

Ferrous metal production and ferrous slags

2

2.1 Introduction

Ferrous, which is different from ferric in chemistry, means iron related, especially iron with a valance of 2 (Fe^{++}) that exists as oxidation state (FeO). Ferrous metals, in general, refer to iron and steel materials. Steel is the major ferrous metal, an alloy of iron and carbon, and is widely used in construction and other applications. Modern steelmaking is an integrated process consisting of blast furnace (BF) ironmaking and basic oxygen furnace (BOF) or electric arc furnace (EAF) steelmaking. Molten steel from BOF or EAF process can undergo a secondary refining process in a ladle furnace, or be sent directly to the continuous caster. During ironmaking, when smelting ore, iron scrap, coke, and flux, BF slag is formed and subsequently discharged. Steel slag is formed and discharged when smelting iron, steel scrap, and flux during the steel-making process. After molten slag is discharged, being air-cooled, or treated under different cooling regimes and processed, slag products for various applications can be produced. Fig. 2.1 is a flow chart to present the iron- and steelmaking processes and the types of slag generated from each stage.

As indicated in Fig. 2.1, the raw materials used in the BF-BOF system include iron ore, coal, fluxes (mainly limestone and dolomite), recycled steel scraps, and alloys. On average, this process uses approximately 1400kg (3086lb) of iron ore, 800kg (1764lb) of coal, 300kg (661 lb) of flux, and 120kg (265lb) of recycled steel to produce 1000kg (2205lb) of crude steel. The EAF process uses primarily recycled steel scraps and electricity. On average, the recycled steel-EAF process uses 800kg (1764lb) of recycled steel, 16kg (35lb) of coal, and 64kg (141 lb) of flux to produce 1000kg (2205lb) of crude steel (World Steel Association, 2014). To make final steel products, other materials may be used, which include manganese, silicon, nickel, chromium zinc, tin, and tungsten.

Unlike manufactured engineering materials, which are produced under quality control required by technical specifications and supplied on demand, ferrous slag is produced as a coproduct simultaneously with iron- and steelmaking and is generated daily. A considerable amount of ferrous slag is produced each year in the world. As the amount of slag tapped from the furnaces is not normally routinely measured and not all of the ferrous slag formed is tapped during a heat, the ferrous slag output levels are normally broadly estimated based on the typical slag to metal production ratios, which in turn are related to the chemistry of the raw materials to the furnaces. For typical high iron ore grades (60–66% iron), a BF normally produces approximately 0.25–0.30 tonne (0.28–0.33 ton) of slag per tonne (ton) of crude iron produced. For lower grade ores, the slag output will be higher, in some cases as much as 1.0–1.2 tonne (1.1–1.32 ton) slag per tonne (ton) of crude iron (USGS, 2013).

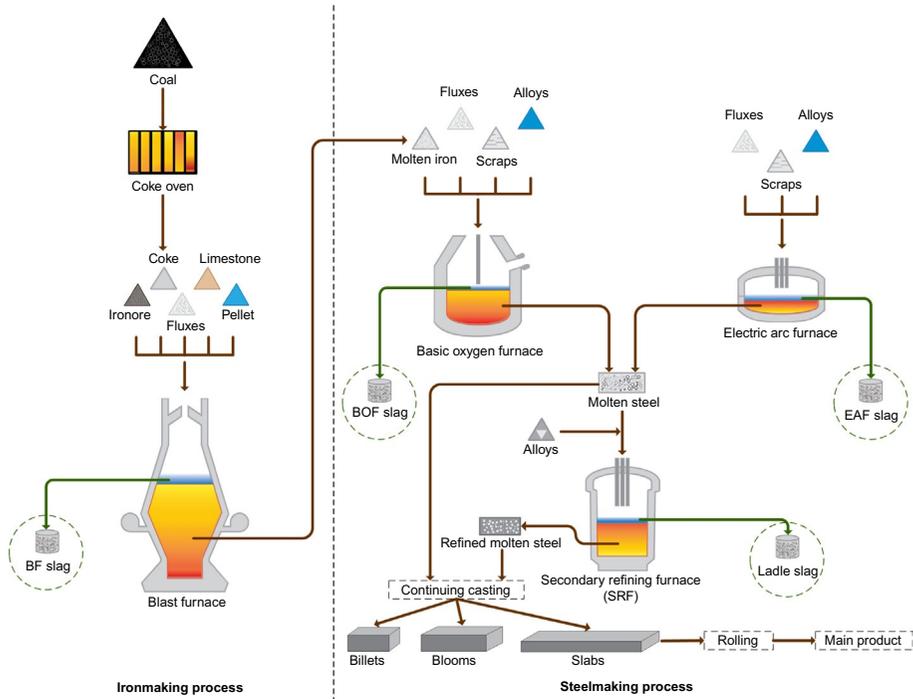


Fig. 2.1 The integrated iron- and steelmaking process and ferrous slag generation.

Adapted from Yildirim, I. Z., & Prezzi, M. (2011). Chemical, mineralogical, and morphological properties of steel slag. *Advances in Civil Engineering*. <http://dx.doi.org/10.1155/2011/463638>.

Steel furnaces typically produce approximately 0.2 tonne (0.22 ton) of slag per tonne (ton) of crude steel. However, up to 50% of this slag is entrained metal, most of which is recovered during slag processing and returned to the furnaces. The amount of marketable steel slag after processing entrained metal is usually between 10% and 15% of the crude steel output (USGS, 2014).

On the other hand, steel will continue to be the most commonly used structural and functional materials in terms of quantity in the future. From 2012 to 2013, the world crude steel production increased by 4.0%. The output of crude steel had increased from approximately 200 million tonnes (220 million tons) in 1950 to 1600 million tonnes (1760 million tons) in 2013 (World Steel Association, 2014). Based on the slag to metal production ratios and the ferrous metal production, the estimated ferrous slag generated in the world in 2013 was approximately 600 million tonnes (660 million tons), which includes 408 million tonnes (449 million tons) of BF slag and 193 million tonnes (212 million tons) of steel slag. Iron BF slag and steel slag make up the largest portion of the slag family, which includes nonferrous slag and nonmetallurgical slag.

In terms of the properties, solidified ferrous slag is a nonmetallic and energy-containing by-product and possesses some chemical, physical, and mechanical properties

that match or are similar to those of some natural or manufactured engineering materials. In addition, due to some special characteristics of ferrous slag, there exists the possibility of altering or modifying physical and chemical properties of the conventional engineering materials to produce special construction materials that can be utilized for special applications. With increasing concern about sustainable development, greenhouse emissions, and emphasis on materials reduction, reuse, and recycling, it is critical that the full potential of the use of ferrous slag is developed to reduce potential environmental impacts and for natural resources sustainability, with financial return, rather than disposal costs. Processed BF, BOF, and EAF slags are being considered to be conventional or nontraditional construction materials. The availability and properties of ferrous slag open avenues for potential engineering utilizations, and also bring scientific, technical, and managerial challenges to people in developing various optimal applications.

2.2 Ironmaking process and BF slag formation

Ironmaking is to convert iron ore or other iron-bearing materials into a form that can be easily transformed into steel. This is done primarily in a BF with other auxiliary facilities to smelt the raw materials, *burden*, to make crude iron that contains high carbon content of approximately 4–5%. This high carbon content makes iron very hard but brittle and limits its use. Steelmaking furnaces are used to make different types of steel that contain lower carbon content, usually less than 1%, and alloys.

2.2.1 Overview of ironmaking

The raw materials charged to a BF consist of iron ore, coke, fluxing stone, hot air, and water for cooling purpose. Mining iron ore or other iron-bearing materials from the ground is the first step to make iron and steel. Iron ores are rocks from which metallic iron can be economically extracted. These rocks are usually found in the form of hematite (Fe_2O_3) or magnetite (Fe_3O_4). Common types of iron ores and their iron contents are shown in Table 2.1. Six major countries in iron ore mine production from 2010 to 2013 are China, Australia, Brazil, India, Russia, and Ukraine. In the United States, in 2013, Michigan and Minnesota produced 99% of the usable iron ore in 11 iron ore mines with 9 concentration plants and 9 pelletizing plants. The United States was estimated to have produced and consumed 2% of the world's iron ore output (USGS, 2014). In BF ironmaking, iron ore accounts for approximately 70% of the total raw materials.

Table 2.1 Common types of iron ores and their approximate iron contents

Iron ore	Hematite	Magnetite	Siderite	Pyrite	Limonite	Taconite	Jasper
Iron compound in the ore	Fe_2O_3 (~70% Fe)	Fe_3O_4 (~72% Fe)	FeCO_3 (~61% Fe)	FeS_2 (~46% Fe)	Fe_3O_4 (~60% Fe)	Various (>16% Fe)	Various (25–40% Fe)

Coke is produced from carefully selected coal. Different grades of coal are stocked separately and blended before transfer to coke ovens. To make coke, coal is washed, crushed, and screened in a preparation tower before being stored. Blended coal is first heated in coke ovens by gas firing for approximately 18h to produce coke. This process is known as *carbonization*. Once carbonized, the coke is pushed out of the ovens and allowed to cool. Gas, accounting for 25% of coal's volume, is released during carbonization that is extracted by the exhausters through the collectors and primary coolers, and used for fuel in the steel plant. Other by-products such as coal tar and phenol are also extracted for other uses. Coke, with few impurities and a high carbon content, is used as the fuel and reducing agent accounting for approximately 25% of the total raw materials in the BF process.

Limestone and dolomite, which are the principal carbonate rocks, are used as flux, accounting for approximately 5% of the total raw materials. Both limestone and dolomite are sedimentary rocks composed mostly of the mineral calcite (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) respectively. Table 2.2 lists some common carbonate minerals and their physical properties.

Table 2.2 Common carbonate minerals used for fluxes and their physical properties

Mineral	Physical properties	Common color
Calcite (CaCO_3)	Hexagonal crystal system, commonly good rhombohedral cleavage. Mohs hardness: 3; specific gravity: 2.72	Colorless or white but may be other colors because of impurities
Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)	Hexagonal crystal system, commonly good rhombohedral cleavage with curved faces. Mohs hardness: 3.5–4.0; specific gravity: 2.87	White or pink
Aragonite (CaCO_3)	Orthorhombic crystal system, Mohs hardness: 3.5–4.0; specific gravity: 2.93–2.95	Colorless, white, or yellow, but may be other colors because of impurities

Data from Freas, R. C., Hayden, J. S., & Pryor, C. A. (2006). Limestone and dolomite. Industrial minerals and rocks, commodities, markets, and uses (7th ed.). Littleton, CO: Society for Mining, Metallurgy, and Exploration, Inc.

The size of limestone and dolomite used in BF is 25–75 mm (1–3 in.). They can be mixed with iron ore to make agglomerates and charged to the furnaces as fluxed pellets or fluxed sinter. Agglomerates are large particles formed from finer ones, which are either fused at high temperature (sinter) or bonded at low temperatures to form a material that is handled easily and transported with minimal degradation. Limestone and dolomite are proportioned to the silica and alumina. The ratio is expressed as the

basicity. For fluxed pellets, the basicity is calculated as the CaO/SiO_2 and MgO/SiO_2 ratios, which reflect only the major components (Kokal, 2006).

To make fluxed sinter, fine-sized ore is first mixed with coke and fluxes, and heated in a sinter plant. Sinter process agglomerate iron ore, dust, or fines with other fine materials at high temperature to create a product that can be used in the BF. This process has a continuous moving belt on which the coke is ignited. The high temperatures fuse the ore particles and fluxes together to form a porous clinker called *sinter*. The sintering process, which has become an important part of the overall ironmaking process, was initially developed because of iron ore in dust form. Using sinter reduces waste and makes the ironmaking process more efficient (UK Steel, 2014), and lessens the amount of raw fluxing stone required in the process.

The amount of flux charged directly to the BF varies widely depending on the amount charged in fluxed agglomerates. The majority of BFs operating with fluxed pellets and/or fluxed sinter require an additional amount of flux of 10–50 kg/t (20–100 lb/ton) of hot metal. Those not using any fluxed burden materials are charging 100–250 kg/t (200–500 lb/ton) of hot metal. Typically, 225–275 kg/t (450–550 lb/ton) is normal, not many modern furnaces approach 200 kg/t (400 lb/ton) (AISI, 1989).

The iron BF is a large steel cylinder up to 30 m (98 ft) high. The maximum diameter, the hearth at the bottom, is typically 9 m (30 ft). The furnace is lined with refractory firebricks, which are water-cooled, and can withstand up to 2000°C (3632°F) temperature. An iron BF can operate more or less for 15 years at pressures up to five atmospheres, and internal temperatures in excess of 1750°C (3182°F), and produce as much as 10,000 tonnes (11,000 tons) of molten iron per day and up to 50 million tonnes (55 million tons) over its service life before the heat-resistant brick lining begins to deteriorate, and then is relined. Fig. 2.2 presents a schematized BF.

An important feature of ironmaking is that the process is continuous. First, coke, iron ore, and sinter are charged into the top of the BF, together with flux. A hot air blast, from which the furnace gets its name, of approximate 1000°C (1832°F), is injected through nozzles, called *tuyeres*, from the base of the furnace. The air injected ignites coke and eventually supplies enough heat to melt the burden. The materials move down through the furnace and are heated from below. The blast air may be oxygen enriched, and coal or oil is sometimes also injected to provide additional heat and reduce coke requirements. The blast fans the heat in the furnace to white-hot intensity, and the iron in the ore and sinter is melted out to form a pool of molten metal in the bottom, or *hearth*, of the furnace. The slag results from fusion of the fluxing stone (limestone and dolomite) together with the gangue (siliceous and aluminous residues from the iron ore) and coke ash in the BF. The molten slag, which is lighter than the metal, floats on top of the molten iron and below the unmelted burden. Both molten materials are drawn off at regular intervals from the continuous process furnace. Because the raw materials are carefully controlled to produce consistent crude iron, the range of slag chemical composition is fairly narrow for a specific ore and furnace operation. The hot air blast to the furnace burns the coke and maintains the very high temperatures that are needed to reduce the ore to iron. The reaction between air and the fuel generates carbon monoxide. This gas reduces the iron oxide, with a valance of 3, in the ore to iron.

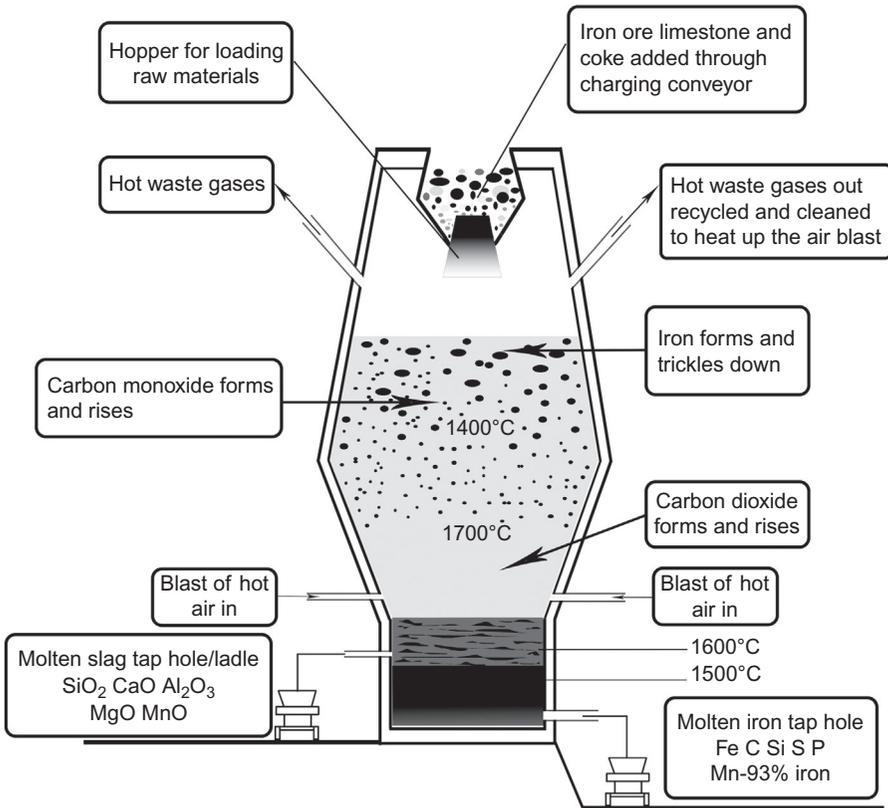
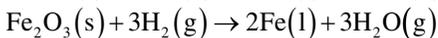
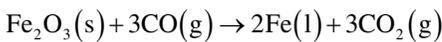


Fig. 2.2 Schematized iron BF.

The main chemical reactions (reduction) in molten iron production are



The hot gas, which contains a lot of carbon monoxide and leaves the furnace, is collected and cleaned and reused as a fuel for other steelmaking processes or to heat up the air blast to the furnace.

When a sufficient quantity of molten iron accumulates in the hearth of the BF, it is tapped off into ladles for steelmaking. As slag builds up on the surface of the molten iron, it is tapped off at regular intervals through a separate notch or taphole. Meanwhile, the raw materials continue to be charged into the top of the furnace, and heated air is blasted in at the bottom. This process goes on throughout the lifetime of the furnace.

2.2.2 BF slag formation

In iron- and steelmaking, flux has two major functions: (i) to make the impurities in the raw materials more easily fusible; (ii) to furnish a substance with which some

impurities may combine in preference to the metal. Fluxing practice, including the type and chemical composition of fluxing stone, proportion, particle size, and the way it is added may affect the formation and properties of the slag. As discussed in Section 2.2.1, limestone and dolomite, which are the major basic fluxes used in iron- and steelmaking, supply lime (CaO) and magnesia (MgO), respectively, in smelting iron ores to form slag with acid components silica (SiO₂) and alumina (Al₂O₃). The ideal flux is low in acids, such as silica, alumina, sulfur, and phosphorus. Typical chemical analyses for limestone, dolomite, and their respective calcined products are shown in Table 2.3. In nature, iron ores are found in impure states, often oxidized and mixed in with silicates of other metals. During smelting, when the ore is exposed to high temperatures, the impurities are separated from the molten metal, combined with the basic oxides in the fluxes to form compounds in the CaO–SiO₂–MgO–Al₂O₃ system, and removed. In many smelting processes, oxides are introduced to control the slag chemistry, assisting in the removal of impurities and protecting the furnace refractory lining from excessive wear. In this case, the slag is termed *synthetic*.

Table 2.3 Major chemical compositions of limestone, dolomite, and burnt lime

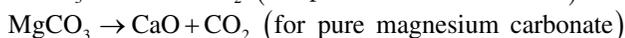
Component	Limestone	Dolomite	Burnt lime	
			High-calcium	Dolomitic
CaCO ₃	95.3	54.5	–	–
MgCO ₃	3.1	42.0	–	–
CaO	53.4	30.6	88.5	56.0
MgO	1.5	20.1	2.5	36.8
SiO ₂	0.7	2.6	1.2	4.7
R ₂ O ₃ ^a	0.3	0.3	0.5	0.5

^a Fe₂O₃ + Al₂O₃ + Cr₂O₃ + TiO₂.

Data from Kokal, H. R. (2006). Fluxes for metallurgy. *Industrial minerals and rocks, commodities, markets, and uses* (7th ed.). Littleton, CO: Society for Mining, Metallurgy, and Exploration, Inc.

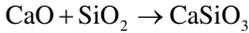
2.2.2.1 Slag formation

In the BF, calcination of limestone begins at temperatures higher than 800°C (1472°F) and dolomite typically begins dissociating at about 700°C (1292°F) (Ricketts, 1992). The melting point of pure lime is higher than process temperatures during smelting of iron ores. However, when lime is added to other components, such as silica, the melting point is lowered and a liquid phase forms. The major chemical reactions of calcination are



These are endothermic reactions, which absorb heat from the furnace. It is important to control the addition of limestone because too much limestone would lower the temperature in the furnace.

Calcium oxide is base and reacts with acidic impurities in the iron ore and other raw materials forming molten BF slag. The liquid slag also absorbs much of the sulfur existing in the various raw materials (Rayner-Canham & Overton, 2006). Calcium oxide reacts with silicon dioxide to produce calcium silicate:



Iron BF slag is controlled to maintain a composition with about 10% Al_2O_3 to achieve a relatively constant melting point and to maintain slag liquid over a wide range of lime and silica combinations. The melting point is typically 1400–1500°C (2552–2732°F). Ferrous iron reacts with silica at much lower temperatures than calcium and alumina, and local melting can occur in the lower part of a BF shaft. One purpose of flux in fluxed pellets is to avoid early melting that results from the formation of iron silicate (Fe_2SiO_4 or fayalite) by preferentially reacting silica in the pellets with lime and magnesia (Ranade, 1992).

2.2.2.2 Flux proportion

The selection of fluxes is governed by well-established physical and chemical laws that apply at smelting temperatures. Once selected, limestone and dolomite are proportioned to the silica and alumina in producing agglomerates. The ratio is expressed as the basicity (Ranade, 1992). Basicity is the ratio of basic oxide components to acid oxide component(s) in the slag and is defined in several ways. Because lime and silica are the most prevalent components in basic slags, the definition of basicity is often given as the lime-to-silica ratio or binary basicity (B_2)

$$B_2 = \text{CaO} / \text{SiO}_2$$

where the weight percent of the chemical components is used to compute the ratio. This ratio is also called the C/S ratio in the manufacture of fluxes pellets. The magnesia-to-silica ratio (M/S ratio) is also specified for fluxed pellets.

The commonly used definition of basicity in BF practice is the four-component basicity (B_4), or total basicity, defined as

$$B_T = B_4 = (\text{CaO} + \text{MgO}) / (\text{SiO}_2 + \text{Al}_2\text{O}_3)$$

Total basicity sometimes is modified to include titania or phosphorus (P_2O_5) as acids (Kokal, 2006). To achieve a fluid slag with adequate capacity to remove sulfides, total basicity (B_T) of iron BF slag is typically between 1.05 and 1.15 (AISI, 1989).

2.2.2.3 Particle size

Traditionally the size of fluxing stone directly charged into an iron BF was approximately 150 mm (6 in.). Nowadays, the size is as fine as 50×12.5 mm (2×0.5 in.) to make them compatible with other raw materials. The smaller particle size will help form complete reactions among the compounds in the BF.

2.2.2.4 Viscosity

Viscosity of liquid slag is another factor to consider for flux additions. Silica can form complex networks in the molten state. These networks comprise chains of silica molecules that result in very viscous flow conditions. Because silica also melts at a high temperature, separation and movement of silica is difficult. The addition of high-calcium lime breaks up the silicate networks, lowers the melting point, and decreases viscosity and is used to minimize the variability of viscosity over a range of slags compositions. However, if sufficient lime is present to precipitate dicalcium silicate (a solid phase), viscosity will increase rapidly (Kokal, 2006).

2.3 Basic properties of BF slag

The chemical and mineral compositions and basic physical properties of solidified BF slag have been well defined by researchers. BF slag is defined by the American Society for Testing and Materials (ASTM) as the nonmetallic product, consisting essentially of silicates and aluminosilicates of calcium and other bases that is developed in a molten condition simultaneously with iron in a BF (ASTM, 2009). Air-cooled BF slag is permitted to solidify under the prevailing atmospheric conditions, either in a pit adjacent to the furnace or in one some distance away to which it is transported in large ladles. After solidification, the cooling may be accelerated by water sprays that produce cracking and facilitate digging of the slag.

2.3.1 Chemical and mineral compositions

2.3.1.1 Chemical composition

The full range of chemical composition of BF slag based on the analyses of over 100 sources from different countries is summarized in Table 2.4. The overall chemical composition can vary over a wide range from different operations depending on the nature of the ore, the chemical composition of the fluxes, the coke consumption, and the type of iron used. It can also change over the years with alterations in the sources and types of ore being smelted. These variations affect the relative contents of the four major constituents (lime, silica, alumina, and magnesia) and also the amounts of the minor constituents (sulfur in the form of sulfide, and ferrous and manganese oxides). However, it is noted that the chemical composition of BF slag from one plant can be within a relatively narrow range. Hewlett (1998) provided the chemical composition of BF slag samples from the United Kingdom, Canada, France, Germany, Japan, Russian, South Africa, and the United States, indicating that CaO ranged from 34% to 43%, SiO₂ from 33% to 37%, Al₂O₃ from 8% to 16%, MgO from 5% to 14%, Fe₂O₃ from 0.3% to 2.0%, MnO from 0.5% to 1.1%, and SO₃ from 0.9% to 2.0%.

Hewlett (1998) also stated that in general the lime content in BF slag may range from 30% to 50%, silica 28% to 38%, alumina 8% to 24%, magnesia 1% to 18%, sulfur 1% to 2.5%, and ferrous and manganese oxides 1% to 3%, except in the special

Table 2.4 Full range of chemical composition of BF slag

Component	Composition range (%)	Component	Composition range (%)
Lime (CaO)	31–50	Iron (FeO or Fe ₂ O ₃)	0.3–2
Silica (SiO ₂)	27–45	Manganese (MnO)	0.1–2.3
Alumina (Al ₂ O ₃)	7–24	Sulfur (S) ^a	0.6–3
Magnesia (MgO)	1–18	P ₂ O ₅	<0.1

^a In the form of calcium sulfide or calcium sulfate.

Data from Dobrowolski, J. A. (Ed.), (1998). *Concrete construction handbook*. New York, NY: McGraw-Hill; Hewlett, P. C. (1998). *Lea's chemistry of cement and concrete* (4th ed.). Burlington, MA: Elsevier; Lee, A. R. (1974). *Blast furnace and steel slag*. New York, NY: John Wiley & Sons; National Slag Association (NSA). (1992). *Properties and uses of iron and steel slags*. MF 182–6. Pleasant Grove, UT: NSA; Nippon Slag Association (NSA). (2014). <http://www.slg.jp/ef/>.

case of ferromanganese prediction when the manganese oxide content of the slag may be considerably higher. Lankford, Samways, Graven, and McGannon (1985) stated that typical iron BF slag contains 32–42% SiO₂, 7–16% Al₂O₃, 32–45% CaO, and 5–15% MgO.

2.3.1.2 Mineral composition

The conditions of cooling control both the growth of mineral crystals and the quantity and size of gas bubbles that can escape before being trapped by solidification of the slag mass. Thus, within the limits imposed by the particular chemical composition, the cooling conditions determine the crystalline structure and the density and porosity of the slag. Although BF slag contains dominantly CaO, SiO₂, MgO, and Al₂O₃, these complex interactions are customarily represented on ternary system phase equilibrium diagrams.

Research by high-temperature microscopy applied to study phase equilibria has concluded that the system CaO–SiO₂–Al₂O₃–MgO accounts for approximately 95% of slag composition (Gutt & Russell, 1977). The crystalline minerals that form BF slag are compounds of the oxides of calcium and magnesium with silica and alumina. Sulfur is also present as sulfides and polysulfides, as sulfates and thiosulfates, and as elemental sulfur in small quantities. There are also small quantities of compounds of iron and manganese, and traces of manganese, titanium, and fluorine.

The possible assemblages of minerals formed by the four major constituents CaO, SiO₂, Al₂O₃, and MgO, in the range of proportions characteristic of slag, cannot be predicted with certainty from phase equilibrium diagrams. Estimates that have been made are, however, in reasonably close agreement with the results of microscopic studies on thin sections or polished etched surfaces of slags.

The most common minerals are melilite, a name applied to any of a series of solid solutions from akermanite, which is represented by 2CaO·MgO·2SiO₂ (C₂MS₂), and gehlenite 2CaO·Al₂O₃·SiO₂ (C₂AS). In slags of low lime and high alumina content, the mineral anorthite CaO·Al₂O₃·2SiO₂ (CAS₂) may appear. In slag having a high lime content, the orthosilicate 2CaO·SiO₂ (C₂S) may be formed. This mineral is known also

as *dicalcium silicate*, and is one that can cause falling, or spontaneous disintegration, when it changes its crystalline structure from β to γ form.

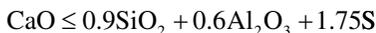
Slags of relatively low MgO content, up to 5%, usually contain melilite as the main constituent. Melilite is the name given to an isomorphous series of solid solutions of which the two principal end members are gehlenite (C_2AS) and akermanite (C_2MS_2). In some slags the solid solution may be replaced by akermanite itself. Other minerals that may occur in slags are bredigite ($\alpha' C_2S$), larnite (βC_2S), γC_2S , pseudowollastonite and wollastonite (CS), rankinite (C_3S_2), merwinite (C_3MS_2), spinel (MA), diopside (CMS_2), monticellite (CMS), anorthite (CAS_2), and forsterite (M_2S). The only one of these minerals that is active and will hydrate is dicalcium silicate in the α' or β form; the γ form is inert. Periclase (MgO) has only been observed in slags of high MgO content exceeding 16% when remelted and heat treated. Theoretically it can occur in the assemblages. Hewlett (1998) provided mineral analyses based on 21 BF slag samples and summarized the results as in Table 2.5.

Some of the minerals can appear in more than one form. Thus both pseudowollaston and wollaston (the high- and low-temperature forms of CS) may be observed, but the former is the more common. C_2S may also appear in more than one form. The higher-temperature forms observed are α' or β into which α' may transform on cooling. Falling slags contain the γ form often mixed with β .

In addition to the above minerals, all BF slags contain calcium sulfide, occasionally in the form of well-shaped but small crystals, but more often having the appearance of a noncrystalline or dendritic mass. Other minor constituents such as alkalis or iron and manganese oxides, when present in small amounts, of the order of 1%, probably occur in solid solution in one of the other minerals. At higher contents, of the order of 3%, they may, however, occur as sulfides (Hewlett, 1998).

2.3.1.3 *Dicalcium silicate*

The compound dicalcium silicate occurs in four different crystalline forms, known as α , α' , β , and γ forms. The α' form occurs at temperature above 1420°C (2588°F), when the slag is in the liquid state. When the temperature falls to about 675°C (1247°F), the dicalcium silicate occurs in the β form. When dicalcium silicate changes from the β to γ form, which it can do at ambient temperatures, it increases in volume by about 10%, and if the silicate is in sufficient quantity this expansion will cause disintegration of the slag matrix. However, studies have shown that dicalcium silicate cannot form in significant amounts when the ratio of the lime and magnesia to the silica and alumina and sulfur is kept within the limits given by either of the formulae



If slag contains partially reduced iron oxides, the oxidation of such constituents leads to expansion that may cause disintegration of the slag. Such instances are rare, but a simple water-immersion test easily detects the expansion (Lee, 1974).

Table 2.5 Some possible minerals from the four-component system in air-cooled BF slag

Number of samples of 21 examined	C_2AS/C_2MS_2 solid solution	C_2MS_2	C_2S	CS	C_3S_2	C_3MS_2	MA	CMS_2	CMS	CAS_2	M_2S	MgO
5	X		X		X							
5	X			X						X		
4	X			X	X							
3	X					X	X					
2	X						X			X		
1		X					X			X	X	
1		X				X	X		X			

Data from Hewlett, P. C. (1998). *Lea's chemistry of cement and concrete* (4th ed.). Burlington, MA: Elsevier.

2.3.2 Basic physical properties

An air-cooled BF is predominantly crystalline in nature, with a cellular or vesicular structure resulting from bubbles of gases that were dissolved in the molten slag. The air-cooled slag crushes to angular, roughly cubical particles with pitted surfaces. Excellent bond is provided with either hydraulic cements or bituminous binder materials. High internal friction angles and particle interlock provide excellent stability. Bulk density is dependent upon grading and particle size; the larger particles contain more internal cells or vesicles and have a lower bulk density. The coarse sizes may have bulk densities as much as 20% lower than natural aggregates with the same gradation, while the fine material (passing a 4.75 mm or No. 4 sieve) is nearly equal to natural sand in density. The aggregate is highly resistant to weathering effects, and does not readily polish to produce slippery surfaces.

Air-cooled BF slag has a low coefficient of thermal expansion and a high fire resistance. It has relatively high water absorption due to its porosity. BF slag is one of the more absorbent types of aggregates. The combination of rough texture and relatively high porosity, together with its alkaline reactivity, produces good adhesion characteristics, particularly in the presence of water.

The physical properties of BF slag from any one plant are reasonably consistent, the variation that do occur being no greater than those that occur in natural rock from a quarry (Lee, 1974). The types of ore used by the plant can, however, produce larger variation in the slag than those found from one plant to another. These variations are caused by the need to adjust the burden charged to the BF to suit the type of ore being used.

The physical properties, such as density, porosity, and particle size, are affected by the cooling rates and chemical composition. Table 2.6 shows some physical properties of air-cooled BF slag.

Table 2.6 Physical properties of air-cooled BF slag

Specific density	Bulk density (kg/m ³)	Water absorption (%)	Impact value dry (%)	Crushing value (%)	Polished stone value (%)	Abrasion value (%)
2.38–2.76	1150–1440	1.5–5	21–42	25–39	50–63	5–31

Data from Lee, A. R. (1974). Blast furnace and steel slag. New York, NY: John Wiley & Sons; Dunster, A. M. (2002). Blastfurnace slag and steel slag as aggregate: A review of their uses and applications in UK construction. Proceedings of the 3rd European slag conference, October 2–4, Keyworth, UK.

2.4 Steelmaking processes and steel slag formation

As seen in Fig. 2.1, crude iron is refined in a BOF or an EAF to become crude steel. It may also undergo a second refining in a ladle furnace. The BOF steelmaking process is currently the dominant steelmaking technology, which makes approximately 60% of the world's total output of crude steel. In the United States, this figure is slowly

declining, from 55% in 2001 to 47% in 2006 (Stubbles, 2014). This is mainly due to the availability of recycled steel scrap, less energy consumption by the EAF process, and the grade of steel produced. However, elsewhere in the world the use of BOF is growing.

2.4.1 BOF steelmaking and slag formation

The primary raw materials for the BOF include approximately 70–80% liquid hot metal from the BF, balanced with recycled steel scrap and flux materials, which are mainly limestone, dolomite, and fluorspar (CaF_2). The quantities of steel scrap are related to factors such as silicon and carbon content and temperature of the molten iron. Pure oxygen (>99.5%) is used to help melt the raw materials.

The principal active ingredients of the limestone and dolomite are CaO and MgO . Fluxes are charged into the furnace, *vessel* or *converter*, to absorb impurities and remove phosphorus and sulfur from the molten iron. Steel slag is formed during this process, which is neutral with respect to the refractory lining of the furnace. To help prevent erosion and dissolution of magnesia brick, 5–12% magnesia is maintained in steel slag. This also aids in controlling the viscosity of steel slag (Kokal, 2006).

The amount of added fluxes usually depends on the silicon, sulfur, and phosphorus contents of the metals, and the purity of the fluxes. By decreasing the silicon content of hot metal and lowering the manganese content, the amount of lime required in steelmaking will decline. Increased use of scrap, along with external desulfurization, also results in lower flux consumption in steelmaking. There is a large number of possible grade of steel that can be produced but at the end of refining, they can be simply classified as high, medium, and low carbon grades. The lower the carbon content, the higher the oxygen level, with more iron oxide generated and usually more limestone and dolomite are needed for slag formation.

The BOF is refractory lined and is open topped to rapidly refine molten iron into steel. Basic refers to the magnesia (MgO) refractory lining, which wears through contact with hot basic slag, molten steel, and raw materials.

The capacity and dimensions of typical BOF vessel are 228 tonne (250 ton), with 10.4 m (34 ft) height, 8 m (26 ft) outside diameter, 0.9 m (3 ft) barrel lining thickness, and 227 m^3 (8000 cu ft) working volume. There are also several modifications to the BOF, such as the Q-BOP (quick-quiet basic oxygen process) and OBM (oxygen bodenblasen Maxhuetten), for which the required oxygen is injected through hydrocarbon shrouded tuyeres located in the bottom of the furnace. Fig. 2.3 is a schematic illustration of a BOF.

The BOF operation, or *heat*, begins when the vessel is tilted about 45 degrees toward the charging aisle and scrap charge is dumped from a charging box into the mouth of the cylindrical BOF. The hot metal is immediately poured directly onto the scrap from a transfer ladle. The charging takes a couple of minutes. Then the vessel is rotated back to the vertical position and lime and dolomite fluxes are dropped onto the charge from overhead bins while the lance is lowered to a couple of meters (a few feet) above the bottom of the vessel. The lance is water-cooled with a multihole copper tip. Through this lance, pure oxygen is blown into the BOF at supersonic velocities.

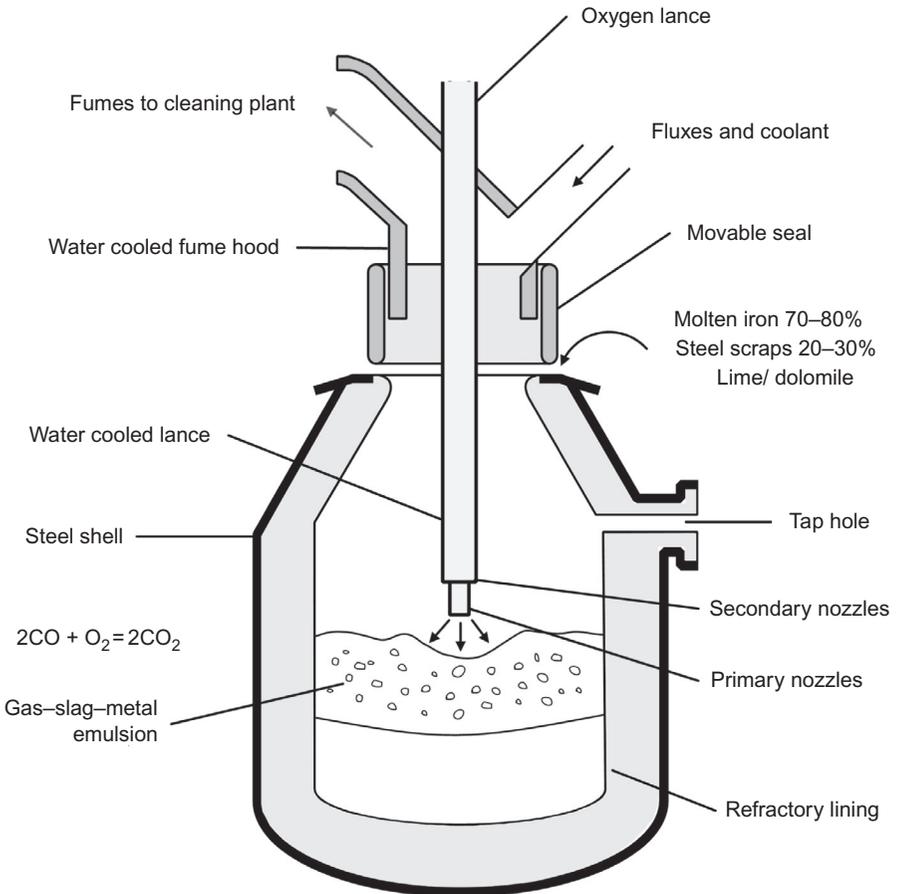


Fig. 2.3 Schematic illustration of BOF.

Heat generated by the oxygen raises the temperature inside the vessel to up to 1700°C (3092°F). This melts the scrap and lowers the carbon content in the molten iron to less than 1% and helps remove sulfur and phosphorus (Stubbles, 2014). The tap-to-tap time is approximately 40 min, and the range is approximately 30–65 min, of which 50% is "blowing time." Blowing continues for a predetermined time based on the metallic charge chemistry and specification.

Nearing the end of the blowing or "refining" cycle, after approximately 20 min, a temperature reading and a sample are taken for analysis. The specified chemical analysis is conducted at 1593–1649°C (2900–3000°F). Once the temperature and chemical composition of the hot metal are known, a computer charge model determines the optimum proportions of scrap and hot metal, flux additions, lance height, and oxygen blowing time. The lance is generally preprogrammed to move to different heights during the blowing period. If the analysis shows that everything is correct, the vessel is tilted and the steel is poured into a ladle. This process is called tapping the steel. At this

time alloying elements are added to bring the steel to the required specification. From here it may undergo further refining in a secondary refining process or be sent directly to the continuous caster where it is solidified into semifinished shapes: blooms, billets, or slabs (Stubbles, 2014; Miller, Jimenez, Sharan, & Goldstein, 1998).

After tapping the steel, the molten steel slag is poured off into a slag cart and carried to the slag-treating bays for air-cooling. The basic operational steps of the BOF process are shown in Fig. 2.4.

Further treatment of the steel takes place in a ladle furnace, including such things as bubbling the steel with an inert gas (eg, nitrogen) to ensure thorough mixing of the alloying elements, injection of materials to refine impurities, and for some special steels, a vacuum degasser is used to remove dissolved gasses, particularly oxygen and hydrogen. Then the steel contains between 0.1% and 1.0% carbon.

2.4.2 EAF steelmaking and slag formation

The important feature of the EAF steelmaking process is that the raw materials are recycled steel scrap and fluxes without the step of iron ore extraction. This results in overall cost of per tonne of annual installed capacity in the range of \$127–182/t (\$140–200/ton) for an EAF-based operation compared to approximately \$1110/t (\$1000/ton) for a BF-BOF-based operation (Jones, 1988).

The EAF is cylindrical in shape. The furnace bottom consists of a spherically shaped bottom dish. The shell sitting on top of this is cylindrical and the furnace roof is a flattened sphere. Most modern furnaces are of the split shell variety. This means that the upper portion of the furnace shell can be quickly decoupled and removed from the bottom. This greatly minimizes downtime due to change out of the top shell. Once the top shell is removed, the furnace bottom can also be changed out fairly quickly. Some shops now follow a practice where the shell is changed out on a regular basis every few weeks during an 8-h downshift.

The furnace sidewall above the slag line usually consists of water-cooled panels. These panels are hung on a water-cooled cage that supports them. The furnace roof also consists of water-cooled panels. The center section of the roof that surrounds the electrode ports is called *roof delta* and is a cast section of refractory that may be water-cooled. The furnace bottom consists of a steel shell with several layers of refractory (Jones, 1988).

Steel scraps are first separated, graded, and sorted into different classes of steel in scrap yards. The scrap yard operator will prepare buckets of scrap according to the needs of the smelter. The scrap is layered in the bucket according to size and density to promote the rapid formation of molten steel in the furnace, and minimize scrap cave-ins, which can break electrodes. The charge may include lime and carbon (Yildirim & Prezzi, 2011).

EAFs are equipped with graphite electrodes and resemble giant kettles with a spout or an eccentric notch on one side. An electric current is passed through three graphite electrodes and forms an arc. The heat generated by this arc melts the scrap. The roof of an EAF can pivot and swing to facilitate the loading of raw materials. The capacity of EAFs have been developed from approximately 135 to 270 tonnes (150–300 tons) of steel per cycle.

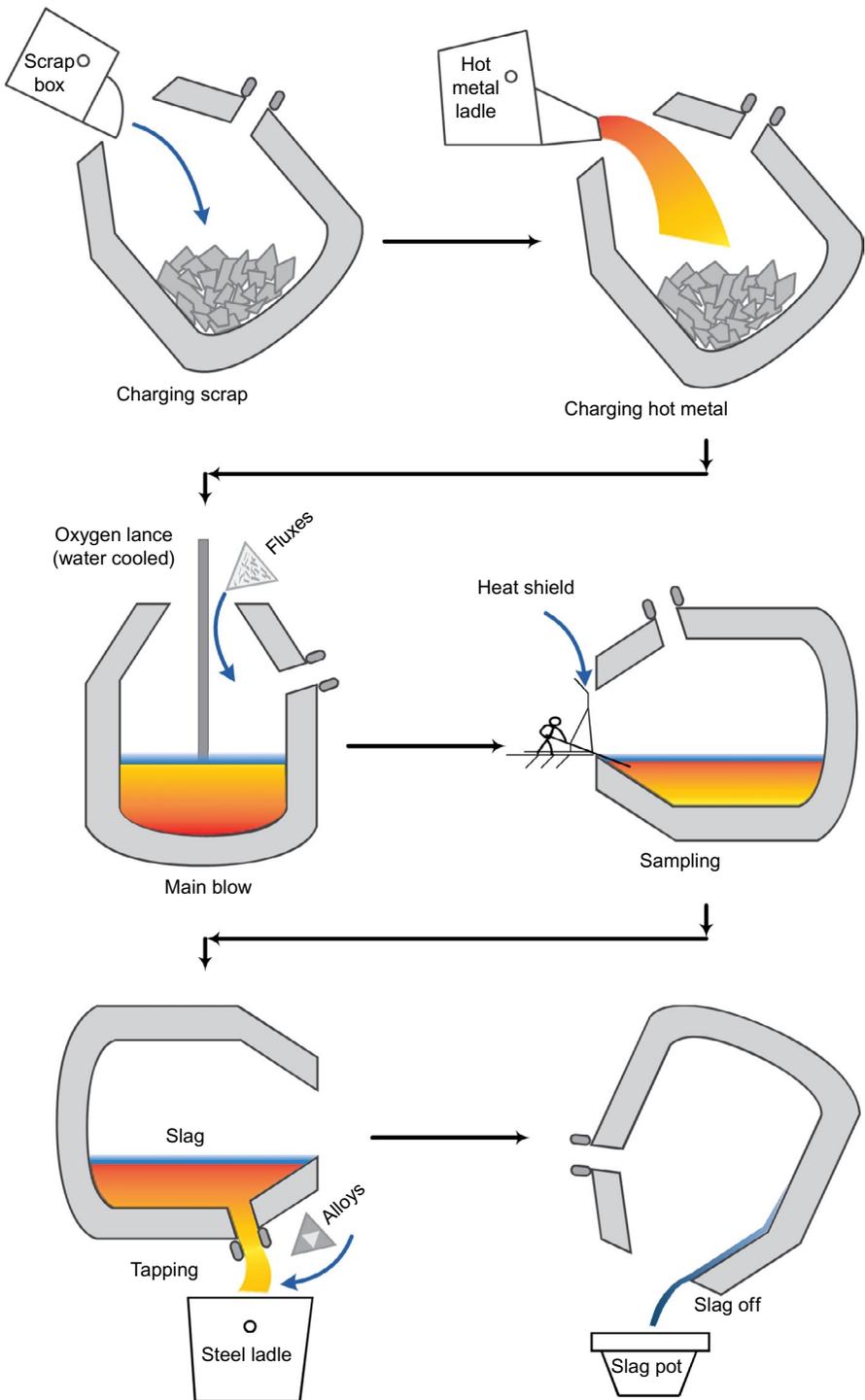


Fig. 2.4 Schematic of operational steps in BOF steelmaking. Adapted from Miller, T. W., Jimenez, J., Sharan, A., & Goldstein, D. A. (1998). Oxygen steelmaking process. In R. J. Fruehan (Ed.), *The making, shaping, and treating of steel* (11th ed.). Pittsburgh, PA: AISE.

The EAF operation starts with the charging of various types of steel scrap to the furnace. The roof and electrodes are raised and are swung to the side of the furnace to allow the scrap-charging crane to move a full bucket of scrap into place over the furnace. Two to three buckets of scrap per heat is normal. Some operations achieve a single bucket charge. The scrap falls into the furnace and the scrap crane removes the scrap bucket. The roof and electrodes swing back into place over the furnace. The roof is lowered and then the electrodes are lowered to strike an arc on the scrap, which causes electricity to travel through the electrodes and the metal itself. The electric arc and the resistance of the metal to this flow of electricity generates the heat. This commences the melting portion of the cycle. As the scrap melts, the electrodes are driven deeper through the layers of scrap. Oxygen may also be injected through a lance to cut the scrap into smaller sizes. Usually, light scrap is placed on top of the charge to accelerate bore-in. Approximately 15% of the scrap is melted during the initial bore-in period. After a few minutes, the electrodes penetrate the scrap sufficiently so that a long arc (high voltage) tap can be used. The long arc maximizes the transfer of power to the scrap and a liquid pool of metal forms in the furnace hearth. Once the molten pool is formed, the arc becomes quite stable and the average power input increases. Calcium oxide, in the form of burnt lime or dolomite, is either introduced to the furnace together with the scrap or is blown into the furnace during melting. After several baskets of scraps have melted, the refining metallurgical operations (eg, decarburization and dephosphorization) are performed. During the steel refining period, oxygen is injected into the molten steel through an oxygen lance. Some iron, together with other impurities in the hot metal, including aluminum, silicon, manganese, phosphorus, and carbon, are oxidized during the oxygen injections. These oxidized components combine with lime (CaO) to form slag. As the steel is refined, carbon powder is also injected through the molten slag floating on the surface of the molten steel, leading to the formation of carbon monoxide. Once the desired chemical composition of the steel is achieved, the EAF is tilted, and the molten slag is poured and carried to a slag-processing unit with ladles or slag pot carriers and steel is tapped out of the furnace into a separate ladle (Seetharaman, 2005). Modern operations aim for a tap-to-tap time of less than 60 min. Fig. 2.5 shows the schematic of an EAF and a ladle furnace.

Traditionally, EAF slag may be classified into oxidizing slag and reducing slag. Oxidizing slag is generated during the oxidation refining stage, and reducing slag is generated during reduction refining. Approximately 70 kg (170 lb) of EAF oxidizing slag and 40 kg (97 lb) of reducing slag are generated for each tonne (ton) of electric furnace steel (NSA, 2014).

2.4.3 Ladle furnace refining and ladle slag

After being tapped from the BOF or EAF, the molten steel produced by the primary processes may undergo further refining to remove additional impurities remaining within the steel, or add alloying elements to obtain the required chemical composition and grade of product. This refining process is called a *secondary steelmaking operation*, *secondary refining*, or *ladle refining* because it is completed within the transfer ladle. The secondary refining process is common to produce high-grade

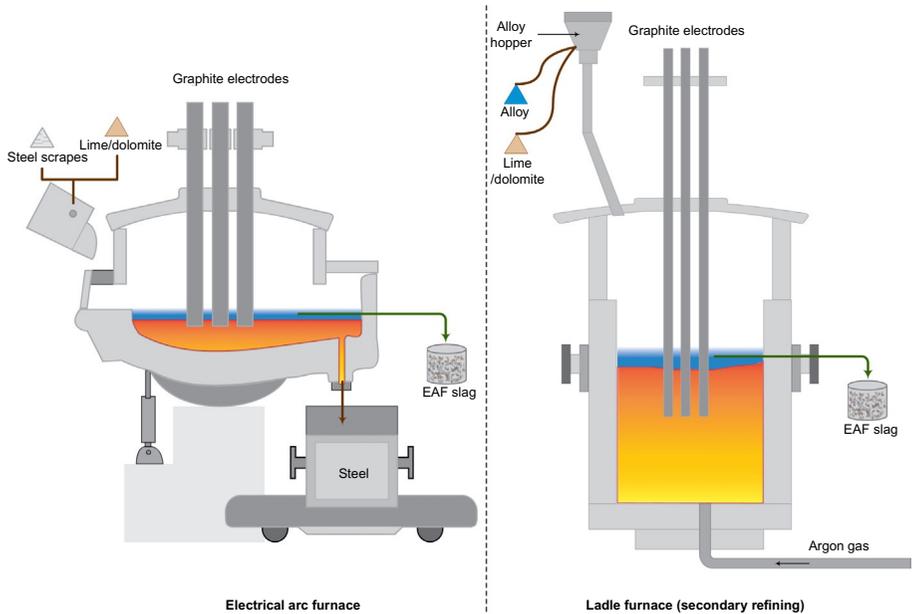


Fig. 2.5 Schematic of EAF and ladle furnace.

steel. The important functions of the secondary refining process are final desulfurization; degassing of oxygen, nitrogen, and hydrogen; removal of impurities; and final decarburization (for ultralow carbon steels). Depending on the required quality, most of the molten steel produced in BOF and EAF processes goes through some or all of the abovementioned refining processes.

Ladle furnaces look like smaller versions of EAF furnaces, having three graphite electrodes connected to an arc transformer used for heating the steel. At the bottom of the ladle furnace, typically, there is a pipeline through which argon gas can be injected for stirring and homogenizing the molten steel in the furnace. By injecting desulfurizing agents (such as Ca, Mg, CaSi, CaC₂) through a lance, the sulfur concentration in the steel can be lowered to 0.0002%. The addition of silicon and aluminum during deoxidation forms silica (SiO₂) and alumina (Al₂O₃). These oxides are later absorbed by the slag generated by the refining process. In addition, to adjust precisely the chemical composition of the steel to produce different grades of steel, the desired alloying elements are added to the molten steel through an alloy hopper that is connected to the ladle furnace. Ladle furnaces also function as a storage unit for the steel before the initiation of casting operations (Shi, 2004; Yildirim & Prezzi, 2011).

During ladle refining, slag is generated by adding fluxes to the ladle, to melt and combine with any carryover of furnace slag for the purpose of absorbing deoxidation products (inclusions), heat insulation, and protection of ladle refractory linings. Because the ladle refining stage usually involves the addition of different fluxes, the properties of these synthetic slags are quite different from those of the furnace slag (Jones, 2014; Shi, 2004).

2.5 Basic properties of steel slag

The chemical and physical properties of a specific steel slag, before undergoing special treating and processing, basically depend on the types of steelmaking process and the grades of steel produced. However, in general, the overall chemical and minerals compositions and physical properties of slag from BOF and EAF are similar.

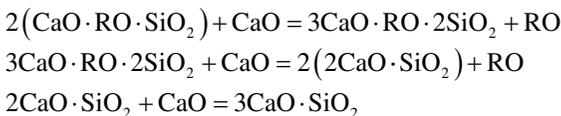
2.5.1 Chemical and mineral compositions

During the steelmaking process, the temperature at the slag-forming stage is up to 1700°C (3092°F). Under this temperature, liquid reaction occurs. Liquid steel slag contains appreciable amounts of CaO, SiO₂, FeO, Fe₂O₃, MnO, MgO, and minor amounts of P₂O₅, Al₂O₃, K₂O, and Cr₂O₃. Obviously, many possible combinations of oxides are available. Studies (Mills & Keene, 1987) on the phase diagram data of steel slag show 11 ternary and quaternary systems possibly composed of CaO, SiO₂, FeO, Fe₂O₃, MnO, and MgO. These systems are CaO-Fe_xO-MgO, CaO-Fe_xO-MnO, CaO-Fe_x-SiO₂, CaO-MgO-MnO, CaO-MgO-SiO₂, CaO-MnO-SiO₂, Fe_xO-MgO-SiO₂, Fe_xO-MnO-SiO₂, MgO-MnO-SiO₂, CaO-Fe_xO-MgO-SiO₂, CaO-Fe_xO-MnO-SiO₂.

2.5.1.1 Chemical composition

Typically BOF slag contains approximately 10–20% SiO₂, 40–50% CaO, 10% MgO, 15–20% iron (mixed oxides), 2–5% Al₂O₃, 10% manganese oxide (MnO), and other oxides. Iron oxides content depends on carbon levels attained in the metal; it generally increases with lower carbon levels. For EAF slag, an oxidizing slag may contain 40–50% CaO, 12–20% SiO₂, 5–35% iron (mixed oxides), 3–10% Al₂O₃, 2–12% MgO, and 5–15% MnO. Typical reducing slag may contain 55–70% CaO, 15–25% SiO₂, 1–3% Al₂O₃, 3–12% MgO, and 0.5–2% FeO and MnO (Kokal, 2006).

In the process of basic oxygen steelmaking, basicity keeps increasing due to the continuous addition of lime and the mineral composition also changes with the change of basicity. The following replacement reactions occur:



The resultant products in the right-hand side are contained in solid slag. The reason for the occurrence of the replacement reactions is that the basicity of CaO is stronger than that MgO, FeO, and MnO. Therefore, if there is sufficient CaO to meet the need of the combination of acid oxides (SiO₂, Al₂O₃, P₂O₅, FeO, Fe₂O₃), solid solution of MgO-FeO-MgO (RO phase) will crystallize.

BOF slag simply falls into two categories: acid slag and basic slag. Most BOF slag belongs to the latter category. There are also different classification methods. EAF slags may be divided into oxidizing slag and reducing slag.

The basicity for steel slag, which was initially proposed by Mason (1947), has been generally adopted. Steel slag is classified on the basicity values (B) for four categories according to the following relationship:

$$B = \text{CaO} / \text{SiO}_2 + \text{P}_2\text{O}_5$$

The basicity of steel slag is classified as follows: $B = 0.9\text{--}1.4$, olivine slag; $B = 1.4\text{--}1.6$, merwinite slag; $B = 1.6\text{--}2.4$, dicalcium silicate slag; $B > 2.4$, tricalcium silicate slag.

Several other basicity definitions, with minor variations, are also proposed (Kuwayama, Mise, Yamada, & Honda, 1989) for steel slag, which are

$$B = \text{CaO} + \text{MgO} / \text{SiO}_2$$

$$B = \text{CaO} + \text{Al}_2\text{O}_3 + \text{MgO} / \text{SiO}_2$$

Chemical compositions of steel slag from different steelmaking processes are reported in some of the literature (eg, Gutt, 1977). The comparison of chemical composition for different steel slags is summarized in Table 2.7. Some steel slags contain trace amounts of V_2O_5 and TiO_2 , which are not included in the table. It is noted that the Al_2O_3 and CaO contents are normally higher for ladle slag.

Table 2.7 Full range of chemical composition of steel slags

Component	Composition range (%)		
	BOF slag	EAF slag	Ladle slag
CaO	35–45	40–60	30–60
SiO_2	12–17	10–30	2–35
Al_2O_3	0.98–3.4	2–9	5–35
FeO	10–25	10–30	0–15
MgO	3–15	3–8	1–12.6
MnO	5–15	2–5	0–5
SO_3	0–0.3	0.1–0.6	0.1–1
P_2O_5	0.2–4	0–1.2	0–0.4

Data from Jones, D.E. (1988). Utilization of ground granulated slag in Australia. In: *Proceedings of concrete workshop* (pp. 307–329), SYD, Australia; Shi, C. (2004). Steel slag—Its production, processing, characteristics, and cementitious properties. *Journal of Materials in Civil Engineering*, 230–236; Wang, G.C. (1992). *The utilization of steel Slag in engineering applications*. PhD Thesis, University of Wollongong, Wollongong, NSW, Australia. Yildirim, I. Z., & Prezzi, M. (2011). Chemical, mineralogical, and morphological properties of steel slag. *Advances in Civil Engineering*. <http://dx.doi.org/10.1155/2011/463638>.

2.5.1.2 Mineral composition of steel slag

The mineral composition of steel slag is related to the forming process and chemical composition. Basic steel slag is composed of $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{SiO}_2$ mixed-crystal of MgO , FeO , and MnO ; that is, $\text{MgO}\cdot\text{MnO}\cdot\text{FeO}$, which is repressed as RO. CaO can also enter RO phase. In addition, there are also $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$, $\text{CaO}\cdot\text{Fe}_2\text{O}_3$, $\text{CaO}\cdot\text{RO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{RO}\cdot 2\text{SiO}_2$, $7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2$, and some other oxides.

2.5.1.3 Free lime and existing form

It is known that a certain amount of uncombined lime (unburnt or free lime) is expressed as free CaO or f-CaO. Uncombined CaO, which has a specific gravity of 3.34, can react with moisture to produce $\text{Ca}(\text{OH})_2$, which has a specific gravity of 2.23, with a resulting volume increase of approximately 90%. This is the primary reason to make some steel slag volumetrically expensive prone.

It is traditionally considered that it is the quantity of f-CaO, rather than its existing form, that contributes to the volume expansion. However, research has found that the existing form of f-CaO plays an important role in it (Geiseler, 1996): (i) f-CaO in solid solution may cause volume expansion; (ii) finer f-CaO particles are not likely the cause of volume expansion.

Analysis has shown that there exist two types of free lime in steel slag: the pure one and the solid solution. The former is free CaO and the latter is $\text{CaO} + x\% \text{FeO}$ ($0\% < x < 10\%$ by weight). They can be distinguished in X-ray diffraction (XRD) patterns, f-CaO having $d=2.41 \text{ \AA}$ and f-CaO in solid solution state having $d=2.38 \text{ \AA}$. Excessive f-CaO, especially in the presence of solid solution with small amounts of FeO, is the primary cause of volumetric unsoundness (Wang, 1992).

From microscopic investigation, Geiseler (1996) found that f-CaO can exist in the form of residual lime and lime precipitated during solidification and subsequent cooling. In both categories, f-CaO exists in different appearance and particle size. The residual f-CaO can be classified into grainy lime with particle size mainly between 3 and $10 \mu\text{m}$ and spongy f-CaO with particle size mainly between 6 and $50 \mu\text{m}$. The precipitated lime can exist on C_2F grain boundaries or within C_3S crystals and has particle size usually less than $4 \mu\text{m}$. All types of f-CaO can hydrate; however, the most significant contributor to expansion is the spongy f-CaO with grain size up to $50 \mu\text{m}$ (Fig. 2.6).

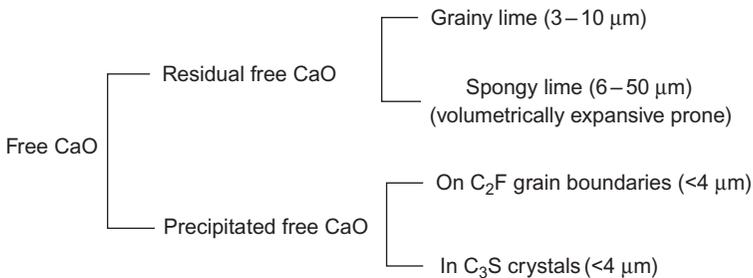


Fig. 2.6 The existing form of free lime.

2.5.1.4 MgO and its crystalline form

Research results show that combined magnesium oxide is not, in fact, the cause of unsoundness of steel slag. Only the free form of MgO (periclase) is expansion prone. Periclase can only be formed in the lower basicity case, whereas in the higher basicity condition, which exists in steel slag, MgO usually forms solid solution mainly with FeO and MnO (ie, RO phase).

From crystallography, it is well known that the ability of two substances to form solid solution is determined primarily by geometrical structure rather than by chemical compositions. If the radii of the substituting atoms differ by not more than about 15%, a continuous solid solution can be formed. The radii of Mg^{++} , Fe^{++} , and Mn^{++} are 0.78 Å, 0.83 Å, and 0.91 Å, respectively; therefore, they can easily form solid solution, especially in the basic liquid reaction.

Microscopic studies have shown that, in steel slag, magnesium oxide exists mainly in solid solution with FeO and MnO, so-called magnesia wüstites, while unbound MgO (periclase) is seldom found. The unbound MgO also includes the macroscopically visible fragments of undissolved refractory lining or dolomite, which were found in some slags.

Based on MgO forming solid solution, Luo (1980) proposed that the percentage ratio (stability factor) by weight of MgO to FeO plus MnO determines whether the MgO is stable or not; where, if $\text{MgO}/\text{FeO} + \text{MnO} < 1$, MgO is stable; if $\text{MgO}/\text{FeO} + \text{MnO} > 1$ MgO is unstable.

Iron mainly exists as bivalent iron (FeO), which accounts for 70% of the total iron content in steel slag (apart from electric arc slag). The ratio is less than 1 for most steel slags. The equation is based on the premise that MgO can form solid solution with FeO and MnO.

Investigations concerning the free magnesia content of steel slags have shown that good dissolution of the added dolomite in the furnace is most important. For this purpose the dolomite should be added at an early stage of the steelmaking process and grain size should be as small as possible to enable the dolomite to dissolve and react completely.

2.5.2 Basic physical properties

Compared to air-cooled BF slags, the steelmaking slags are much heavier, harder, denser, and less vesicular in nature. They have unusually high resistance to polishing and wear in pavement surface.

Solid steel slag exhibits both block shape and honeycomb shape. The former steel slag possesses luster; the latter is nonlustrous and more brittle. The specific gravity of steel slag is dependent on viscosity, surface tension of liquid steel slag and amount of dioxide contained, ferrous materials, and porosity. Moisture content of steel slag is 0.2–2.0%, specific gravity is 3.2–3.6, compressive strength is between 169 and 300 MPa (43.5 ksi), and the Mohs scale number is between 5 and 7. Grindability of steel slag is less than that of BF slag. Hardness and specific gravity are greater than those of BF slag. Like air-cooled BF slag, steel slag exhibits excellent skid-resistance properties. Some basic physical properties of steel slag are shown in Table 2.8.

Table 2.8 Basic physical properties of steel slag

Bulk density (kg/m ³)	Specific gravity	Crushing value	Impact value	Abrasion value	Polish stone value
1150–1440	2.38–2.76	25–39	21–42	5–31	50–63

Data from Lee, A. R. (1974). *Blast furnace and steel slag*. New York, NY: John Wiley & Sons.

2.6 Summary

Slag is generated as a by product during iron and steelmaking which result in considerable compositional and physical variability to various slags. However, after it is poured, the molten slag will go through special treating, handling, and processing, and various slag products can be produced with well established quality control procedures. The current annual production of ferrous slag throughout the world is approximately 600 million tonnes (660 million tons). To correctly and successfully use a particular ferrous slag mainly depends on the understanding of its chemical, mineral, and physical properties, and the technical requirements of the end products and utilization. Processed BF slag is usually considered to be a conventional construction material. Acceptance has been growing for steel slag applications.

Depending on the cooling method, different types of slag products can be produced for different applications; for instance, air cooled, granulated, expanded, and pelletized BF slags. The review of iron and steelmaking processes and slag formation will form a foundation for further exploration of slag processing, utilizing, establishing usability criteria, and property measuring and testing for various utilizations.

Questions

- 2.1 What are the raw materials and the approximate proportion of the raw materials for ironmaking?
- 2.2 Describe the process of BF ironmaking.
- 2.3 Why does the crude iron contain such a high percentage of carbon?
- 2.4 How is BF slag formed?
- 2.5 Describe the process of BOF and EAF steelmaking.
- 2.6 How are BOF and EAF slag formed?
- 2.7 What are the differences between BOF and EAF steelmaking?
- 2.8 What are the functions of fluxes in ironmaking and steelmaking?
- 2.9 In iron-BF production, what is the range of basicity of slag?
- 2.10 What are the main chemical and mineral compositions of BF slag?
- 2.11 What are the main chemical and mineral compositions of BOF and EAF steel slag?
- 2.12 How does the type of flux affect the chemical and mineral compositions of slag?
- 2.13 Can the properties of slag be modified by adjusting ironmaking and steelmaking processes?

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