CHAPTER 12.34

Steelmaking

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Steel is an iron-based engineering material, often containing carbon as the principal strengthening element, and is the most-produced metallic material; more than 1.6 billion t (metric tons) of crude steel was produced in 2016. The many different grades of steel provide a wide range of properties, ranging from soft and ductile interstitial-free steel to tool steels that can retain their strength even when red hot; stainless steels contain more than 12% chromium for improved corrosion resistance. Steels that combine high strength and high ductility at reasonable cost are currently being developed and improved for use in automobiles.

The properties of steel depend on the chemical composition and physical processing of the material. In this overview, the focus is on production of crude steel from raw materials. Detail on processing routes and reactions can be found in comprehensive reviews (Fruehan 1998; Remus et al. 2013; Seetharaman et al. 2014).

Steelmaking is the conversion of raw materials to liquid steel—with the correct chemical composition and temperature—for subsequent solidification into intermediate products such as slabs, blooms, billets, beam blanks, or ingots. Simplified flow sheets are shown in Figure 1.

The main metallic raw materials are hot metal (the carbon-rich product of blast furnace [BF] ironmaking), scrap (recycled steel), and other metallics such as direct reduced iron (DRI). The step labeled "Steelmaking" in Figure 1 involves several other steps. As discussed in subsequent sections, hot metal is normally processed by converter steelmaking, often after an initial pretreatment step to remove phosphorus and sulfur. Electric furnace steelmaking mainly uses scrap and DRI. These initial operations (primary steelmaking) remove oxidizable impurities by injecting oxygen: Carbon is removed in gaseous form (as CO); phosphorus and silicon are converted to oxides and captured in slag. Slag is the molten (or largely molten) mixture of oxides that floats on top of the steel; slag originates from elements and compounds in the raw materials and fluxing additives (such as limestone). Slag–metal reactions are essential to many of the refining reactions and can be manipulated by changing the overall slag composition, operating the process under relatively oxidizing or reducing conditions, and by stirring. Slag is a major by-product of steelmaking.

Following the primary steelmaking step, dissolved oxygen is normally removed from the crude steel by the addition of deoxidizers. Subsequent processing (*secondary metallurgy*) involves control of dissolved impurities (such as sulfur, hydrogen, and nitrogen) and of second-phase impurities (nonmetallic inclusions).

Quality control of steelmaking relies on discrete measurements of composition (typically using optical emission spectroscopy and inert-gas fusion of *lollipop* samples taken from liquid steel), temperature (taken with immersion thermocouples), and activity of dissolved oxygen (measured with electrochemical probes). Some variables are or could be continuously monitored during processing, including off-gas composition, cooling-water flow rate and temperature, and steelmaking vessel acceleration.

Steelmaking involves physical and chemical processing, manipulated by stirring (electromagnetically or by gas bubbling); physical separation of metal, slag, and gas; and control of reaction equilibria by temperature, slag composition, vacuum, and redox conditions. This rich variety of processing options allow tight and economical control of steel compositions.

Steelmaking costs vary by geographical location but are typically dominated by the cost of raw materials. As indicated by Figure 2, approximately two-thirds of the variable cost is scrap (for electric arc furnace [EAF] steelmaking) or coal (for coke production) and iron ore (for BF/basic oxygen furnace [BOF] steelmaking). The estimates are based on hypothetical

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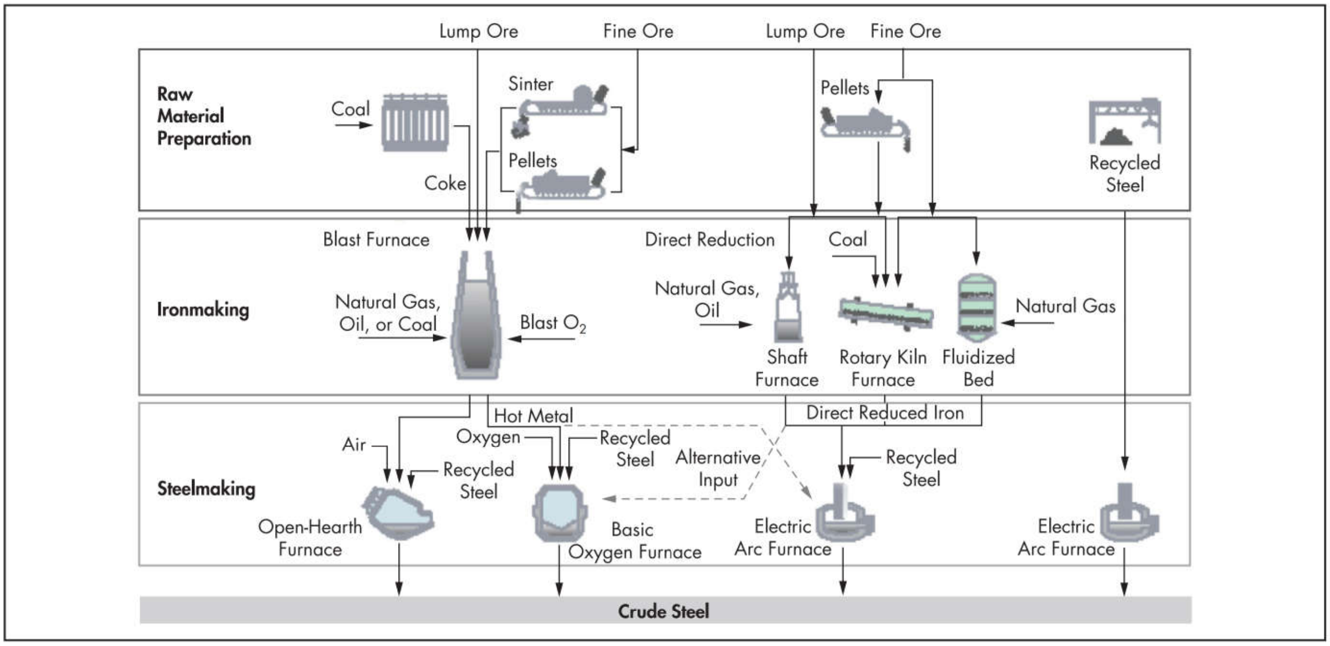
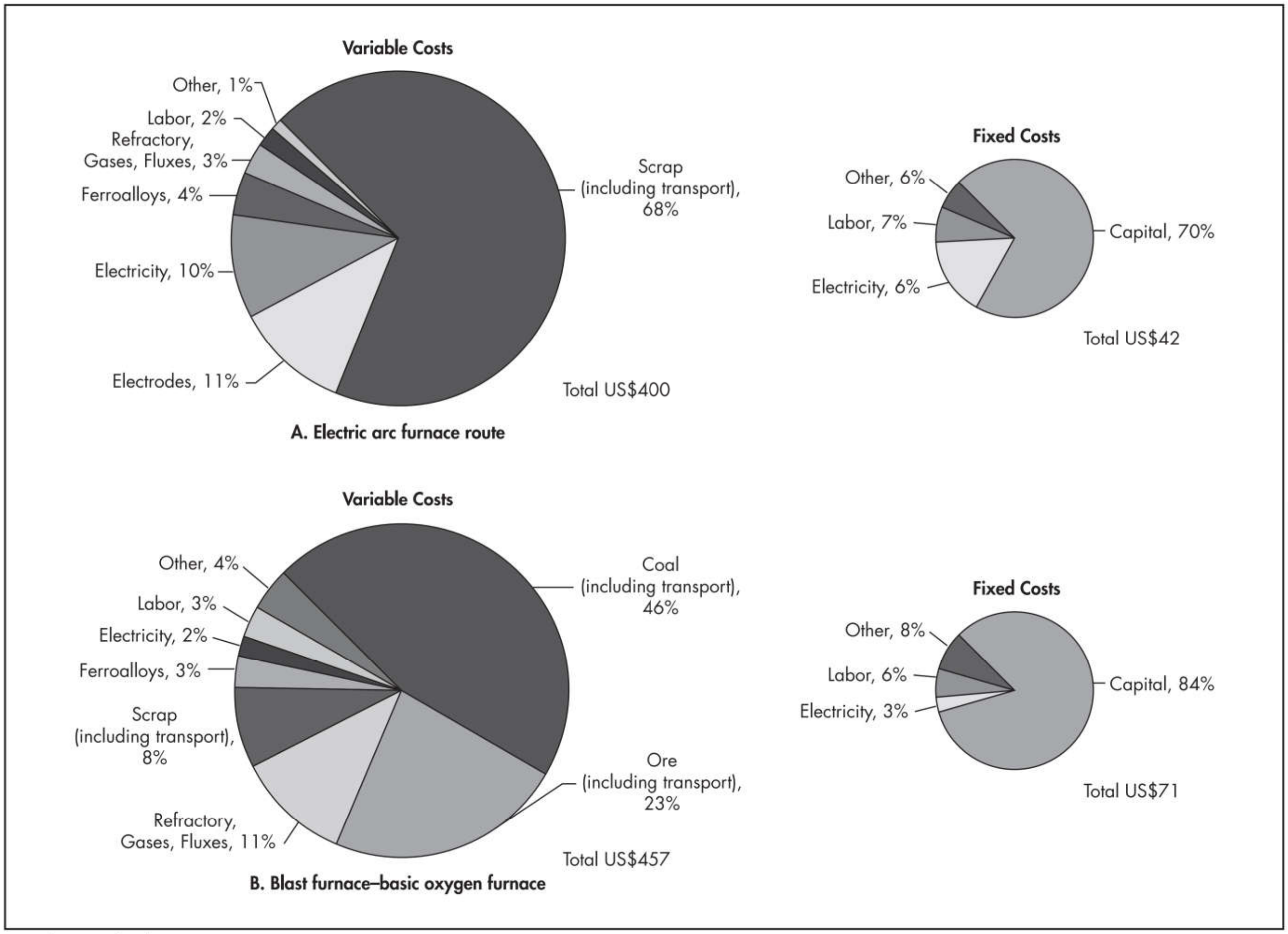


Source: World Steel Association 2018

Figure 1 Steel production routes for basic oxygen furnace and electric arc furnace



Data from steelonthenet.com

Figure 2 Indicative costs of (A) electric furnace steelmaking and (B) integrated steelmaking

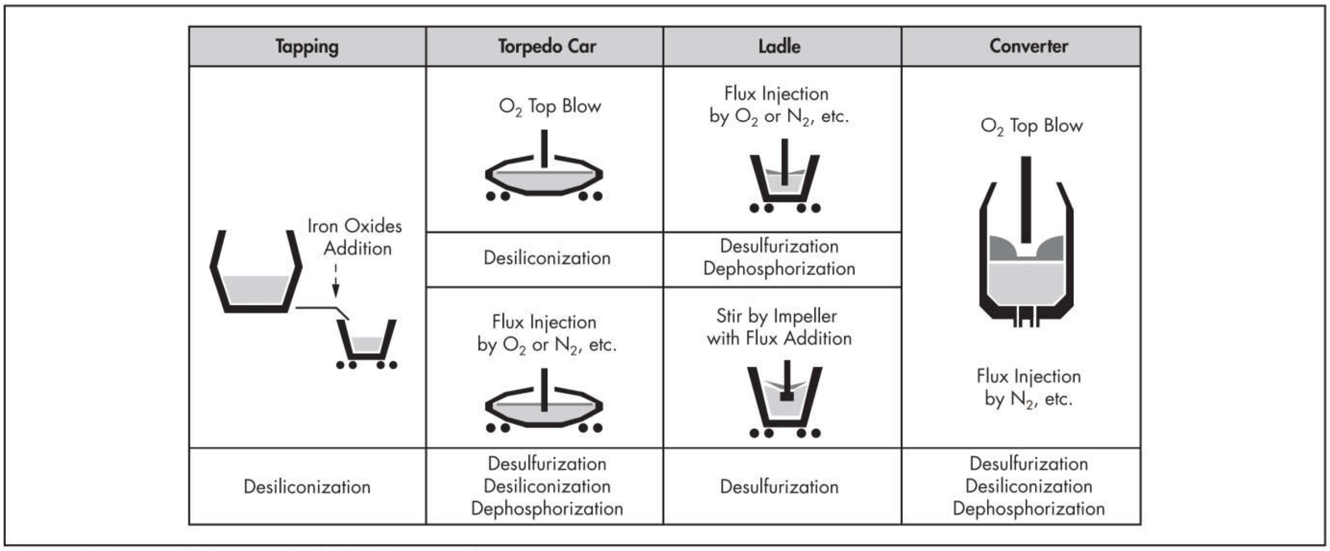


Figure 3 Some refining methods for hot metal pretreatment

coastal Japanese plants in 2017. Credits for by-products and export gas are not included in the costs.

Steelmaking occurs by batch processing; that is, a quantity (*heat*) of material is processed until it achieves the required chemical composition and temperature. In contrast, ironmaking (in BFs and direct reduction) is typically a continuous process.

HOT METAL PRETREATMENT

Hot metal pretreatment is a typical first step in integrated steelmaking, that is, the process that uses hot metal from the BF for oxygen steelmaking. The aim is to remove most of the sulfur and phosphorus when their concentrations in hot metal are much higher than the requirement of the final product. Hot metal pretreatment is normally conducted during the transportation period after the tapping of hot metal from the BF and before charging into the converter for decarburization. A torpedo car, ladle, or converter is used as a refining vessel. Several examples of refining methods and their functions for hot metal pretreatment are compared in Figure 3 (Fuwa et al. 1984; ISIJ 2006; Kitamura et al. 1990; JFE 21st Century Foundation 2003; Kawabata et al. 2002; Kanbara et al. 1972; Kraemer et al. 1968; Mukawa and Mizukami 1994; Ogawa et al. 2001; Sasaki et al. 2013). In the following sections, some thermodynamics and kinetics considerations for desulfurization, desiliconization, and dephosphorization are introduced.

Desulfurization

Desulfurization of hot metal by slag can be expressed as Equation 1 when using solid calcium oxide (CaO) as reactant. In principle, the desulfurization reaction can be promoted by using basic slags, such as soda ash (Na_2CO_3), and CaO-based slags, and by a low oxygen activity in the metal. Desulfurization is commonly not based on slag reactions, however, but on injection of solid calcium carbide or co-injection of magnesium and calcium oxide (Fruehan 1998).

$$\mathrm{CaO(s)} + [\mathrm{S}]_{\mathrm{metal}} = \mathrm{CaS(s)} + [\mathrm{O}]_{\mathrm{metal}} \qquad \textbf{(EQ 1)}$$

Under thermodynamically favorable conditions for desulfurization, mass transfer of sulfur in hot metal is the rate-controlling step. Therefore, the shape and size of refining vessel, size of added flux and addition method, and stirring intensity are important factors for designing the desulfurization process. Flux injection and mechanical stirring as shown in Figure 3 are commonly used to improve kinetics. Rate control by mass transfer of sulfur in the hot metal implies first-order kinetics. This leads to a semilogarithmic relationship between the extent of desulfurization and the amount of reagent needed (Delhey et al. 1989).

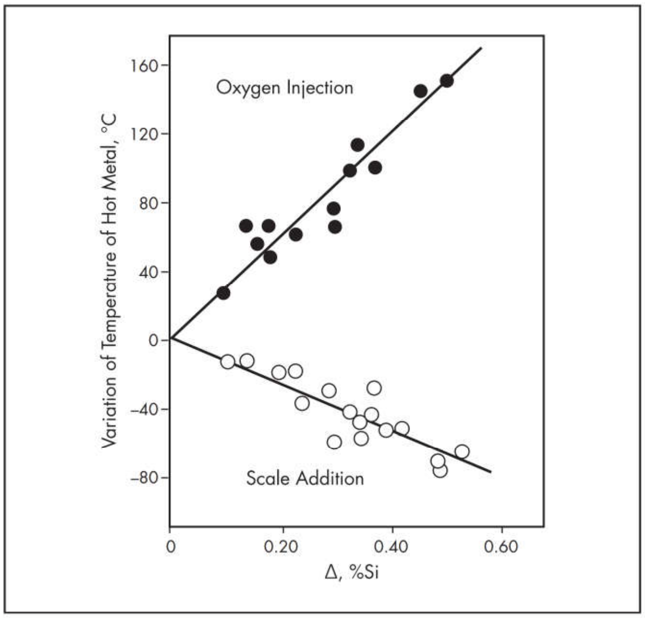
Desiliconization

Both silicon and phosphorus are removed from hot metal by oxidation—the opposite of desulfurization, which requires reduction. BF hot metal typically contains 0.5%–1% Si by mass. Traditionally, desiliconization was often adopted to decrease the CaO consumption and shorten the refining time in the following processes, such as dephosphorization and decarburization. However, because low-basicity slag can be used for dephosphorization (Mukawa and Mizukami 1994; Ogawa et al. 2001), today, desiliconization is not conducted separately in some steelworks but rather occurs as a first step before dephosphorization.

Oxidizers such as iron oxides (mill scale, sinter ore, etc.) and gaseous O_2 are used for desiliconization. Iron oxides are added during tapping or injected into the torpedo car, and O_2 is introduced by top blowing or injection, as shown in Figure 3. Desiliconization changes the hot metal temperature: O_2 injection increases hot metal temperature, whereas use of iron oxides decreases it (Figure 4).

Dephosphorization

Dephosphorization of hot metal pretreatment requires oxidation; see Equation 2. Use of basic slags, a higher oxygen activity, and lower temperatures all promote dephosphorization. Dephosphorization typically involves a basic iron oxide (FeO)-containing slag reacting with hot metal that contains carbon. This slag and metal cannot coexist at equilibrium: Some carbon is oxidized in parallel with oxidation of phosphorus. The relative extents of these competing reactions depend on both the thermodynamics (temperature and slag



Source: Kawauchi et al. 1983

Figure 4 Oxygen injection and scale addition affect temperature

composition) and kinetics. An empirical equation has been proposed to quantify the joint effects of temperature, slag, and carbon in hot metal (Ogawa et al. 2001), and kinetic models have been used to quantify the competitive reactions (Kitamura et al. 2014).

$$[\mathrm{P}]_{\mathrm{metal}}+\frac{5}{4}\mathrm{O}_2+\frac{3}{2}(\mathrm{O}^{2-})_{\mathrm{slag}}=(\mathrm{PO}_4^{3-})_{\mathrm{slag}} \quad \textbf{(EQ 2)}$$

In Equation 2, [P] is phosphorus dissolved in the metal, O_2 is gaseous oxygen, O^{2-} is anionic oxygen in the slag, and $PO_4{}^{3-}$ refers to phosphate ions in the slag.

CaO-based slag is often used for the dephosphorization process, either of high CaO-to-silicon dioxide (SiO_2) ratio with low FeO content or low CaO/SiO_2 ratio with high FeO content. During the dissolution of CaO into slag, $2CaO{\cdot}SiO_2$ solid solution forms a layer surrounding the CaO particle (Hamano et al. 2006), and $2CaO{\cdot}SiO_2$-$n3CaO{\cdot}P_2O_5$ solid solution also forms within and near this layer (Saito et al. 2009). This phenomenon concentrates phosphorus oxide (P_2O_5) from liquid phase to solid phase, maintains a low P_2O_5 concentration in the liquid slag, and therefore promotes the transfer of phosphorus from metal to slag.

CONVERTER STEELMAKING

The converter process is the main steelmaking method, responsible for nearly 75% of world steel production. The modern oxygen converter evolved from air-blown Bessemer and Thomas converters developed in the second half of the 19th century. These processes had high productivity but also quality problems caused by high nitrogen content from air. As blowing was through the vessel bottom, the technique could not use pure oxygen because of overheating and catastrophic lining wear. The problems of oxygen injection were solved by top blowing with a water-cooled lance, first realized in Linz, Austria, in 1951. The process is known as LD (Linz-Donawitz) or basic oxygen process (BOP)/BOF steelmaking. The new method emerged rapidly during the 1960s and became the dominant steelmaking process (Michaelis 1979; Jalkanen and Holappa 2014).

Oxygen bottom blowing was successfully resolved by using annular nozzles, in which O_2 is blown through the inner tube and a shrouding gas (hydrocarbons [C_xH_y], Ar) blown through the outer annulus. The first OBM/Q-BOP (oxygen-bottom-Maxhütte/quick, quiet, quality BOP) was commissioned in 1967. Since then it has spread and currently accounts for about 10% of the overall converter capacity (Brotzmann 1979). Experiences from the OBM process clearly revealed the principal drawback of top blowing: the relatively weak stirring effect of the oxygen jet, resulting in over-oxidation of the slag and of the metal bath.

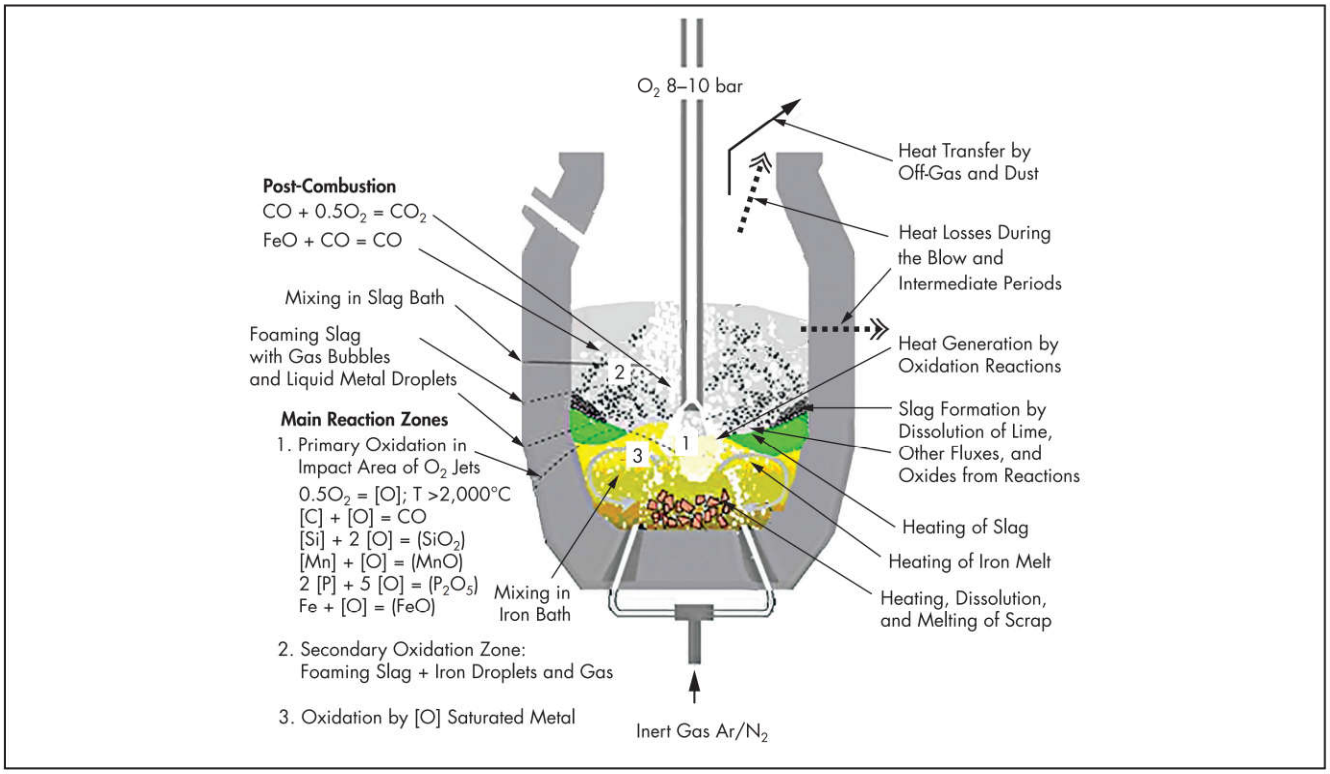
The benefits of both processes were combined into one process; numerous combined-blowing processes were developed since the middle 1970s, most based on the LD process with inert-gas bottom blowing. A great majority of the converters today are these *hybrid* processes. The advantages compared to pure top blowing are reported to be increased blowing efficiency owing to strongly intensified melt stirring, lower FeO in the slag, increased refractory lining life, better accuracy in target end composition and temperature because of better homogeneity, as well as less splashing and spitting of slag (Jalkanen and Holappa 2014). The following section describes the features of the modern oxygen top blowing plus inert-gas bottom stirring practice.

Process Description

Hot metal from BFs typically contains about 94.5% Fe, 4.5% C, 0.3%–0.4% Si, 0.1%–0.3% Mn, and 0.03%–0.05% S plus varying amounts of other impurities (such as P, Ti, and V), depending on the raw materials for sinter, pellets, coke, and coal. High-phosphorus ores used to be more common but were discarded during the last 50 years. However, two categories still exist. In Asian plants, typical hot metal has 0.08%–0.13% P, whereas in Europe and the United States, the typical level is 0.05%–0.07% P (Jalkanen and Holappa 2014). For these reasons, special processes for hot metal dephosphorization are in use in Japan, Korea, and China (Kitamura 2014). For low-phosphorus hot metal, external dephosphorization is not needed. Sometimes, iron ore contains significant concentrations of other impurities, such as vanadium, resulting in up to 0.1% V in BF hot metal and requiring special attention in the BOF process. This section focuses on decarburization, which is the main goal of the converter process.

Figure 5 shows the main features (reactions and zones) of a BOF vessel and the physical and chemical phenomena that occur during converting (Jalkanen and Holappa 2014). A heat starts with charging of steel scrap and liquid hot metal. The permissible amount of scrap depends on the thermal balance of the process, considering physical and chemical heats, as well as input and output temperatures of the system phases. Most of the heat generation comes from oxidation of carbon and a smaller share from oxidation of silicon and iron and other reactions. Typical scrap rates are 15%–25%. Even higher fractions are possible, for example, by utilizing post-combustion or addition of extra fuel (such as coke or ferrosilicon) (Dubois et al. 2003).

As seen, carbon oxidation occurs not only in the impact area of the oxygen jet but also in the slag and at the slag–metal interface. The slag has other refining roles: It binds the condensed-state oxidation products (mainly SiO_2, MnO, FeO, and P_2O_5) and protects the basic refractory lining. Lime (CaO)

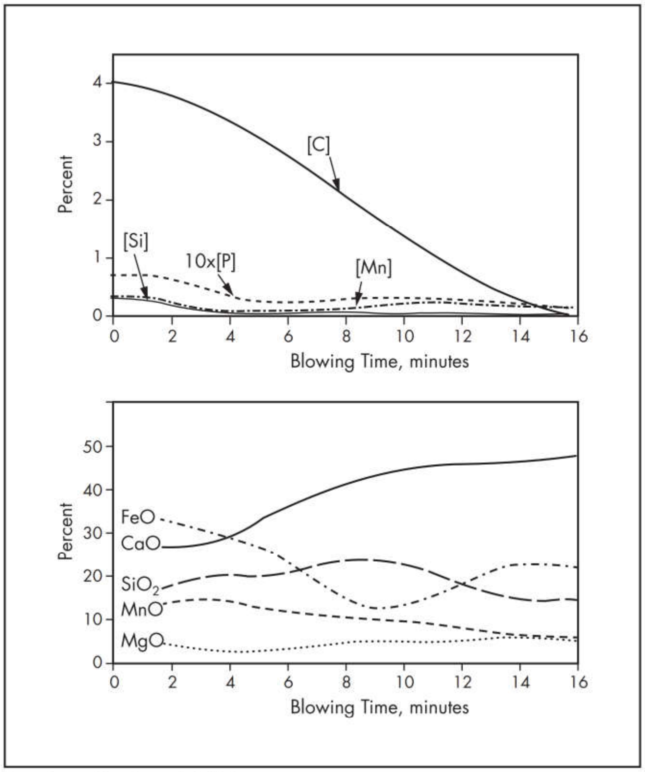


Source: Jalkanen and Holappa 2014

Figure 5 Basic oxygen furnace converter with oxygen lance and bottom-blown inert gas

is added before the start of the blow and during blowing to attain a high slag basicity value (the CaO/SiO$_2$ mass ratio is often larger than 3), which is favorable for dephosphorization and lining protection. Typical composition evolution in the metal bath and slag during the oxygen blow period is shown in Figure 6. For more information about the phenomena behind the features of the curves, see Jalkanen and Holappa (2014). The lines were drawn as trend lines based on the experimental data (Cicutti et al. 2000) and generally known phenomena taking place in a typical process.

During blowing, the temperature increases from the hot metal temperature, typically 1,300°–1,350°C, to the steel target temperature in the 1,650°–1,700°C range. The heat generation from reactions (Figure 5) and the amounts of cooling materials, scrap and other additions, lime, doloma lime, iron ore, as well as heat losses, define the end temperature. The main targets of process control are that the carbon concentration should be less than a prescribed maximum and the temperature higher than a set minimum; often a maximum phosphorus concentration is an additional target. If all targets are not attained, re-blow is needed. The carbon target depends on the final C content of the steel to be produced: For high–C grades $[C]_{max}$ can be up to 0.7% C, and for ultra-low-carbon (ULC) grades, for example, 0.04% C. The target temperature depends on the steel grade, but also on the subsequent process stages, which often include the possibility for heating in a ladle furnace. In such a case, the optimum temperature is related to the requirements of both converter process and ladle metallurgy. Process control systems are generally based on a static model with mass and heat balance calculations, which calculates the amount of oxygen, scrap, and other additions.



Data from Cicutti et al. 2000

Figure 6 Evolution of composition of iron bath and slag during oxygen blowing

The model starts from measured input values (analyses of hot metal, scrap, etc., and temperatures) and output values (target C, T, P), then calculates reactions in the metal bath and in the slag phase. The target values (C, T) are then attained via iteration. The hit rate can be improved by adaptive control using experimental data from previous heats. Today, dynamic control systems are common in large converters, often utilizing a sub-lance device for direct measurement of T, [C] and/or $a_{[O]}$ with probes. The measurement is performed 1–2 minutes before the predicted blow end to have enough time for corrective actions. Another method for carbon control is a cumulative calculation of carbon oxidation by applying continuous off-gas analysis and flow measurement. Strict control improves productivity by shortening average time from converter tapping to next tapping. Typical tap-to-tap times are 35–40 minutes, which is compatible with other downstream unit processes.

ELECTRIC ARC FURNACE STEELMAKING

Increased steel stock worldwide results in the generation of steel scrap, and thus a suitable recycling process is required. The major steel recycling process is EAF steelmaking, in which steel scrap is melted and refined. EAF steelmaking is also a major process for the production of special grades of steel, for example, stainless steel or highly alloyed steel.

EAF steelmaking has also become a major steelmaking process in newly developed countries because of its relatively low initial investment and lesser technical and metallurgical difficulty compared with integrated ironmaking and steelmaking (that uses iron ore and reducing agents). Today, some steel mills use large-production-capacity EAFs with tap sizes of up to 400 t.

Furnace Type

The majority of EAFs use alternating current (AC), converting electrical energy to thermal energy by using electric arcs produced by three-phase AC. The energy is used for melting and refining the steel. Direct current arc heating is also utilized in some furnaces. There are several systems to improve the energy efficiency of operation. Because much of the energy input into the furnace is lost as sensible heat in the off-gas (Table 1), systems are available to use this heat to preheat steel scrap before charging to the EAF furnace. These include conveyor and shaft systems, in which scrap is continuously preheated by off-gas from the EAF. However, there are various technical challenges; therefore, preheating systems are still under development and not widely utilized in commercial operating furnaces.

Raw Materials

The main raw material for EAF steelmaking is various grades of steel scrap. Selection of steel scrap grade depends on the quality and type of steel to be produced. Heavy steel scrap has a known composition and fewer impurities, while some steel scrap, such as waste household appliances or automobile shredder residue, contain various kinds of metallic impurities. During oxidizing refining of molten steel, some elements cannot be removed, including copper, tin, and nickel. Contamination of steel products by copper has become a serious problem. Although some special refining processes have been proposed to remove copper, these are impractical, and other economically feasible countermeasures, such as scrap sorting, are required.

In some regions, the supply of steel scrap cannot satisfy the demand of EAF steel producers. In such a case, steel scrap is imported from other countries, or other iron resources, such as cold pig iron, DRI or hot briquetted iron, are used as raw materials.

Typical Energy and Electricity Consumption

A typical thermal energy balance for a Japanese EAF is summarized in Table 1. Modern operations utilize a large proportion of chemical reaction energy to increase productivity and reduce electricity consumption. In addition, various lances and injectors are used in modern EAFs. Oxygen or oxygen and gas coherent burners are used for scrap cutting, steel refining, and supplying supplementary energy. Immersed lances are used for coal and coke injection into slag, mainly for slag foaming. The other essential technology for energy utilization is post-combustion above the furnace melt, where oxygen gas is injected to burn CO gas generated through slag–carbon reaction and the combustion energy provides further heating.

Efficient energy utilization, less thermal damage to the furnace body, and stabilized arcing are promoted by covering the electric arc with foamy slag.

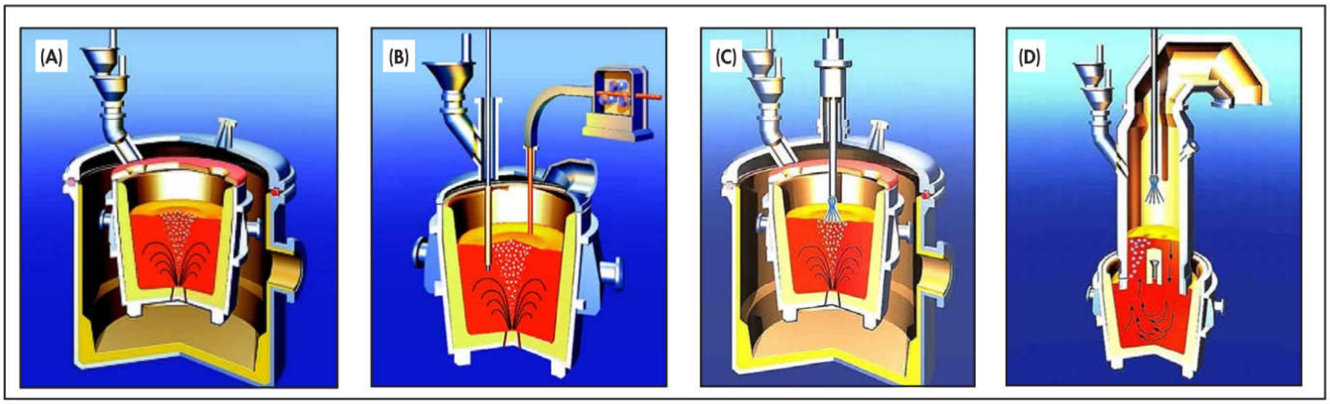
Operation

EAF operations are divided into four steps: (1) raw material charging, (2) melting, (3) refining, and (4) tapping. Except for furnaces equipped with a scrap preheating system, raw materials, such as steel scrap, DRI, or cold pig iron, are put into a charging bucket according to a prescribed recipe. The recipe prescribes not only the chemical composition but also the layering order by scrap density, size, and other feedstocks, for smooth melting and furnace protection. The charging bucket is transferred onto the furnace body and the bucket bottom is opened for charging. The furnace is subsequently covered by a water-cooled roof, and the graphite electrodes (three electrodes for an AC furnace) are lowered.

The melting process, during which the melted and unmelted materials coexist, should be completed as quickly as possible; this requires a well-considered procedure depending on type of raw materials and their mixing ratio, furnace size, electric power input, auxiliary materials, other inputs, and use of a hot heel (molten material retained from the previous heat). Some furnaces that consume a large proportion of DRI continuously feed this material (through one or more ports in the furnace roof) during arcing.

Table 1 Typical thermal energy balance of a Japanese electric arc furnace

Input	kW·h/t	Output	kW·h/t
Electricity	313	Molten steel	396
Metal heel	41	Slag sensible heat	54
Slag heel	11	Remaining metal heel	40
Scrap sensible heat	170	Remaining slag heel	11
Fuel burning	20	Electric energy loss	11
Oxidation of electrode	12	Cooling water	58
Oxidation of auxiliary materials	192	Off-gas	189
Slag formation heat	5	Furnace radiation heat	9
		Others	–4
Total	**764**	**Total**	**764**



Courtesy of SMS Group

Figure 7 (A) Vacuum tank degassing, (B) ladle treatment station, (C) vacuum oxygen decarburizing, and (D) Ruhrstahl Heraeus degasser with oxygen blowing units for secondary refining

The conventional EAF operation also refines the steel. Decarburization and dephosphorization reactions proceed during the initial refining stage in oxidation mode. The generated slag is continuously removed from the furnace as a foamy slag. During an optional last stage of refining, desulfurization, iron or chromium recovery, and temperature tuning can be achieved under reducing conditions. Commonly, secondary refining processes are available in the steel plant, in which case it is not necessary to refine the steel in the EAF under reducing conditions.

Tapping of molten steel is conventionally conducted by tilting the furnace. Modern EAFs have a bottom tapping hole (eccentric bottom tapping) to remove molten steel without moving the furnace, promoting quick tapping and avoiding entrapment of slag. A portion of the molten steel is retained in the furnace as a *hot heel* to smoothly melt steel scrap in the next heat.

SECONDARY STEELMAKING

Decarburization and (to some extent) dephosphorization are carried out during primary steelmaking. Final adjustments of composition, cleanliness, and temperature are performed in a separate vessel after primary steelmaking. Generally, this step is referred to as *secondary steelmaking* (refining) or *ladle metallurgy*. Ladle metallurgy is important in the production of high-quality steel.

Alloying

Usually basic alloying is performed during tapping, which is the process of transferring liquid steel from the BOF/EAF furnaces to a ladle; the kinetic energy of the tapping stream is utilized to intensify alloy melting and promote homogenization in the ladle. Secondary additions are then made during ladle treatments. For small additions, such as trimming of major components and micro-alloying, a special technique, wire injection, is often used. The alloying system in vacuum tank degassing and wire feeding at a ladle treatment station are schematically shown in Figures 7A and 7B.

Gas Stirring

Inert gas (argon) is generally used to stir the steel in the ladle. The gas rising through the liquid steel induces a turbulent recirculatory motion that provides the necessary bath agitation for increasing the rates of various heat- and mass transfer–controlled processes (such as melting of deoxidizer and alloying additions and their dissolution and dispersion). As the injected gas escapes to the surroundings, the redirected bulk flow from the spout region (plume eye) pushes the slag layer radially outward, exposing the melt surface. This plume eye is a potential site for reoxidation, nitrogen pickup, and slag entrainment phenomena and hence can influence quality of steel profoundly. Therefore, during the final stage of ladle refining and immediately prior to continuous casting, it is customary to practice gentle stirring to ensure a small plume eye area.

Temperature and Composition Control

Temperature and composition control are routinely carried out in a ladle furnace following furnace tapping. A top cover is placed on the ladle and graphite electrodes are lowered into the ladle through holes in the cover. An arc is struck between the electrodes and steel, transferring heat to the melt by convection and radiation. Convection generated by argon bubbling helps to distribute heat within the melt; relatively large argon flow rates are employed. The top cover also provides significant protection from atmospheric oxidation and radiation heat losses.

Degassing

Degassing is the removal of carbon, nitrogen, and hydrogen. The carbon content cannot be reduced to very low levels in the BOF because oxidation of iron increases strongly when [C] decreases below approximately 0.03%. The maximum carbon requirements for ULC steel can be as low as 20–30 ppm (by mass). This is achieved by vacuum degassing. As subsequent carbon contamination (pickup) cannot be fully avoided, the aim value after vacuum treatment is 10–20 ppm. In certain processes, oxygen is blown while placing the steel under vacuum to promote deep decarburization (Figures 7C and 7D).

Hydrogen in steel originates from ambient moisture (in air), either directly or indirectly from added lime and other hygroscopic slag formers, and from other sources such as alloying materials and moisture in refractory linings. Typical [H] contents in steel produced by EAF and BOF processes are in the range of 4 to 6 ppm and 2 to 4 ppm, respectively. Hydrogen removal is done by vacuum degassing; [H] contents less than 2 ppm are readily attained. For some critical grades, the aim value after hydrogen removal can be less than 1 ppm, requiring a long and efficient vacuum treatment. For efficient dehydrogenation, the pressure in the vacuum chamber should be below 1 mbar.

Nitrogen in steel originates from N_2 in air dissolving as nitrogen atoms. In the BF process, some nitrogen is dissolved in iron, and typical values are about 50 ppm (or less) in hot metal. In the BOF converter, the CO gas evolution efficiently flushes the liquid steel, and [N] contents down to 10–20 ppm are attained. During tapping, the steel is contaminated by air, causing some [N] pickup. Because of the high solubility of nitrogen in steel and kinetic limitations, only limited nitrogen removal can be achieved by vacuum degassing.

Desulfurization

Desulfurization can be understood as an electrochemical exchange reaction, as shown in Figure 8, where dissolved elemental sulfur (in the steel) receives two electrons and turns into a sulfide anion that dissolves in the slag. The electrons are obtained from free oxygen ions in the slag; [O] atoms are formed and transferred to steel as dissolved oxygen, which can further react with deoxidizing elements such as silicon and aluminum.

The sulfide capacity quantifies the partitioning of sulfur from steel to slag. The sulfide capacity strongly increases as the composition approaches CaO saturation, indicating better thermodynamic conditions for desulfurization.

It has been commonly concluded that the overall desulfurization rate is controlled by mass transfer of sulfur in molten steel, which is promoted by strong argon stirring (Roy et al. 2013). However, mixed control (by mass transfer in both steel and slag) may arise in some cases: For less-basic slags with a viscosity greater than about 1.1 dPa·s (poise) and an equilibrium S partition ratio L_S lower than about 400, the overall mass transfer coefficient is affected by a change in the physicochemical properties of the slag (Kang et al. 2017).

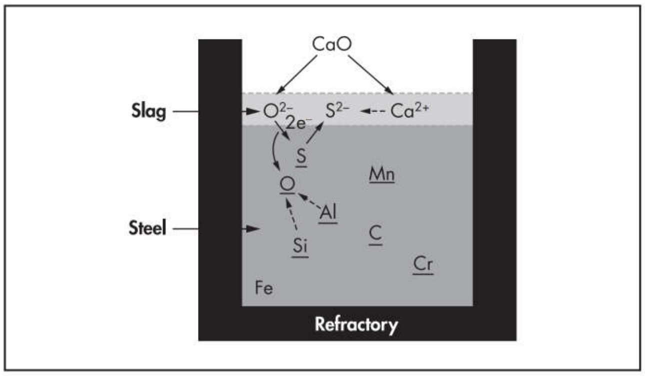
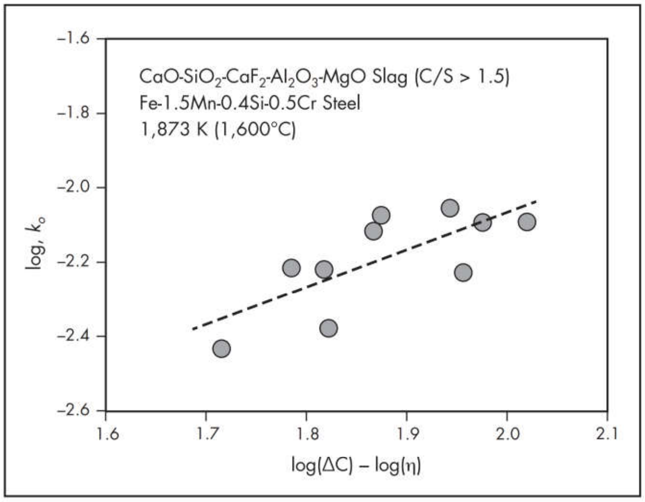


Figure 8 Transfer of sulfur from steel to slag, coupled to transfer of oxygen from slag to steel



Source: Park and Park 2016

Figure 9 Apparent rate constant of inclusion removal reaction and slag parameter relationship

Deoxidation and Inclusion Control

After the BOF converter process or scrap melting and oxygen blowing in EAF steelmaking, the crude steel has a high concentration of dissolved oxygen (typically in the range of 200 to 800 ppm). Currently, most steelmaking aims at complete *killing* (lowering dissolved oxygen to around 50 ppm or less) by addition of strong oxide-forming elements (deoxidants) such as aluminum and silicon.

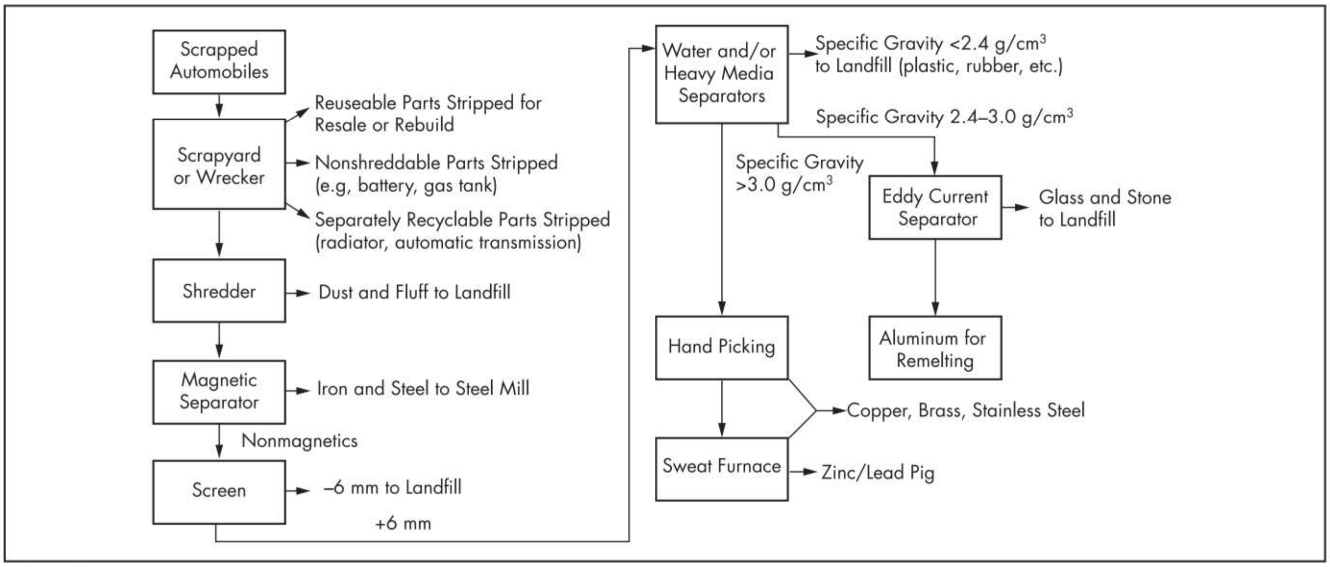
When deoxidants are added into liquid steel, intensive nucleation results in many small inclusions. After initial nucleation, the inclusions grow by diffusion, coalescence, and collisions; collisions are regarded as the main growth mechanism (Linder 1974). Because of the rapid initial deoxidation reaction, the dissolved oxygen content decreases to a value close to the equilibrium shortly after deoxidant addition and can be regarded as almost constant until steel casting (Patil and Pal 1987). However, the total oxygen content, which is the sum of the dissolved oxygen and the oxygen bound in inclusions (deoxidation products), decreases relatively slowly during the subsequent ladle metallurgical operations. The decrease in total oxygen directly reflects removal of inclusions from the steel to the top slag. It has been suggested that the dissolution rate of inclusions into the slag phase is proportional to the ratio of the driving force for inclusion dissolution (expressed as a concentration difference, ΔC) to slag viscosity (η) (Valdez et al. 2006). This implies that the inclusion removal rate would strongly depend on the physicochemical slag properties as shown in Figure 9, where k_{ox} represents the apparent rate constant of inclusion removal (Park and Park 2016), including the driving force of the chemical dissolution of alumina (Al_2O_3) and the viscosity of the slag.

ENVIRONMENTAL ISSUES

Efficient scrap recycling, valorization of the steelmaking by-products (such as slag, dust, and sludge), and innovative process development for reducing carbon intensity of steelmaking contribute to lowering the environmental effects of steelmaking.

Scrap Recycling

The steel industry has been recycling steel scrap for more than 150 years. Increased consumption of scrap reduces the needs for additional resource extraction and hence the environmental impact.



Adapted from Spoel 1990

Figure 10 Recycling scrapped automobiles

Scrap Source

The three main sources of steel scrap are home scrap, prompt scrap, and obsolete scrap. Home scrap is generated within the steel mill during production of iron and steel. It presents no major problems of collection, transportation, and sorting. This scrap has a known composition and is easily recycled to steelmaking. Prompt scrap is generated from the manufacturing process of steel products. It is recycled as part of normal industrial housekeeping as well as for economic reasons. Obsolete scrap consists of obsolete machinery, industrial equipment, agricultural equipment, household appliances, and automotive steel. Because of the wide variety of chemical and physical characteristics, old scrap often requires significant preparation for its recycling, such as sorting, de-tinning, and de-zincing, prior to consumption in mills.

Scrap Processing

Using a variety of equipment, scrap dealers collect and process scrap into a physical form and chemical composition that steel mill furnaces can consume. Figure 10 shows a flow-sheet example for recycling of scrapped automobiles (Spoel 1990). The largest and most expensive equipment is the shredder. The shredder can fragment vehicles into fist-sized pieces of various metals, glass, rubber, and plastic. Hydraulic shears, which have cutting knives of chromium-nickel-molybdenum alloy steel for hardness, slice heavy pieces of ship plate, railroad car sides, and structural steel into chargeable pieces. Various separation processes are applied for sorting and preparation of steel scrap, including magnetic, eddy current, and heavy medium methods; separation by other physical and chemical characteristics; and incineration. Recently developed scrap-sorting technologies include portable optical emission spectrometers, color sorting, and laser-induced breakdown spectroscopy (Yellishetty et al. 2011). Baling presses are used to compact scrap into manageable bundles, thereby reducing scrap volume and shipping costs.

Scrap in Steelmaking

Steel plants melt scrap in BOFs, EAFs, and, to a minor extent, BFs. The proportion of scrap in the charge of a BOF is limited to less than 30%, whereas that in an EAF can be up to 100%. Steel and iron foundries use scrap in EAFs and cupola furnaces. Scrap recycling in steelmaking allows the BF to be bypassed, eliminating the cost of using expensive equipment, labor, energy, iron ore, and coke, resulting in significant primary resource savings and reductions of CO_2 emission and waste generation. One published estimate is that, on average, recovery of 1 t of steel from scrap conserves 1,030 kg of iron ore, 580 kg of coal, and 50 kg of limestone (Fenton 2003). Another estimate can be made: 1.1 t of scrap is needed to produce 1 t of EAF steel, avoiding use of 1.5 t of ore to produce 1 t of BOF steel (steelonthenet.com, n.d.). This means that 1 t of scrap conserves approximately 1.4 t of iron ore.

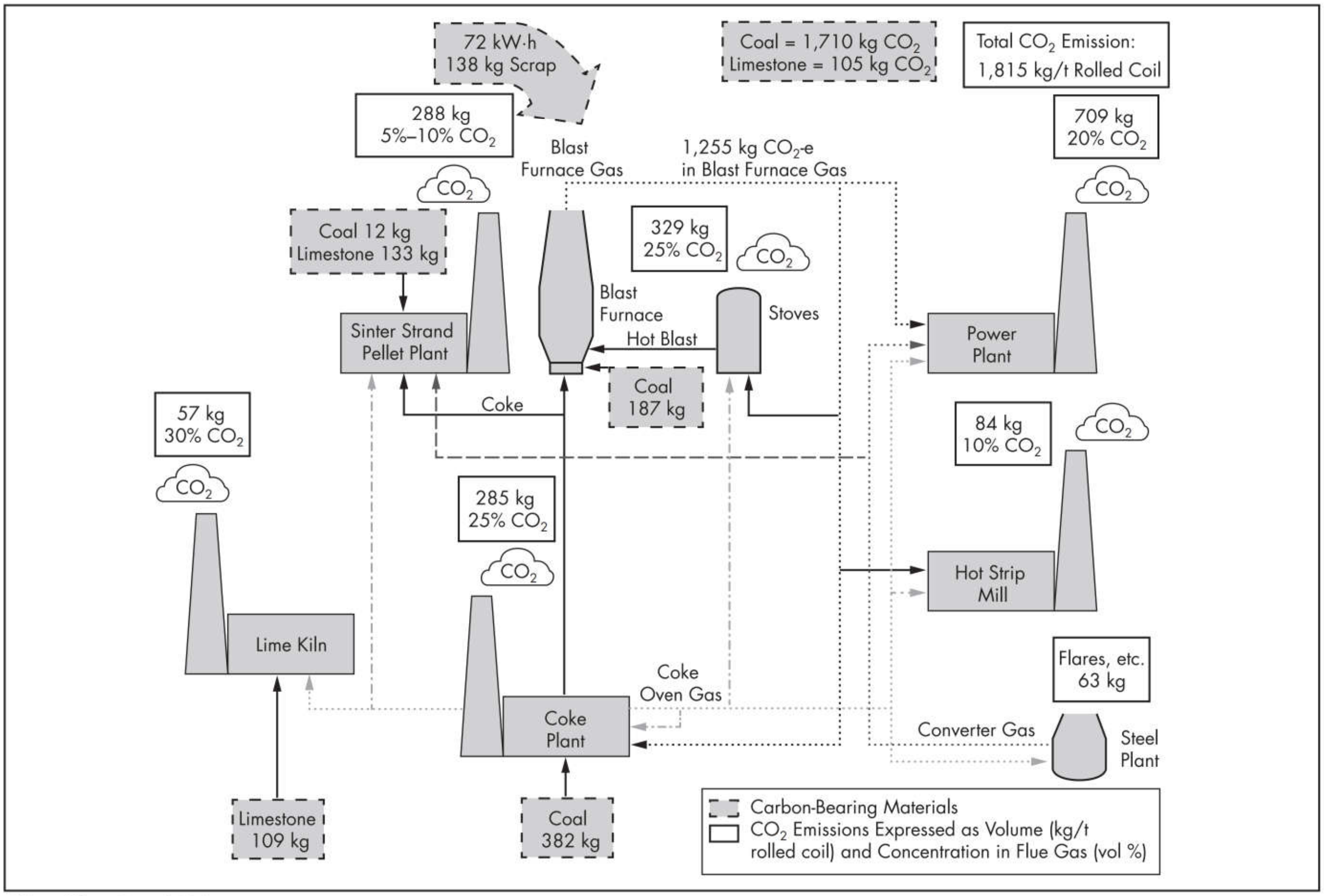
A major issue of the scrap recycling in steelmaking arises from tramp elements (Cu, Sn, Zn, Pb, Mo) in scrap. For example, automotive scrap contains copper and tin from the electrical systems. These tramp elements are hard to remove in steelmaking, degrading the steel quality, complicating the slag chemistry, and causing refractory degradation (e.g., lead oxide can penetrate refractory bricks and damage the furnace).

Carbon Intensity of Steelmaking

Currently, iron and steel production is the largest industrial source of CO_2 emissions, at 6%–7% of global anthropogenic CO_2 emissions. This is attributed to using carbon-based fuels and reductants and the large volume of steel produced (1,630 Mt [million metric tons] in 2016) (World Steel Association 2017).

CO_2 Emissions in Steel Production

The main CO_2 emissions in steel production are from BFs where iron ore reacts with a reducing agent, like coke, ultimately producing large volumes of CO_2. The carbon intensity of iron and steel production varies considerably between



Adapted from Birat 2009

Figure 11 Typical steel plant CO_2 emission

the production routes, ranging from around 0.4 t CO_2/t crude steel for scrap EAFs, to 1.7–1.8 t CO_2/t crude steel for the integrated BF/BOF, and 2.5 t CO_2/t crude steel for coal-based DRI processes (Carpenter 2012). Figure 11 shows the principal CO_2 sources for a typical integrated steel plant producing hot rolled coil. The figure gives a simplified carbon balance, indicating the major entry sources (coal and limestone) and the stack emissions, in volume (kilogram per ton of hot rolled coil) and concentration of CO_2 (volume percent). The BF (69% of emissions) is the largest emitter of CO_2, followed by the sinter/pellet and coking plants.

Reducing Carbon from Steelmaking

Available technologies for reducing CO_2 emissions from iron- and steelmaking processes include (1) minimizing energy consumption and improving the energy efficiency of the process; (2) using clean energy and low-carbon materials in the process; and (3) capturing the CO_2 and storing it.

CO_2 emissions can be reduced by recovering heat from the various gaseous steams and solid and liquid products. The calorific value of off-gases can be recovered before these are emitted to the atmosphere. The gases can also be utilized as a fuel, to produce steam for internal use or to generate electricity. Condensed-phase streams suitable for heat recovery include liquid slag (by dry granulation) and hot coke (by dry quenching; recovering around 80% of the sensible heat of coke and generating around 160 kW·h/t coke [Carpenter 2012]).

CO_2 emissions would be significantly cut if steel plants could switch to clean energy and low-carbon materials, for example, scrap as charge materials (in EAF and BOF), hydrogen (or biomass) as a reducing agent, and using electricity generated in hydroelectric or nuclear power plants or from renewable energy.

Finally, CO_2 emissions could be cut by equipping steel plants with carbon capture and storage. In-process CO_2 capture with oxygen operation could also reduce CO_2 emissions from BFs. In addition, mineral sequestration has been proposed for storage of CO_2: Some minerals (e.g., in magnesium-rich ultramafic rocks) can react with CO_2 to form stable carbonates. However, application of the mineral sequestration is limited by the reaction kinetics.

Steelmaking By-Products

Depending on technological level, production route, and charging materials, approximately one ton of solid wastes or by-product is generated per ton of steel produced from steel industries. These solid wastes (Table 2) or by-products include slag, sludge, dust, and mill scale, and contain valuable metals and minerals.

Ironmaking Slag

Ironmaking slag (approximately 300–400 kg/t of pig iron) is produced during BF processes, from the gangue in the raw materials and fluxing additions. The slag contains mainly

Table 2 Solid and liquid waste generated from steel plants

Solid and Liquid Wastes	Mass Relative to Hot Metal, kg/t	Source of Generation
Coke breeze	—	Coke oven
Nut coke	—	Coke oven
Coke dust and sludge	—	Coke oven
Blast furnace slag	300–400	Blast furnace
Blast furnace dust and sludge	28	Blast furnace
Sintering plant sludge	—	Sinter plant
Basic oxygen furnace slag	100–200	Steel melting shop
Lime fines	15–16	Steel melting shop
Electric arc furnace slag	100–200	Steel melting shop
Electric arc furnace dust	11–20	Steel melting shop
Gas-cleaning-plantsludge	—	Steel melting shop
Carbide sludge	—	Acetylene plant
Mill scale	22	Mills
Mill sludge	12	Rolling mills
Refractory, bricks	11.6	Steel melting shop, mills, etc.
Sludges and scales	—	Water treatment plant
Fly ash	—	Power plant

Source: Das et al. 2007

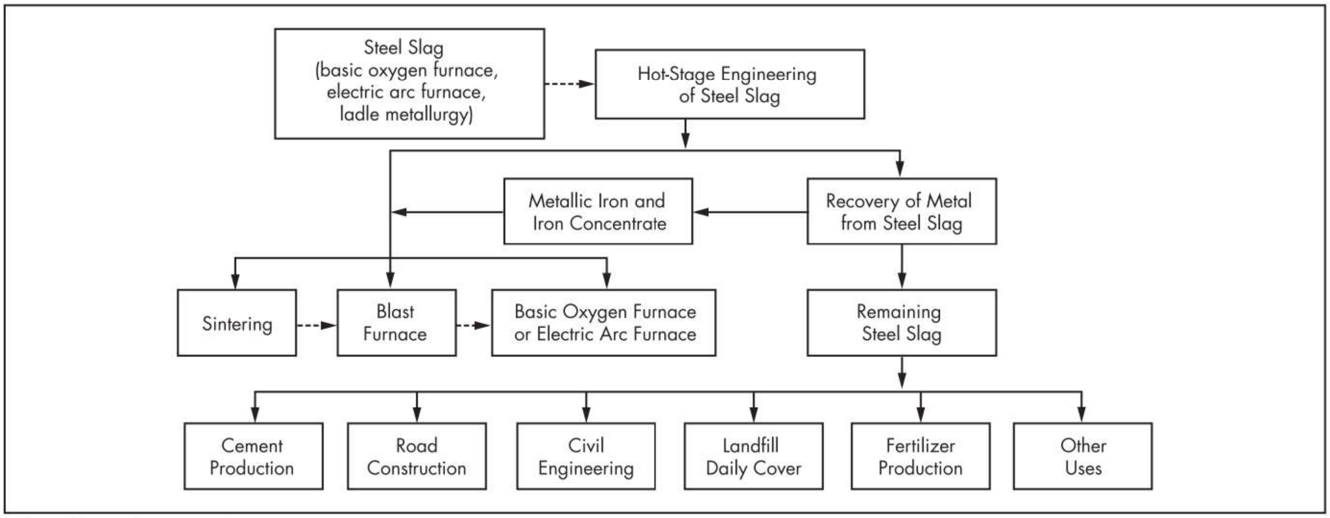
inorganic constituents such as 30%–35% SiO_2, 28%–35% CaO, 5%–10% MgO, 10% Al_2O_3, 1% iron oxide (expressed as Fe_2O_3). Because BF slag contains little iron and is high in CaO, it is used in cement production. The slag is either air-cooled or granulated. Air-cooled slag is used as aggregate in road construction, and granulated slag is used for cement making. Almost 100% of BF slag is utilized in many areas, such as cement production, road construction, civil engineering work, fertilizer production, landfill daily cover, soil reclamation, and others. Recovery of metals from BF slag is not important because of its low iron content (Fe <2%). In leaching studies, the concentrations of hazardous elements (including As, Ba, Cd, Cr, Pb, Hg, Se, and Ag) were much lower than the toxicity characteristic leaching procedure criterion, indicating that the elements are very tightly bound and not released from the matrix (Proctor et al. 2000).

Steel Slag

Steel slag (100–200 kg/t of liquid steel) is formed in steelmaking from oxidation of Si, P, Mn, and Fe in BOF and EAF steelmaking; other impurities; and addition of fluxes. The main components in steel slags are CaO, Fe, SiO_2, MgO, and MnO. Iron is present as metallics (7%–10%), iron oxide, and iron-bearing minerals. Figure 12 summarizes the recycling of steel slag (Okumura 1993). The metallic iron can be separated by mineral processing technology and recycled by sintering, BF ironmaking, and steelmaking. After metal recovery, the high content of 30%–50% CaO, 3%–10% MgO, and MnO in steel slags can be used to substitute for a part of limestone, dolomite, and manganese ore in steelmaking. However, 50%–90% of the total steel slag (Das et al. 2007) has higher concentrations of phosphorus and sulfur, limiting direct recycling to the ironmaking and steelmaking. Such slag is usually subjected to metal recovery and then applied outside ironmaking and steelmaking.

Difficulties in steel slag reuse include poor volume stability (with BOF slag, hydration of free CaO and MgO; with argon oxygen decarburization slag, C_2S disintegration), high iron oxide content (unsuitable for cement making), high alkalinity (with BOF slag, pH of 10–12.5), and heavy metal (e.g., Cr in EAF stainless-steel slag) (Horii et al. 2015). Hot-stage slag engineering can improve slag properties. Approaches include (1) additions to molten slag for reduction and separation of a metallic phase and/or stabilization of minerals (e.g., C_2S, free CaO and MgO); and (2) selection of appropriate cooling paths to obtain a desirable microstructure. Currently in most steel plants, however, liquid slag is simply cooled slowly to ambient temperatures in slag yards; minimal additions take place, and granulation is not widely practiced.

Steel slag has been recycled in different applications, including aggregate for road construction, metallurgical powder for desulfurization of steel, cement and concrete for preparing building materials, phosphorus-rich fertilizers in agricultural application, soil stabilizer and soil conditioner, use for wastewater treatment, application in CO_2 capture, and flue gas desulfurization (Chand et al. 2016).



Adapted from Okumura 1993

Figure 12 Recycling of steel slag

Dust and Sludge

Dust and sludge are generated during iron and steelmaking from the top of the furnaces (BF, EAF, and BOF). The BF flue dust is a mixture of iron oxides (50% Fe_2O_3) and coke fines (30% C) (Das et al. 2007). It also contains SiO_2, CaO, MgO, and trace elemental oxides. Direct recycling of the BF dust is not possible because of undesirable elements (like Zn, Pb, and alkali metals) causing BF operational difficulties. Sometimes the dust contains toxic elements (Cd, Cr, and As), and a suitable beneficiation method is needed to recycle it within the plant, avoiding landfill.

During EAF steelmaking, around 11–20 kg of EAF dust is formed per ton of steel; the EAF dust is rich in oxides of iron (20%–45%) and zinc (14%–35%) and has been classified as a hazardous waste by the Environmental Protection Agency because it contains leachable cadmium, lead, and chromium (Suetens et al. 2014). Currently, 80% of EAF dust is recycled to recover iron and zinc by using the Waelz kiln process.

BOF sludge consists of the fine particles recovered after wet cleaning of the off-gas from BOF converters, with high levels of FeO (61%–64%), CaO (10%), and some zinc and lead, depending on the type of limestone and chemistry of scrap used in BOF steelmaking. The high moisture content of the BOF sludge (35%–40%) is a major obstacle in its recycling to the sinter plant. Because it becomes sticky and forms agglomerates after long exposure to the atmosphere, the sludge must be dried before recycling. Mill scale (from the rolling process) contains more than 70% Fe; 70%–100% of mill scale is recycled by briquetting or sintering. Technologies to recycle steel sludge and dusts range from simple agglomeration to thermal, hydrometallurgical, and physical beneficiation methods. An example is a briquetting plant, commissioned at the then National Steel Corporation, Great Lakes, to recycle 300,000 t of waste materials such as BOF sludge, BF dust and sludge, mill scale, and other materials (Landow et al. 1997).

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