CHAPTER 12.9

Copper Pyrometallurgy

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About three-quarters of the world's mined copper ore is processed using a combination of beneficiation (using minerals processing techniques described elsewhere in this volume) and high-temperature technology that ultimately produces purified copper for sale. Figure 1 illustrates the generalized flow sheet for pyrometallurgical-based copper production, which includes four high-temperature unit processes: smelting, converting, fire refining and anode casting, and remelting. This flow sheet is the descendent of technology first developed a century ago, and although some of the unit processes have seen considerable advances in recent decades, others are ready for changes that might come about soon. This chapter presents a snapshot of current technology; it is a summary of material published in more extensive form elsewhere (Schlesinger et al. 2011).

CONCENTRATES

There are several inputs to the copper smelting and refining process. The most important is the copper concentrate produced by the beneficiation process described elsewhere. Other inputs include oxygen-enriched air, carbonaceous fuel, flux, converting slag and reverts, and purchased copper scrap.

Copper concentrates primarily consist of copper and iron sulfide minerals, along with gangue minerals from the original ore. Their grade (wt % copper) ranges between 22 and 35, depending on mineral processing strategy and practice. In addition to copper, concentrates contain varying levels of impurities, usually in solid solution in the sulfide minerals; these include valuable impurities such as gold, silver, selenium, and tellurium, and undesirable impurities, in particular antimony, arsenic, and bismuth. Concentrates also contain 8%–10% moisture, in part to reduce the risk of fire. The percentages of these impurities vary considerably from ore to ore, and thus from concentrate to concentrate. Most smelters blend concentrates obtained from numerous mines; some custom smelters purchase all of their concentrates from independent mining and milling operations.

The value of copper concentrates is determined by a smelter schedule, an example of which is shown as Table 1 (Hustrulid et al. 2013). The percentages refer to the daily market price of each metal (copper, gold, or silver). The only penalties charged by this smelter are for mercury and fluorine content; most copper smelters also charge penalties for antimony, arsenic, and bismuth; for excess moisture content; and for excessive gangue levels. The prices quoted in this schedule vary substantially from smelter to smelter, and are the result of negotiation between the smelting facility and the mine supplying the concentrate.

In addition to concentrates, many smelting operations make extensive use of purchased scrap as a source of copper. The scrap is added to converting furnaces as cold dope to absorb excess heat from the converting reaction. Some smelting operations purchase large amounts of electronic waste as well. The e-waste contains a high percentage of copper; it also contains gold, silver, and platinum-group metal content that can be recovered during the refining process. Copper is also obtained from reverts (skulls from ladles and trimmings from casting operations) and from the converter slag that is often added to smelting furnaces.

Smelting reactions use the oxygen in air to oxidize the sulfur, iron, and other impurities in copper concentrate and transfer them to a separate phase. Over recent decades, it has become common to enrich the air to 24%–28% O_2 by adding pure oxygen. This increases reaction temperatures and thus process kinetics, reduces nitrogen flow-through and the heat losses that result from it, and reduces off-gas volumes and the size of the equipment required to handle it. Copper smelting operations are usually big enough to afford oxygen production facilities of their own; smaller smelters instead rely on purchased oxygen supplied by larger-scale producers. The other gas purchased by copper smelting operations is natural gas, used for providing energy to smelting and refining furnaces. This is typically supplied by pipeline. On rare occasions fuel oil is used instead.

Copper smelting and converting furnaces require a flux to react with the iron oxide generated during oxidation of concentrates and produce a low-melting-point slag. This is usually silica, produced from nearby quarries. The silica contains a few percent of other mineral oxides (Al_2O_3, CaO, Fe_2O_3, MgO) as impurities. Furnaces that use a calcium ferrite slag

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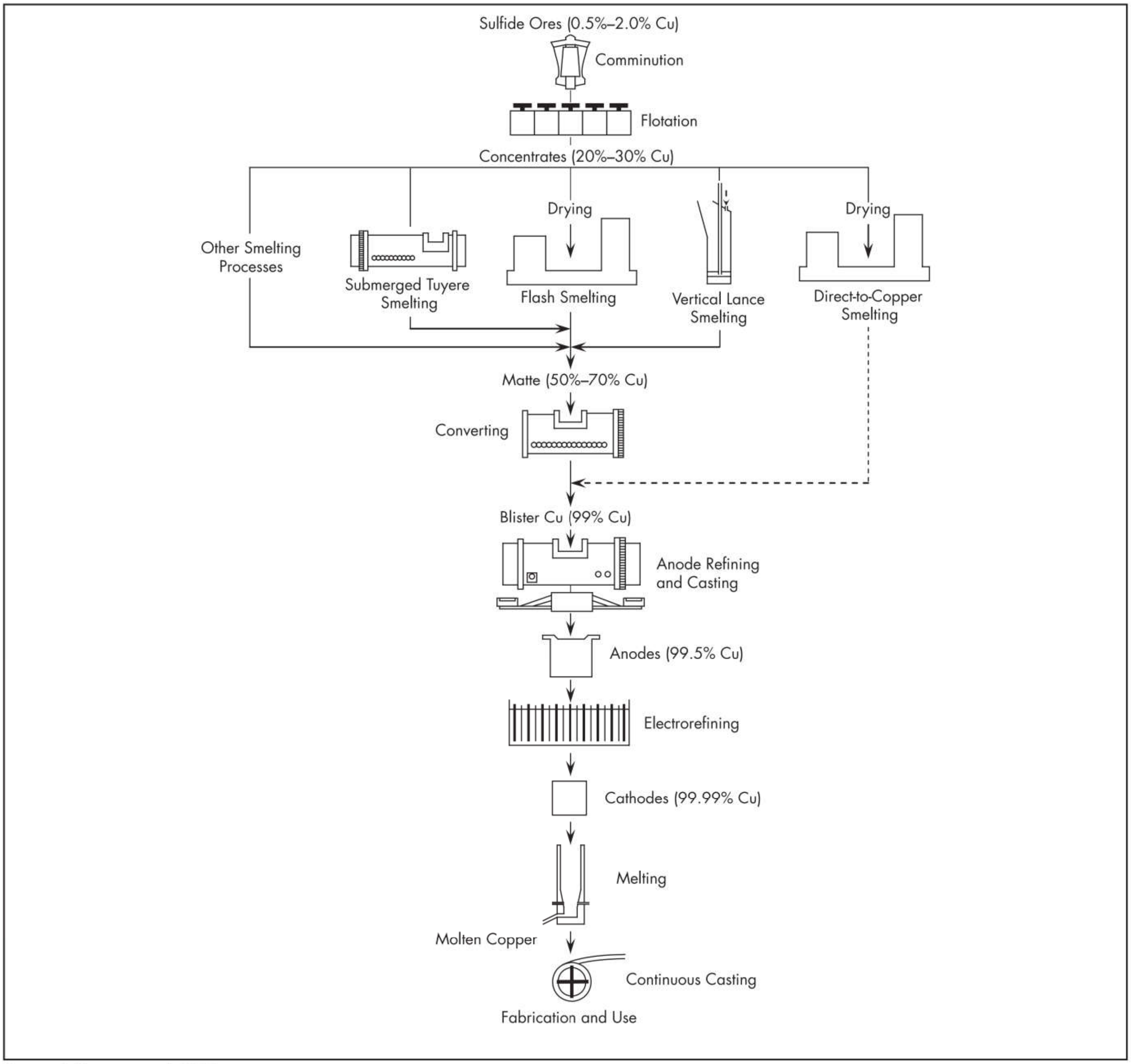


Source: Schlesinger et al. 2011

Figure 1 Generalized flow sheet for pyrometallurgical processing of copper concentrates

in place of the typical fayalite slag use burnt lime (CaO) as a flux instead.

PREPROCESSING

Copper concentrates are sometimes fed directly to smelting furnaces. However, for flash smelting, thermal preprocessing is performed. The common unit operation is drying, which reduces the moisture content to 0.5 wt % or less. This is done at smelters using flash furnaces. Drying keeps clogs from forming in concentrate burners and improves ignition of concentrates. Drying is normally performed using indirect heating of concentrates. A common type of dryer is the steam dryer shown as Figure 2. The steam (generated using the hot off-gas from smelting) is fed at 16–20 bar gauge pressure through tubing bundles in the sides of the vessel; the vessel rotates to ensure good contact and faster drying. The length of these dryers is 9.0–12.5 m, and the diameter is 3.5–4.5 m. Processing capacities range from about 100 to 240 t/h of concentrate. Steam dryers like these are replacing the rotary and flash dryers that were previously used. The use of indirect heating by the steam flowing through the tubing bundles reduces the amount of off-gas produced by the dryer, and eliminates CO_2 and SO_2 emissions that result from the combustion of fossil fuel and reaction of off-gases with the sulfide concentrate. Dust emissions are reduced as well.

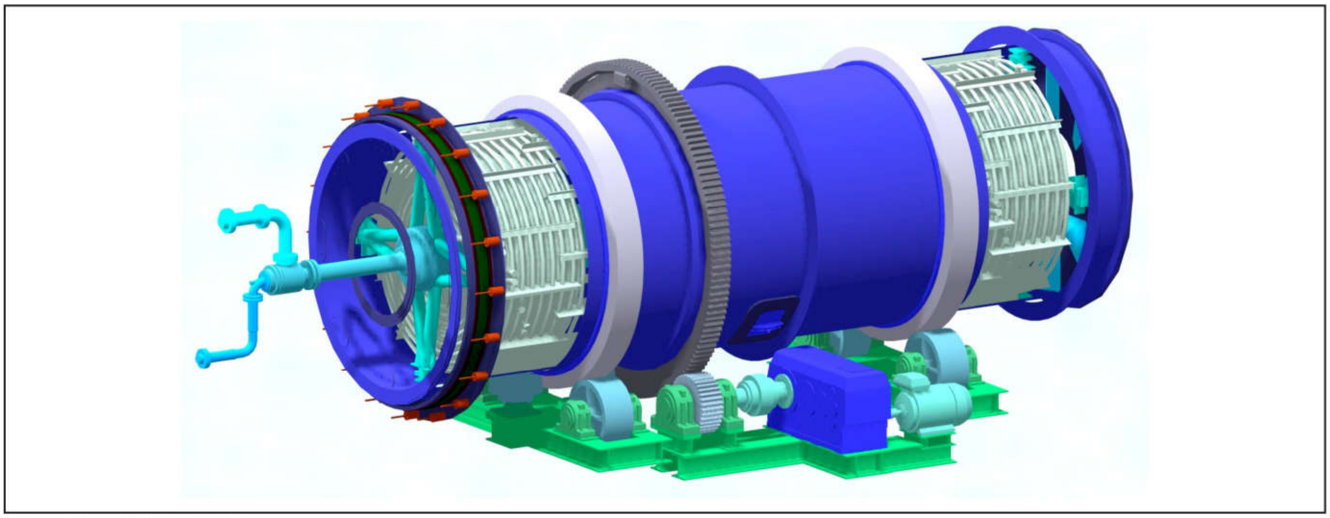
The high concentration of impurities (particularly arsenic) in some new sources of copper concentrate has revived interest in partial roasting as a pretreatment process. The

Table 1 Model smelter schedule for copper concentrates*

Payments	Copper	Pay for 95% to 98% of the copper content at market value. Minimum deduction of unit (1% of a ton) per dry metric ton for copper concentrates grading below 30%. Unit deductions and treatment charges may be higher for concentrates about 40% Cu.
	Gold	Deduct 0.03 to 0.05 oz/dmt (troy ounces per dry metric ton) and pay for 90% to 95% of the remaining gold content at market value.
	Silver	Deduct 1.0 oz/dmt and pay for 95% of the remaining silver content at market value.
Deductions	Treatment/refining charges	Treatment changes in annual contracts for 2011 varied between \$56.00 and \$90.00/t (per metric ton) concentrate with refining charges of \$0.056 to 0.090/lb Cu.
	Price participation	Prior to mid-2006, contracts often included price participation clauses. Most contracts settled after late 2006 either eliminated price participation clauses or have capped the price participation to \$0.04–\$0.10/lb Cu at a basis of \$1.20/lb Cu or above. In 2011 none of the contracts reported a price participation clause.
	Complex concentrates	Treatment charges for "complex" concentrates are typically \$15 to \$25/t higher than charges for clean concentrates. In addition, copper concentrates grading over 40% may be charged up to \$10/t more for treatment. This extra charge varies depending on the tightness of the concentrate market. Currently, no smelters are imposing this charge on high-grade concentrates.
	Refining charges	Range from \$6.00 to \$8.00/oz of payable gold and \$0.50 to \$0.75/oz of payable silver.
Penalties	Deleterious element assessments	Copper concentrates containing excessive amounts of the following elements may be penalized or rejected: lead, zinc, arsenic, antimony, bismuth, nickel, alumina, fluorine, chlorine, magnesium oxide, mercury. Lead, zinc, and arsenic levels about 2% each often result in rejection. For fluxing ores, iron must be less than 3% and the alumina at low levels so that the available silica fluxing content remains high.
	Moisture	High moisture content may also be penalized due to material handling difficulties.

Source: Infomine USA 2012, as cited in Hustrulid et al. 2013

*Spot treatment charges since 2008 have fluctuated widely from treatment charges between \$5–\$120/t and \$0.005–\$1.20/lb refining. Mid-year 2011 spot contracts were reported lower at \$42–\$44/t.



Adapted from LS-Nikko 2007

Figure 2 Kumera stream dryer for copper concentrates

primary purpose of this roasting process is to react arsenide minerals with oxygen to generate As_2S_3 vapor:

$$2Cu_3AsS_4(s) + heat = Cu_2S(s) + 4CuS(s) + As_2S_3(g)$$

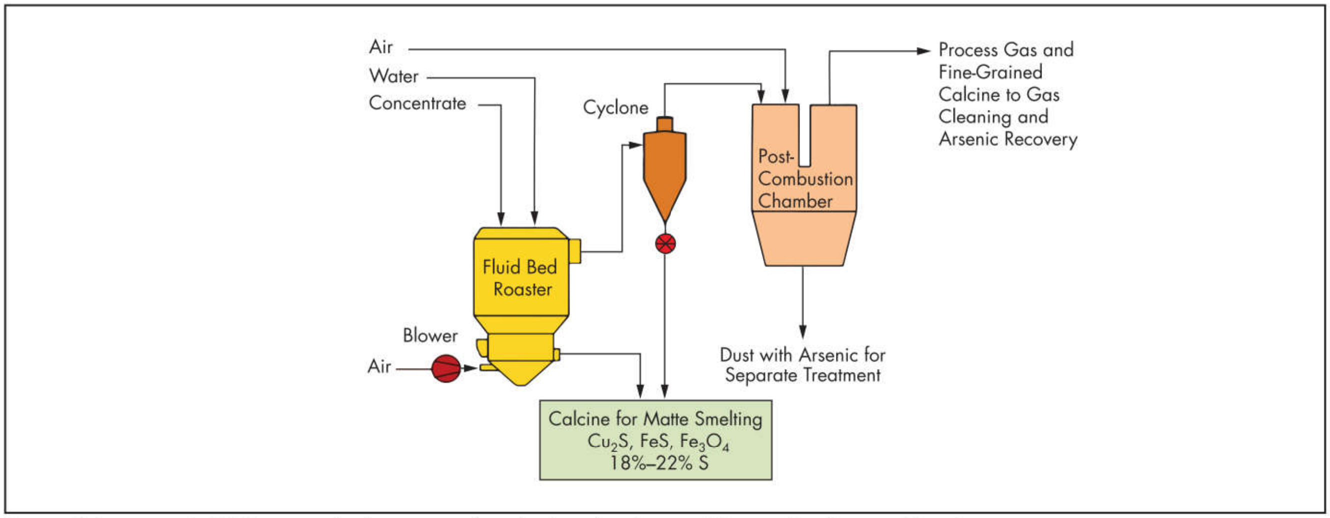
The arsenic sulfide vapor is then oxidized to produce arsenic trioxide (As_2O_3), which is then condensed and recovered for further processing. Some oxidation of sulfide minerals also occurs:

$$3FeS_2(s) + 8O_2 = Fe_3O_4(s) + 6SO_2(g) + heat$$

$$4CuFeS_2(s) + 7O_2 = 2Cu_2S(s) + FeS(s) + Fe_3O_4(s) + 5SO_2(g) + heat$$

The heat produced by these combustion reactions is used to decompose the arsenides in the concentrate.

Figure 3 illustrates the partial roasting of high-arsenic copper concentrates (Holmström et al. 2014). The fluid bed roaster at left is a replacement for the rotary kilns and multiple-hearth roasters used in previous decades. Typical temperatures are 680°–720°C, and oxygen input is controlled at less than 5% of the input sulfur rate to minimize oxidation of the sulfur in the concentrate. The roasting process also volatilizes mercury from the concentrate, allowing its capture; this minimizes subsequent mercury emissions during smelting and converting. Roasting of this sort is currently uncommon but may become more widespread as dirtier concentrates are processed.



Source: Holmström et al. 2013, reprinted with permission from the Canadian Institute of Mining, Metallurgy and Petroleum

Figure 3 Partial roasting process for high-arsenic concentrates

SMELTING

The primary goal of copper production is to separate the copper in minerals such as chalcopyrite ($CuFeS_2$) and bornite (Cu_5FeS_4) from the iron and sulfur, achieving a recovered copper stream with (1) high purity, (2) high overall recovery of the input copper, (3) minimized cost, and (4) minimized emissions of pollutants. Theoretically, it is possible to directly react copper minerals with oxygen to produce metallic copper, iron oxide, and sulfur dioxide (SO_2) gas:

$$4CuFeS_2(s) + 11O_2(g) = 4Cu(l) + 2Fe_2O_3(s) + 8SO_2(g)$$

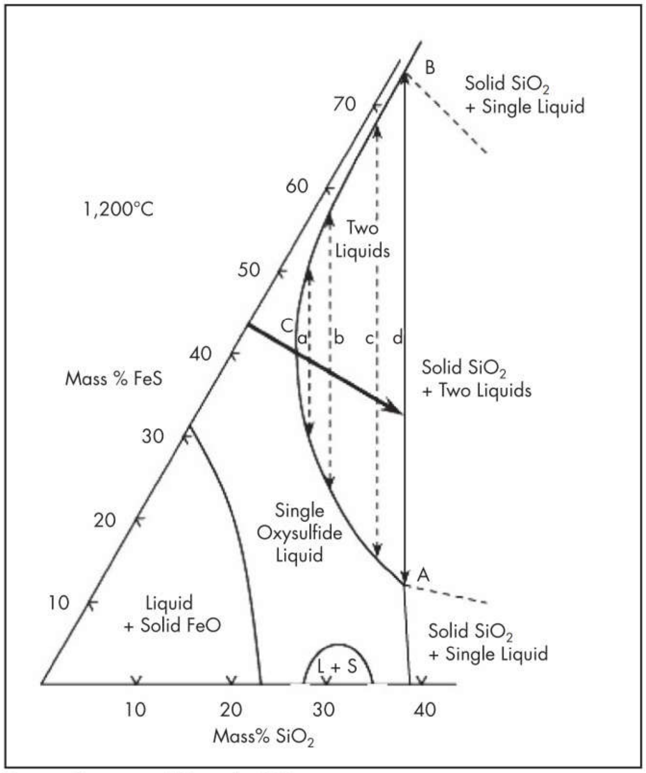
The overall reaction is exothermic and should generate enough heat to produce a molten copper phase that can be separated from the hematite (iron oxide) produced by the oxidation of copper. However, in practice this reaction does not work. The primary reason is that much of the copper metal reacts with oxygen to generate cuprite (Cu_2O), which is lost to the process. A means is needed to remove as much of the iron as possible without oxidizing the copper, to minimize losses when the final oxidation step is performed.

Figure 4 shows the Cu_2S-FeS-SiO_2 phase diagram, which is the basis of matte smelting. The diagram shows a large miscibility gap between a molten oxide–based iron silicate slag and a sulfide-based melt known as a matte. When SiO_2 flux is added to concentrate along with air, the resulting reaction oxidizes some of the iron to form a molten slag, leaving nearly all of the copper in a molten Cu_2S-FeS matte. This removes most of the iron in the concentrate, as well as some of the sulfur, without oxidizing the copper at the same time. Nearly all sulfide concentrates are smelted in this manner, using a variety of technologies that are discussed later in this chapter.

Matte smelting is a balancing act. It would be nice to eliminate as much of the iron in the concentrate as possible, producing a matte with a high grade (% Cu). However, as the fraction of copper sulfide in the matte grows, an exchange reaction with iron oxide in the slag is pushed to the right:

$$Cu_2S\ (matte) + FeO\ (slag) = Cu_2O\ (slag) + FeS\ (matte)$$

This results in higher levels of copper dissolved in the slag, and thus greater losses of copper from the concentrate. Figure 5 shows the percent of copper in slag in equilibrium with matte of varying grades. As can be seen, producing matte with more than 65% Cu has drawbacks.

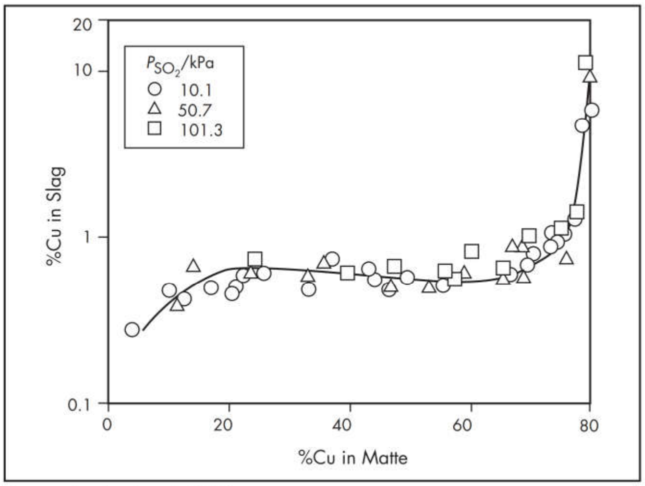


Source: Yazawa and Kameda 1953

Figure 4 Cu_2S-FeS-SiO_2 phase diagram

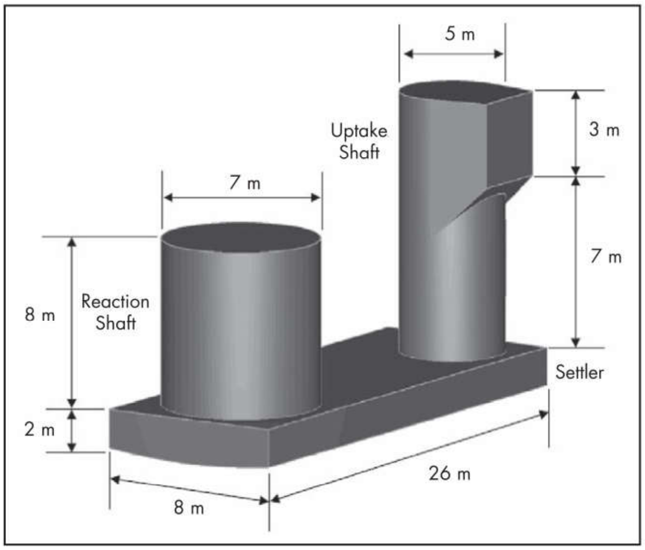
Temperature control of matte smelting is also a balancing act. Typical matte temperatures are 1,200°–1,250°C. Low temperatures increase refractory life. However, at low temperatures, wüstite (FeO) dissolved in the slag will oxidize to form magnetite, which is less soluble and precipitates as a solid:

$$3FeO\ (slag) + ½O_2 = Fe_3O_4(s)$$



Source: Roghani et al. 2000

Figure 5 Copper content in smelting slag as a function of matte grade



Source: Schlesinger et al. 2011

Figure 6 Outotec (Outokumpu) flash furnace

This can block air flow into the melt through the furnace tuyeres and is difficult to remove from the furnace. As a result, a higher temperature is often used to reduce most of the magnetite and keep it dissolved in the slag.

The heat generated by oxidation of sulfur and iron during smelting should be sufficient to make the process autothermal—sufficient to produce molten matte, slag, and off-gas from room-temperature concentrate, flux, and air. However, in practice this is difficult because reverts such as converter slag and e-waste are often added to the charge. These generate little or no energy when smelted and require heat from the rest of the melt. In addition, heat losses from the system impact the energy balance. As a result, the energy balance needs to be improved. This can be done by burning fossil fuels such as natural gas or coal, or by enriching the air with added oxygen. The reduced amount of nitrogen in enriched air reduces heat losses from the system and raises the temperature in the smelting furnace. Improving the reaction kinetics also helps the smelter heat balance, in addition to improving furnace productivity. As a result, current smelter design is centered around technology that improves smelting kinetics. Several designs of smelting furnaces are in use around the world; however, most are one of two types: flash furnaces or bath smelters.

Flash Smelting

Figure 6 illustrates the basic design of the Outokumpu (now Outotec) flash furnace, developed in the late 1940s. The furnace features (1) a concentrate burner mounted in the roof of the reaction shaft at left; (2) an uptake shaft where hot off-gases from the smelting reaction are removed, allowing dust to settle back into the reactor; and (3) a settling area where molten matte and slag are allowed to separate into two immiscible layers. Matte is removed through several tapholes located near the bottom of the settling unit, and slag is removed through a separate taphole located closer to the top of the settling area. The interior of the furnace is lined with direct-bonded magnesia-chrome refractories, backed by water-cooled copper cooling jackets in the walls to reduce wear. Flash furnaces have a range of sizes and capacities but can process up to 4,200 t/d of concentrate.

Concentrates are fed as a dry powder to the concentrate burner, to avoid clumping. They are usually mixed with dusts recovered from the smelting operation, sludges from wastewater treatment, and reverts (skulls and oxide crusts from ladles and other molten-material containers). Flux consists primarily of crushed and ground quartzite rock added to the concentrate before being fed to the burner. The air mixed with the concentrate is enriched to 45%–80% O_2, depending on concentrate grade and smelting strategy; this adjusts the energy balance so that fossil fuels are rarely needed. Controlling the oxygen percentage in the enriched air and the total O_2-to-concentrate ratio allows the smelter to set the output temperature of the matte and slag, as well as the matte grade. (The more iron and sulfur in the concentrate oxidized, the higher the matte grade and temperature.)

The smelting reactions that occur when the concentrate is combusted generate droplets of molten matte and slag, which fall through the reaction shaft to the settling area. As this molten mixture flows toward the other end of the reactor, these separate into two molten layers, the less dense slag on top. Higher temperatures encourage quicker settling; lower temperatures increase the immiscibility of the two phases, reducing the percentage of copper in the slag. Lower temperatures also encourage the deposition of solid magnetite on the bottom and sides of the reactor; although too much is undesirable, a layer of magnetite protects the refractory from the molten matte and slag, lengthening its life. Matte and slag are typically tapped at 1,250° and 1,220°C, respectively.

The molten matte tapped from the furnace has a grade of 60%–70% Cu (75%–87% Cu_2S). The remainder is mostly FeS, but other minor elements in the concentrate also wind up in the matte. These include gold, silver, lead, nickel, and some of the antimony, arsenic, bismuth, selenium, and tellurium. Matte is tapped into ladles and taken away for charging to the converter.

Molten smelter slag is based on fayalite (Fe_2SiO_4) but contains a small amount of sulfur and up to 2% copper. (Less than 1% Cu is more common.) If the percentage is high, the slag may be subjected to mineral processing after it solidifies to try and recover some of the copper; if not, the slag will be dumped, used as roadfill, or mixed into cement.

The off-gas from the process consists primarily of SO_2 produced by the smelting reaction and N_2 from the combustion air. Since smaller droplets of matte and slag settle slowly, a tall off-gas chamber at the right is provided to minimize the dust carried out of the furnace. Even so, some dust remains, and a series of gas-treatment steps are applied to recover it. This dust will be charged back to the furnace. The off-gas, which has a strength (% SO_2) of up to 70%, will be treated to produce sulfuric acid. The higher strength makes this process easier, and was one of the significant advantages of the flash furnaces over the reverberatory smelting furnaces originally used for processing copper concentrates.

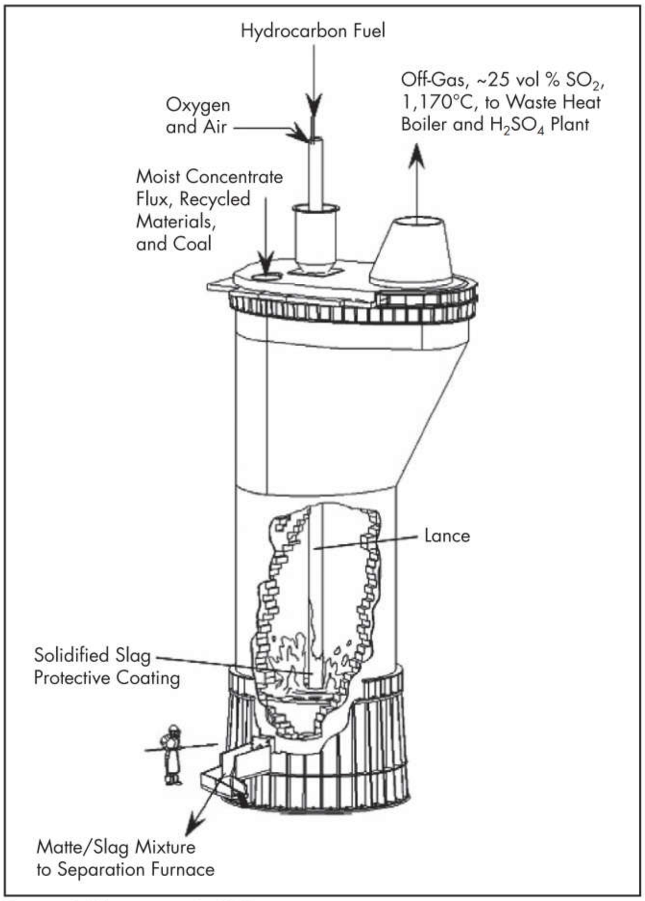
Flash smelting is still the most common method for producing matte from copper concentrates, especially in larger smelting operations. Other technologies, particularly bath smelting, are competing to be the long-term future for this unit process.

Bath Smelting

This technology was first developed in Australia in the 1970s, and several types are now in use. Figure 7 illustrates the best known, the top submerged lance (TSL) furnace. This furnace is sold commercially as IsaSmelt or Ausmelt technology (the two types are similar) and is the fastest-growing smelting device. The furnace shown is 3.5–5 m diameter and 12–16 m high, and is lined with the same type of mag-chrome refractory used in flash furnaces. TSL furnaces have somewhat higher capacities than flash furnaces (up to 5,000 t/d of concentrate) but a much smaller footprint per unit capacity. The furnace also features a lance consisting of a stainless-steel outer pipe (up to 0.5 m diameter) and a carbon-steel inner pipe. Air and oxygen are mixed with hydrocarbon fuels and blown through this lance into the molten bath inside this furnace; the air is typically enriched to 50%–65% O_2. A separate feed port is provided for solids, including concentrates, converter slag, reverts, and powdered coal for additional combustion energy. Efforts are being made to include shredded copper scrap in the feed as well.

Pelletized concentrates are fed moist to TSL furnaces, to avoid dust generation; as a result, no drying is needed. The feed falls into and dissolves in a molten bath consisting of an emulsion of matte and slag, kept agitated by the gas blown in through the lance. The reaction of the air with the concentrate dissolved in the bath produces high smelting kinetics; the height of the shaft allows dust or droplets of molten emulsion to settle back into the bath. Periodically, some of the emulsion is tapped through the bottom either to a ladle or directly into a separate settling furnace where matte and slag are allowed to separate. The high bath temperature (1,250°C) and agitation wear the lance away, and periodically a new lance is attached at the top to make up the loss. Off-gases are lower strength than those produced by a flash furnace, because of the additional air needed to burn the fuel and coke. The agitation also results in greater refractory wear, which is made up for by installing cooling panels or using thicker refractory.

Smelting in a TSL furnace is currently a semicontinuous process, as in a flash furnace. However, efforts are being made to make the process continuous by linking furnace output directly to a settling furnace and a converter. The ability to produce impure molten copper directly from concentrate has long been a goal of copper producers. The need to use a reducing environment for smelting, followed by an oxidizing environment for converting, is what has made this goal difficult to accomplish.

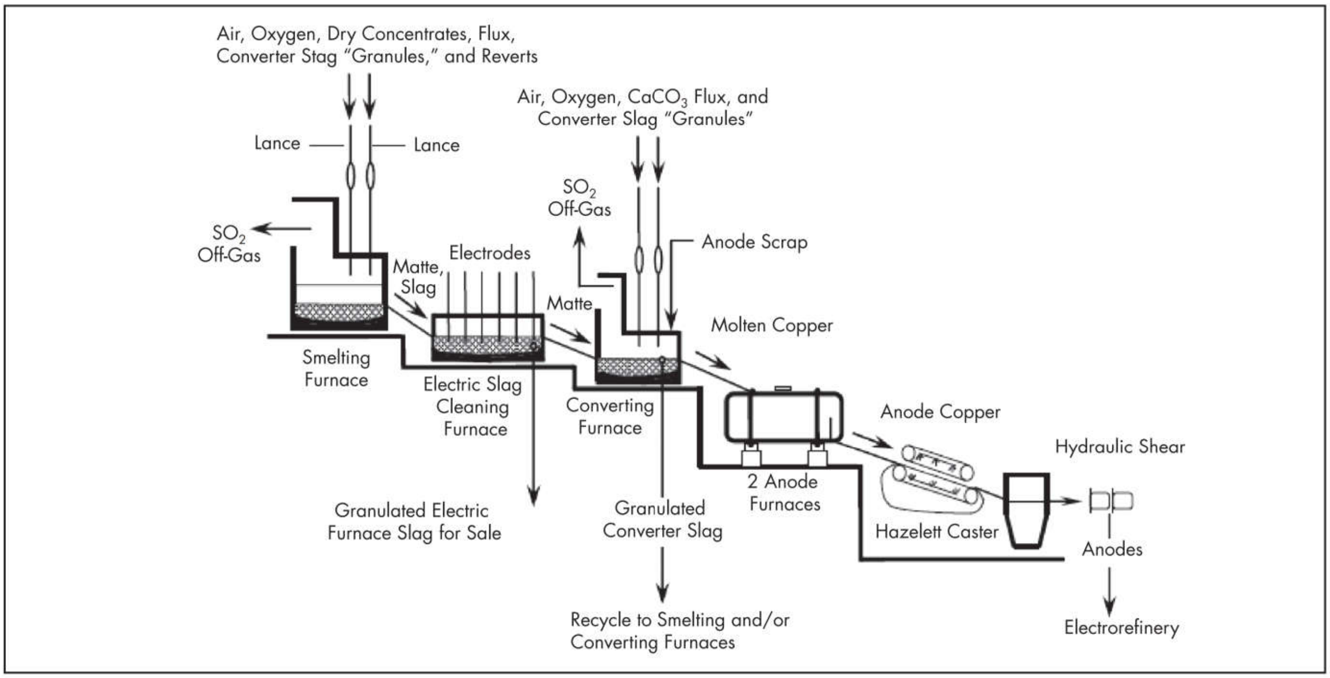


Source: Schlesinger et al. 2011

Figure 7 Cutaway view of an IsaSmelt TSL bath smelting furnace

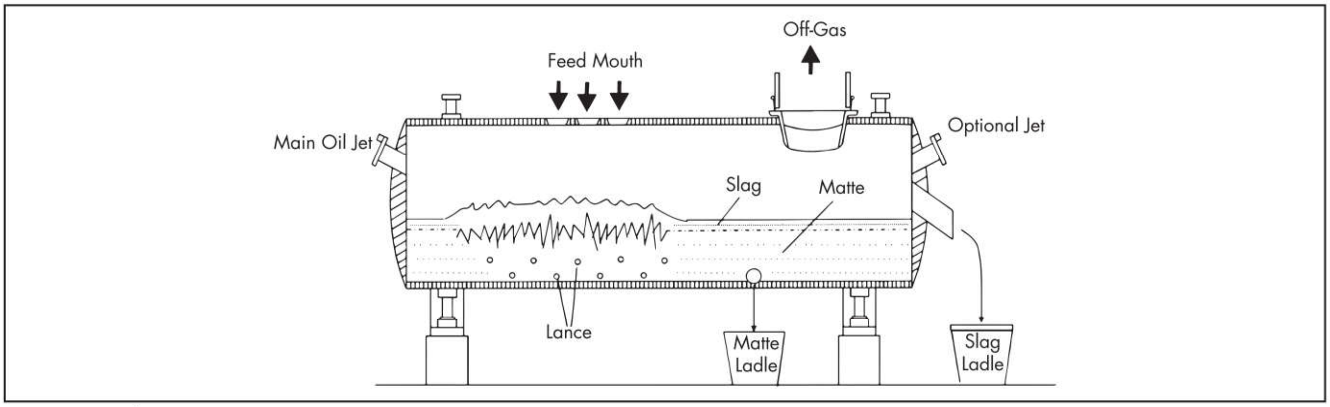
Figure 8 illustrates an early process designed to accomplish direct-to-copper smelting, the Mitsubishi process. This process uses three linked furnaces. The first, the S-furnace, is where smelting takes place. Lances are used to inject both concentrate and enriched air onto the surface of a molten bath; because the lance is not inserted into the bath, it tends to wear at a lower rate than in a TSL furnace. Smelting reactions produce matte and slag as before; these are continuously tapped and flow to the second cleaning furnace, or CL-furnace. Matte and slag are allowed to settle in the CL-furnace and tapped separately; the slag is handled as described previously, whereas the matte flows to the third C-furnace, where conversion to molten impure copper is completed. This process eliminates the need for ladles and tapping, and should produce matte and slag of consistent quality and temperature. In practice, it is difficult to keep the three furnaces operating in tandem, and as a result, the number of Mitsubishi-type furnaces worldwide is small.

A third type of bath smelter is more recent. Figure 9 depicts the bottom-blown oxygen smelting furnace that has been installed over the past 10 years by several Chinese copper producers (Cui et al. 2013). This design is a long, cylindrical, refractory-lined device (4.4 m diameter × 16.5 m length)



Source: Ajima et al. 1999. Copyright 1999 by The Minerals, Metals & Materials Society. Used with permission.

Figure 8 Process flow sheet for the Mitsubishi process



Source: Cui et al. 2013

Figure 9 Chinese bottom-blown smelting furnace

with openings at the top for solid feed input and off-gas removal. The feed is moist pelletized concentrate, along with plant reverts, slag, and the concentrate produced by beneficiation of smelter and converter slags. Enriched air (70% O_2) is blown into the molten matte/slag emulsion in the furnace through lances inserted through the refractory at the bottom; the lances are similar in construction to those used in TSL furnaces. Some fuel oil is burned at the top to keep the slag molten. The lances are located toward the left side of the vessel; this allows matte and slag to settle as they flow toward the right. Slag is tapped from the right side of the vessel; matte is tapped from the bottom. The off-gas is high–strength (68% SO_2), reducing the volume of gas to be handled. The smelter processes slightly less than 2,000 t/d of concentrate.

Operating practice with this device produces a high-grade (70% Cu) matte. This means that the slag has higher levels of copper (2%–3%) than other smelting devices. The bottom-blown smelter was designed to handle lower-grade concentrates (~25% Cu), which have higher Fe/Cu ratios than other concentrates. This means that much more FeO is generated during smelting. The smelter produces a slag with higher Fe/SiO_2 ratios than other smelting furnaces, and so magnetite formation is a concern. The claim is made that enriched air injection through the matte layer limits oxidation of FeO in the slag, minimizing magnetite. This smelter also operates at lower temperatures (1,150°–1,170°C), which reduces refractory wear but makes the tapping of slag more difficult. Future practice may include using dried feed instead of moist, which would improve the energy balance and further improve off-gas strength (Jie 2013). This device appears to be more suited for smaller smelting operations.

Submerged-Tuyere Smelting

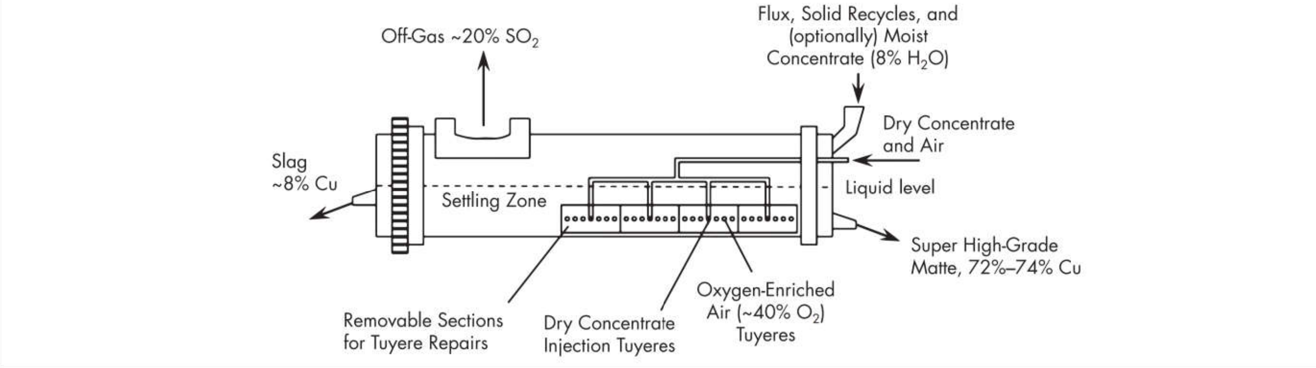
This type of smelting technology is a descendant of the Peirce–Smith converter and operates on similar principles. The three main types are the older Noranda and Teniente smelters, and the newer Vanyukov smelting furnace. They are much less common than flash furnaces and bath smelters.

Figure 10 illustrates a typical Teniente smelting furnace. The length of these furnaces ranges from 14 to 23 m, and the inside diameter is 4–5 m. As with other smelting furnaces, mag-chrome brick is used as the lining. The right-hand side of this view shows 35–50 tuyeres, 5–6 cm diameter; the left-hand side is a “quiet zone” where matte and slag settle in separate layers for tapping. The tuyeres are mounted into panels for easier replacement as they wear. The device is mounted on trunnions so that it can be rotated to expose the tuyeres for inspection and repair. Tapping of slag is performed at the left end, and tapping of matte at the right. Tapping temperatures are typical: 1,240°C for slag, 1,250°C for matte. A variety of materials can be fed to the Noranda smelter, including moist or dry concentrates, flux, dust, reverts, and in some cases considerable solid scrap. Oxygen-enriched air (40% O_2) is blown in through the tuyeres, and ordinary air is used to blow in dry concentrates. Because the degree of enrichment is lower than in other smelting furnaces, more nitrogen reports to the off-gas stream. This dilutes the strength of the off-gas to 20% SO_2. Teniente furnaces typically process 2,000–2,500 t/d of concentrate.

Teniente smelters were designed to produce very-high-grade matte (72%–74% Cu). This minimizes the amount of time required to convert it and reduces the amount of converter slag. However, it also means the smelter produces very-high-copper slag (~8% Cu). This slag must be subsequently processed to recover the copper, increasing costs elsewhere in the process. No water cooling of the refractory is needed, because of the reduced agitation of the bath compared with flash furnaces or bath smelters.

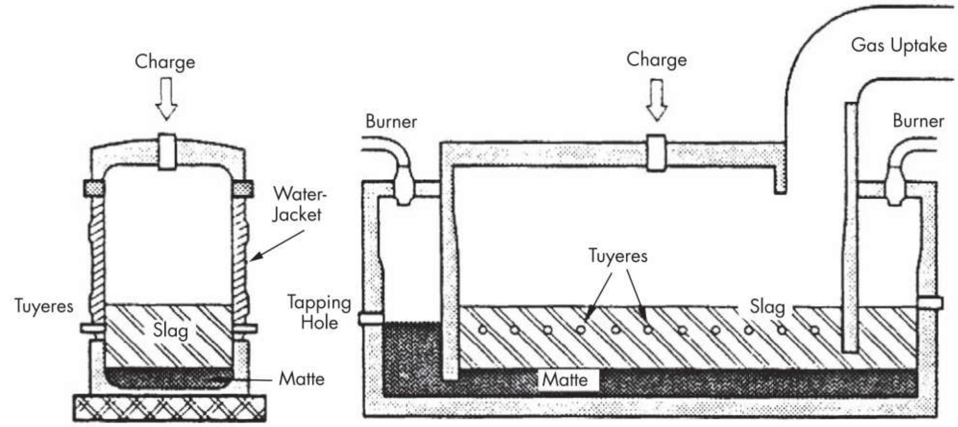
The design of Noranda smelters is similar to that of Teniente furnaces, but there are some differences. Matte is tapped from the same side of the furnace as slag. Dry concentrate is fed through the tuyeres rather than from the top, but other feed (reverts, flux, slag concentrate) is input through a slinger belt that throws the material into the furnace, ensuring better distribution. About 10% of the feed consists of scrap, including shredded electronic scrap. Recent installations have a higher smelting capacity (3,000 t/d) than most Teniente furnaces.

Figure 11 shows the cross section of a Vanyukov smelting furnace, invented in the former Soviet Union and installed in a



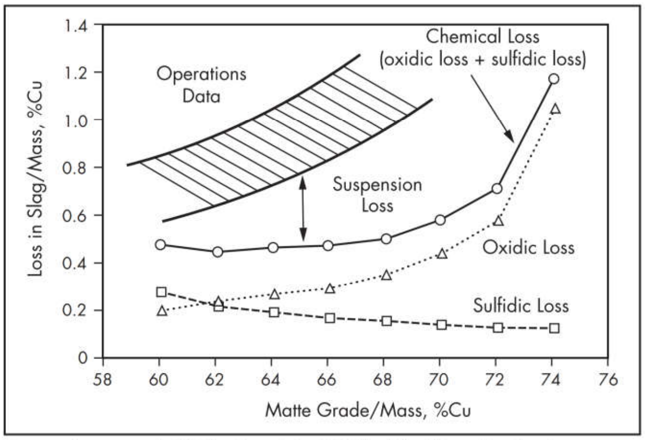
Source: Schlesinger et al. 2011

Figure 10 Schematic of Teniente smelting furnace



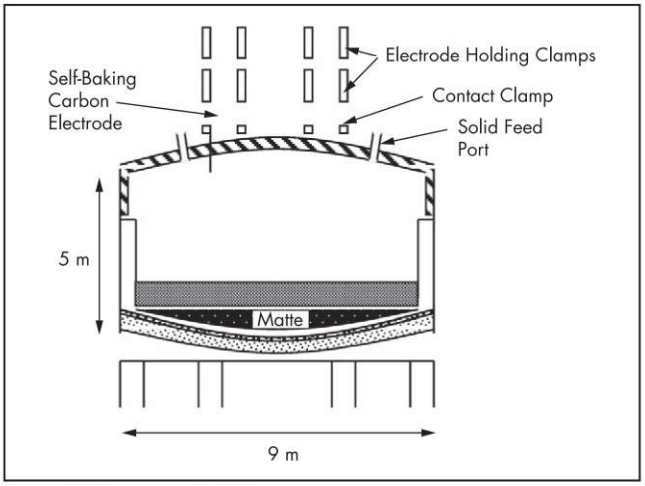
Source: Kellogg and Diaz 1992. Copyright 1992 by The Minerals, Metals & Materials Society. Used with permission.

Figure 11 Sketch of Vanyukov smelting furnace



Source: Furuta et al. 2006. Copyright 2006 by The Minerals, Metals & Materials Society. Used with permission.

Figure 12 Copper loss in slag as a function of matte grade



Source: Schlesinger et al. 2011

Figure 13 Cross section of a slag cleaning furnace

limited number of locations. Unlike the Noranda and Teniente smelters, it does not rotate to clear the tuyeres for cleaning or replacement. Feed is input through a hole in the top, and enriched air is blown in through the tuyeres. An advantage of the Vanyukov furnace is the use of weirs to separate the matte and slag tapping zones from the rest of the furnace. This allows better settling and reduces the copper of the slag to 2% or less. A variety of matte grades are produced in this furnace, depending on concentrate grade and Cu/Fe ratio.

SLAG PROCESSING

Slag is produced by both smelting and converting furnaces. The amount of copper in these slags depends on the type of furnace, the grade of matte or molten copper being produced, and the oxidation potential of the furnace environment. Figure 12 illustrates this point (Furuta et al. 2006). The graph shows the percentage of copper in smelting slags as a function of matte grade. Copper occurs in slag in three forms: dissolved copper sulfide, dissolved copper oxide, or entrained particles of sulfide matte that have not had sufficient time to settle out of the slag. The concentration of dissolved sulfidic copper decreases slightly as the matte grade increases. This is the result of increasing immiscibility between the matte and slag phases, which decreases overall sulfur solubility in the slag. The concentration of oxidic copper increases rapidly, because of the shifting equilibrium of the reaction described earlier:

$$Cu_2S\ (\text{matte}) + FeO\ (\text{slag}) = Cu_2O\ (\text{slag}) + FeS\ (\text{matte})$$

As the increasing grade of the matte increases the activity of Cu_2S, the activity (and thus the concentration) of Cu_2O goes up as well. The fraction of suspended matte in the slag is the difference between the overall percentage of copper in the slag (the shaded area in Figure 12) and the percentage of dissolved copper. Factors that increase the level of suspended matte in the slag include high slag viscosity (which increases required settling time) and inadequate settling time because of poor furnace design. The lengthy settling area of flash furnaces minimizes the amount of suspended matte in slags produced by flash furnaces; the low operating temperature of Chinese bottom-blown smelters increases slag viscosity and thus dissolved suspended matte in these slags.

Smelter slags can contain 0.5%–8% or more copper; converter slags analyze 4%–12% copper. This percentage, multiplied by the mass of slag produced in these furnaces, means that a considerable fraction of the copper in the input raw materials (concentrates, reverts, dusts, scrap) would be lost to the slag if it were simply disposed of. As a result, most smelters treat their process slags to recover as much of this as is feasible, using one or more of several techniques.

If the slag is still molten, simply giving it more time to settle may remove most of the suspended matte. Figure 13 shows a typical electric slag-cleaning furnace, popular since the 1960s. These furnaces are commonly used to treat both high-copper smelting slags from submerged-tuyere smelters like the Noranda and Teniente furnaces and the matte-slag emulsions tapped from TSL furnaces (Ausmelt, IsaSmelt, Mitsubishi). This is an AC furnace with three carbon graphite electrodes, usually the self-baking Søderberg type. Heat is generated by passing current through the slag layer at the top, which minimizes turbulence and improves settling. Power use is 15–70 kW·h/t of slag treated, depending primarily on the furnace input and the required residence time for complete settling. The furnace sidewalls are typically water cooled to reduce refractory wear and increase furnace life.

Besides molten slag or emulsion, inputs to the slag-cleaning furnace may include converter slag or reverts, along with a reducing agent such as coal, coke, natural gas, or ferrosilicon. The reducing agent minimizes dissolved copper oxide by reducing it to metal, which is slightly soluble in matte:

$$C + Cu_2O\ (\text{slag}) = CO + 2Cu\ (\text{matte})$$

Adding reducing agent also reduces magnetite (Fe_3O_4) in the slag to wüstite (FeO). This decreases slag viscosity and increases settling rates. Fuel-fired slag-cleaning furnaces are sometimes used instead of electric, depending on costs.

Most furnaces are tapped on a semicontinuous basis, although the slag-cleaning furnaces for TSL smelters are more likely to operate on a continuous basis. The products of slag-cleaning furnaces are low-copper slag (0.6%–1.3%), and normal-grade matte (65%–70% Cu).

When high-copper converter slags cool, the dissolved copper oxide is partially reduced to metallic copper:

$$Cu_2O + 3FeO = 2Cu(l) + Fe_3O_4$$

This copper exsolves as small metallic particles as the solid solidifies. Crushing and grinding the converter slag by typical comminution technology and using froth flotation to recover the metallic copper eliminates the need for a slag-cleaning furnace. This is especially true in plants using a flash furnace, which normally produce a smelter slag with sufficiently low copper content for disposal without further processing.

CONVERTING

The molten matte produced by copper smelting and matte settling consists mostly of Cu_2S and FeS, along with minor amounts of several impurity elements. Metallic copper can be produced by reacting the matte with oxygen, a process known as converting:

$$Cu_2S\ (\text{matte}) + O_2 = 2Cu(l) + SO_2$$

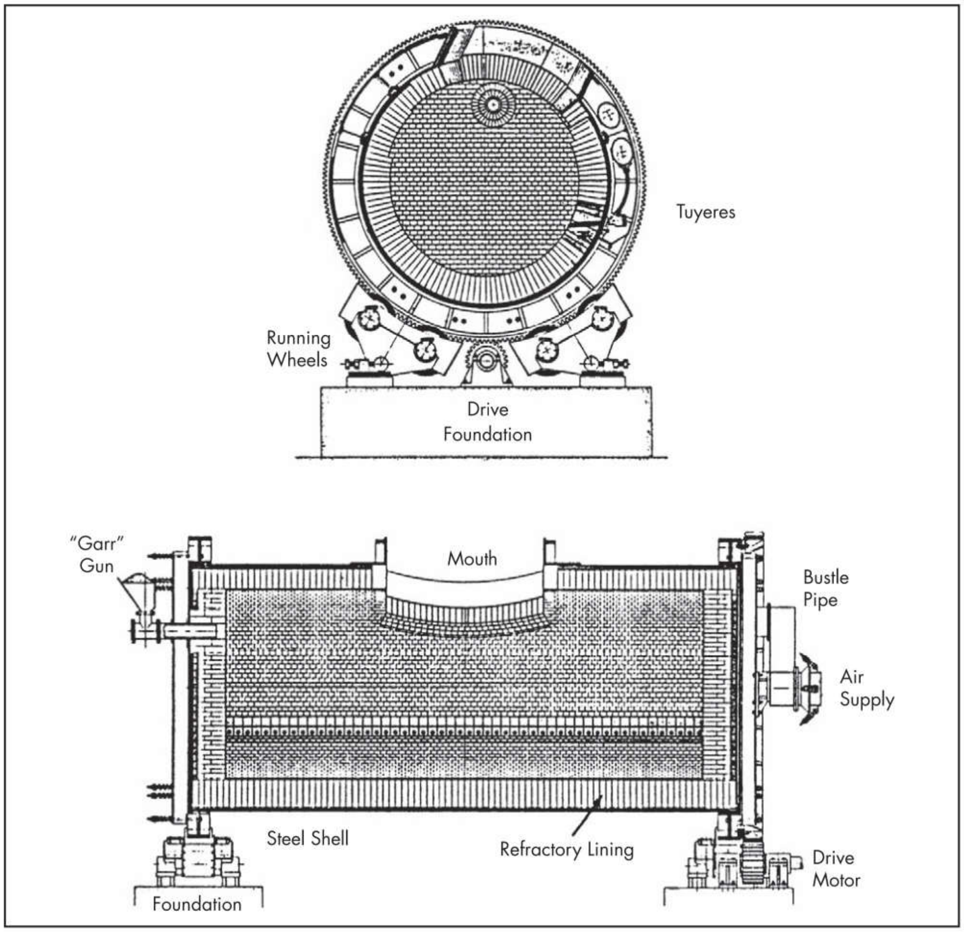
The FeS in the matte oxidizes to form FeO, which dissolves in the slag. Some of the copper also oxidizes to form dissolved Cu_2O in the slag:

$$Cu_2S\ (\text{matte}) + \tfrac{3}{2}O_2 = Cu_2O\ (\text{slag}) + SO_2$$

This produces a slag with high dissolved copper content, 4%–8%. However, because most of the iron in the concentrate was oxidized during smelting, the amount of slag produced during converting is relatively small, so the amount of copper lost in it is relatively small as well. The reprocessing of the converter slag described in the previous section will recover most of this copper, minimizing overall losses to the disposal slag. Converting of copper matte has been practiced for over a century, using technology that is only now undergoing significant changes.

Peirce–Smith Converting

Figure 14 illustrates a Peirce–Smith converter, used to produce most of the world's copper. This is a cylindrical vessel mounted on trunnions so it can be rotated back and forth for charging, blowing, and tapping. Dimensions vary, but a typical size is 4.5 m diameter × 12 m length. Like smelting furnaces, the vessel is lined with mag-chrome brick. The vessel treats 600–1,000 t/d of matte and produces 500–900 t of molten impure blister copper in the process. It features numerous tuyeres throughout its length, through which enriched air (24%–29% O_2) is blown into molten matte. A large opening in the top is where molten matte is charged, and where molten matte and copper are drained from the furnace after converting; it is also the exit from which off-gas (a mixture of N_2 and SO_2) is emitted during the process. A hood is placed over the opening to collect the off-gas during converting; this hood is removed during tapping and emptying, which is one of the disadvantages of the Peirce–Smith furnace. Converting is



Courtesy of Harbison–Walter Refractories, Pittsburgh, Pennsylvania

Figure 14 Peirce–Smith converter

operated as a batch process, so the vessel is completely emptied after a 6- to 12-hour cycle.

The converting process involves several separate steps. The first is charging. During this step, the vessel is rotated about 15 degrees from vertical to allow molten matte to be poured from the ladle by which it was transported from the smelter. Most of the charge consists of matte, but other material is also added: flux (either silica or calcium carbonate, depending on the type of slag being produced), purchased scrap, and in some cases plant reverts. The reactions that take place during converting are exothermic and generate more heat than is needed to produce blister copper and slag, so the added scrap and reverts known as cold dope absorb this excess heat.

When the vessel has been filled, it is rotated back to the vertical position and the hood is replaced. At this point, blowing through the tuyeres begins. The oxidation of iron sulfide is kinetically favored, so this occurs first, producing converter slag and almost-pure molten Cu_2S, better known as white metal. When this is complete, the vessel is rotated by 80 degrees and the converter slag is skimmed off the top into a ladle for copper recovery. Typical slag temperature is 1,220°C.

When the vessel is rotated back to vertical, the final blowing step begins. This oxidizes the white metal and produces molten copper with 0.01%–0.05% dissolved sulfur and 0.1%–0.8% dissolved oxygen. Some impurities in the matte also wind up in the copper; gold, silver, selenium, and tellurium are desirable, whereas antimony, arsenic, bismuth, and lead are not. When the final step is complete, the vessel is rotated to a horizontal position, and the copper (~1,200°C) is emptied into a ladle for fire refining.

The strength (% SO_2) of the off-gas varies throughout the process but averages about 10%. The two main reasons are (1) the low level of enrichment of the air blown through the tuyeres, which means high nitrogen throughput, and (2) air leakage into the hood during converting. The hood is operated under low pressure to prevent fugitive vapors from leaking out into the plant environment, and this causes outside air to be sucked into the hood, further diluting the off-gas. One reason for preferring higher matte grades in the smelter is that it reduces the length of the converting process, thus reducing the amount of this low-strength off-gas being produced.

Traditionally, converter slag has been produced by adding silica and generating the same type of fayalite ($FeO\text{-}SiO_2$) slag produced in smelting furnaces. In recent years, some converting furnaces have begun to replace the silica with limestone ($CaCO_3$) or burnt lime (CaO), which results in a calcium ferrite ($CaO\text{-}Fe_2O_3$) slag. This slag has lower solubility for Cu_2O, which reduces copper losses in the slag. It also absorbs more antimony, arsenic, and bismuth, removing more of these undesirable impurities from the molten copper. However, it is more aggressive toward refractories and requires more careful control to avoid magnetite precipitation.

Peirce–Smith technology has been used to convert copper mattes for more than a century. During that time, several shortcomings of the process have become apparent. These include slow processing time, low off-gas strength, fugitive vapors, vessel maintenance, frequent refractory replacement, and the inefficiency of a batch process. As a result, numerous modifications have been tried over the years, including the following:

- The Hoboken converter, which uses a syphon attached to one side of the unit as a semipermanent seal to eliminate the need for sucked-in air.
- The Mitsubishi converter, which uses lances to replace the tuyeres. This eliminates the need for the vessel to rock, allowing a permanent seal with the off-gas ductwork.
- The Noranda continuous converter, which is similar in construction to the Teniente/Noranda smelter shown earlier. This converter is actually semicontinuous, with periodic charging and tapping. The device is never entirely drained of converter slag and therefore never has to be turned for skimming. This eliminates the need for rotation, again allowing a better seal with the off-gas system.

Over the long term, none of these devices has been successful enough to take the place of the Peirce–Smith furnace. However, in recent decades, other converting furnaces have been introduced that may be the future of this process. The first of these is a flash converter, based on the flash furnace smelter described earlier. It uses solidified and crushed matte from the smelter, mixed with lime flux and sprayed through a burner in the top to react with highly enriched air (82%–88% O_2). As the matte "burns," slag and molten copper form; these are given a chance to settle in the same sort of arrangement as a flash smelting furnace. A second tower gives dust a chance to settle and allows evacuation of the off-gas. The off-gas has higher strength (30%–40%) and a steadier composition. Dusts are also recycled to the converter. Molten slag and blister copper are periodically tapped from the side and bottom, similar to a smelter. Because the flash converter uses solidified matte, it is decoupled from the smelter and can be operated on stored matte when the smelter is down for maintenance or repair. The flash converter was designed to use a calcium ferrite slag, and therefore lime is charged with the matte to the burner.

Perhaps the most promising new converting technology is based on the TSL bath smelting furnace described earlier. Both Ausmelt and IsaSmelt have developed converters based on this furnace, with the Ausmelt C3 converter more widely used at this time. Bath converting is performed in a vessel similar to that shown in Figure 7. The vessel is charged through the feed port with molten matte, along with flux and small amounts of cold dope. Enriched air (30%–40% O_2) is blown in through the lance, and an emulsion of slag and molten copper is tapped from the bottom and allowed to settle. Because no separate slagging step is used, copper losses in the slag can be high; therefore, high matte grades are encouraged to reduce the overall amount of converter slag produced. Bath converting has many potential advantages. A sealed system eliminates fugitive vapor and produces stronger off-gas; semicontinuous operation means that the vessel is operating more often than the batch-process Peirce–Smith converter; consistent operating conditions mean consistent off-gas strength and furnace temperatures. Efforts are being made to link TSL converting to TSL smelting and settling to produce a truly continuous copper extraction process.

FIRE REFINING

As mentioned previously, the impure copper produced by smelting and converting contains 0.01%–0.05% dissolved sulfur and 0.1%–0.8% dissolved oxygen. If this copper is cast directly, the dissolved sulfur and oxygen react as the metal cools:

$$\underline{S} + 2\underline{O} = SO_2 \text{ (gas)}$$

The SO_2 bubbles formed by this reaction leave behind small bubbles called blisters as they rise to the surface of the solidifying copper, hence the name *blister copper*. Blister copper also contains numerous additional impurities that are in violation of product-quality standards. As a result, the copper must be refined before it can be sold. For copper produced by smelting and converting, there are two refining steps: fire refining (covered here) and electrorefining (see Chapter 10.17, "Electrorefining"). The primary purpose of fire refining is to remove the dissolved sulfur and oxygen; electrorefining primarily removes/recovers the other impurities.

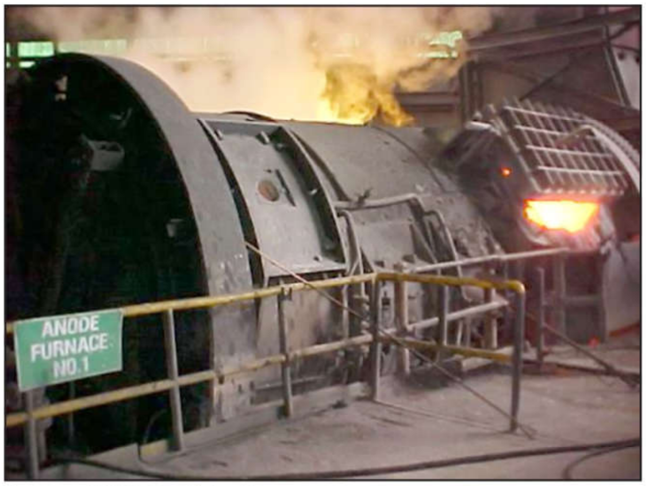
Figure 15 illustrates a typical anode furnace used for fire refining of blister copper. The vessel design is roughly similar to a Peirce–Smith converter. The biggest difference is the reduced number of tuyeres; there are two instead of the 30–50 used for a converter. The reactions taking place in an anode furnace are not exothermic enough to keep the contents warm, so a fossil fuel—typically natural gas, occasionally propane or naphtha—is burned. Both the fuel combustion air and the air blown in through the tuyeres are unenriched. The vessel tilts in the same way as a Peirce–Smith converter to accept input through the hole at the top, and tilts over the same way to let purified molten copper flow out after refining is complete. A hood is provided for the removal of product gases, although the strength (% SO_2) is negligible.

The refining cycle in an anode furnace begins when enough blister copper (250–300 t) has been charged. This is equal to several ladles of molten metal. At this point, air is blown in to oxidize most of the remaining sulfur in the metal:

$$\underline{S} + O_2 = SO_2$$

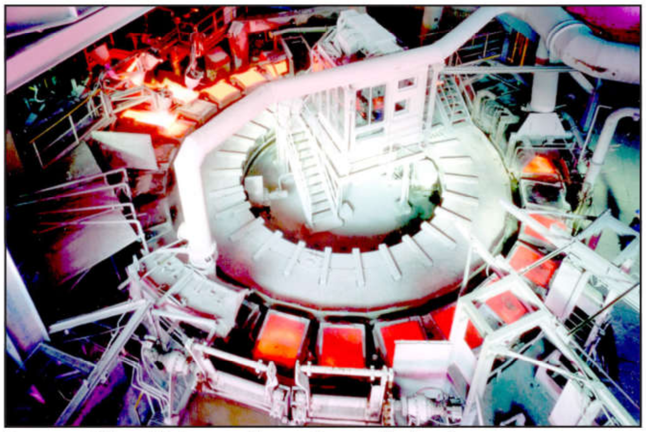
This happens until the dissolved sulfur is reduced to ~30 ppm (0.03 wt %). During this one-hour process, the concentration of dissolved oxygen in the molten blister increases, so a second refining step is needed to remove the oxygen. This is accomplished by blowing in hydrocarbons through the tuyeres. The hydrocarbons react with dissolved oxygen to produce water vapor and carbon monoxide, which leave the furnace. This effectively removes the $\underline{O}$, without dissolving any new impurities in the metal. This second step often requires about two hours to complete. When the process is complete, the vessel is rolled over and the molten anode copper is poured into a trough that leads to the casting wheel.

Figure 16 shows the final step in the pyrometallurgical processing of copper, the casting of molten copper into molds that will become anodes for electrorefining upon solidification. The anodes (16–32, depending on plant capacity) are placed in a continuously rotating casting wheel. Each is roughly 1 m × 1 m, and thick enough to produce an anode 360–410 kg in mass. They are sprayed with a barite slurry before being rotated under the spoon from which molten metal is poured into them, to make removal of the solidified anode easier. When the wheel has rotated about 270 degrees after being filled, an automatic pin and raising mechanism picks the anode up and removes it from the mold. The now-empty mold is sprayed with more barite and rotated back under the spoon to be filled again. About 50–100 t/h copper is cast this way. The process is designed to produce very flat anodes of uniform thickness and mass to ensure good results from electrorefining. Some copper producers use a continuous anode casting line that produces an anode-thick slab of solidified copper that is then sheared into anodes. This eliminates the need to maintain the molds, but maintaining uniform results is difficult. As a result, its use is not widespread.



Courtesy of Palabora Mining Company

Figure 15 Anode furnace in operation



Courtesy of Miguel Palacios, Atlantic Copper, Huelva, Spain

Figure 16 Anode casting wheel

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