO).

### 3.1.1.1 Magnesia

Modern high-purity magnesias are produced in well controlled processes. The principal sources of magnesias are brines (often deep well type) and seawater. Magnesium hydroxide, $Mg(OH)_2$, is precipitated from these sources by reaction with calcined dolomite or limestone; one source uses a novel reactor process. The resultant magnesium hydroxide slurry is filtered to increase its solids content. The filter cake can then be fed directly to a rotary kiln to produce refractory grade magnesia, but more commonly now the filter cake is calcined at about 900–1000°C (1650–1830°F), usually in multiple-hearth furnaces, to convert the magnesium hydroxide to active magnesia. This calcined magnesia is then briquetted or pelletized for firing into dense refractory-grade magnesia, usually in shaft kilns which reach temperatures around 2000°C (3630°F). The end product is sintered magnesia.

Fused magnesia is produced by melting a refractory grade magnesia or other magnesia precursor in an electric arc furnace. The molten mass is then removed from the furnace, cooled, and broken up to begin its path for use in refractories.

The impurities in magnesia are controlled by the composition of the original source of the magnesia (brine or seawater), the composition of the calcined dolomite or limestone, and the processing techniques. In particular the amounts and ratio of CaO and $SiO_2$ are rigorously controlled, and the $B_2O_3$ is held to very low levels. The end results are high-grade refractory magnesias which are ready for processing into refractory products. Tables 3.1 through 3.4 show the compositions of different grades of magnesia.

**Table 3.1   Selected Sintered Magnesias Produced in North America (high CaO/SiO$_2$ ratio)**

| Reference Code | SM-1 | SM-2 | SM-3 |
|---|---|---|---|
| Chemical Analysis (wt%) | | | |
| CaO | 2.2 | 2.2 | 0.8 |
| $SiO_2$ | 0.7 | 0.35 | 0.1 |
| $Al_2O_3$ | 0.1 | 0.20 | 0.1 |
| $Fe_2O_3$ | 0.2 | 0.20 | 0.1 |
| $B_2O_3$ | 0.015 | 0.02 | 0.005 |
| MgO | 96.7 | 96.3 | 98.8 |
| CaO/SiO$_2$ ratio | 3.1 | 6.3 | 8.0 |
| Bulk Density (kg/m³) | 3400 | 3420 | 3400 |
| Average Crystallite Size ($\mu$m) | ∼ 80 | ∼ 90 | ∼ 100 |

*From Ref. 2.*

**Table 3.2   Selected Sintered Magnesias Produced in Europe and the Middle East (high CaO/SiO$_2$ ratio)**

| Reference Code | SM-4 | SM-5 | SM-6 |
|---|---|---|---|
| Chemical Analysis (wt%) | | | |
| CaO | 1.90 | 0.65 | 0.7 |
| $SiO_2$ | 0.20 | 0.15 | 0.03 |
| $Al_2O_3$ | 0.05 | 0.06 | 0.03 |
| $Fe_2O_3$ | 0.20 | 0.50 | 0.04 |
| $B_2O_3$ | 0.015 | 0.008 | 0.005 |
| MgO | 97.5 | 98.5 | 99.2 |
| CaO/SiO$_2$ ratio | 9.5 | 4.3 | 23.3 |
| Bulk Density (kg/m³) | 3440 | 3450 | 3430–3450 |
| Average Crystallite Size ($\mu$m) | 150–160 | ∼ 100 | 70-90 |

*From Ref. 2.*

**Table 3.3   Selected Fused Magnesia Produced in North America**

| Reference Code | FM-1 | FM-2 |
|---|---|---|
| Chemical Analysis (wt%) | | |
| CaO | 0.95 | 1.8 |
| $SiO_2$ | 0.30 | 0.5 |
| $Al_2O_3$ | 0.11 | 0.2 |
| $Fe_2O_3$ | 0.16 | 0.5 |
| $B_2O_3$ | 0.0025 | 0.01 |
| MgO | 98.50 | 97.0 |
| $CaO/SiO_2$ ratio | 3.2 | 3.6 |
| Bulk Density (kg/m³) | 3530 | 3500 |
| Average Crystallite Size ($\mu$m) | ~ 780 | ~ 800 |

*From Ref. 2.*

**Table 3.4   Selected Sintered Magnesias Produced in North America (low $CaO/SiO_2$ ratio)**

| Reference Code | SM-7 | SM-8 | SM-9 |
|---|---|---|---|
| Chemical Analysis (wt%) | | | |
| CaO | 0.7 | 0.80 | 0.9 |
| $SiO_2$ | 0.7 | 0.60 | 2.1 |
| $Al_2O_3$ | 0.1 | 0.20 | 0.15 |
| $Fe_2O_3$ | 0.2 | 0.20 | 0.35 |
| $B_2O_3$ | 0.1 | 0.10 | 0.23 |
| MgO | 98.2 | 98.05 | 96.2 |
| $CaO/SiO_2$ ratio | 1.0 | 1.3 | 0.4 |
| Bulk Density (kg/m³) | 3330 | 3340 | 3260 |
| Average Crystallite Size ($\mu$m) | 50-60 | ~ 60 | ~ 40 |

*From Ref. 2.*

High purity is quite important because MgO has high refractoriness and good resistance to basic slags. Minimizing the total impurities content in magnesias is quite important because impurities affect refractoriness and performance. A high $CaO/SiO_2$ ratio, preferably 2:1 or slightly higher, is optimum for maintaining high refractoriness in magnesias. As the total impurities are reduced to about 1% or less, the $CaO/SiO_2$ ratio has less and less significance. High density reduces infiltration and dissociation of magnesia grain by slag. Large crystallite size (best achieved in fused magnesias) provides less surface area for slag attack. Low $B_2O_3$ content ensures high strength at elevated temperatures for burned brick. Low lime to $SiO_2$ ratios are required in certain products where MgO is used with other raw materials (such as $Cr_2O_3$) or for maximum resistance to hydration.

### 3.1.1.2 Dolomite

The natural double carbonate dolomite ($CaCO_3 \cdot MgCO_3$) can be converted to refractory dolomite ($CaO \cdot MgO$) by high temperature firing. A limited number of dolomite deposits exists in the world with satisfactory uniformity, purity, and calcining behavior to be processed into high purity, refractory dolomite at a reasonable cost. High purity dolomite is greater than 97% CaO + MgO and