# METALLURGY, EXTRACTIVE

## 1. Introduction

Extractive metallurgy deals with the extraction of metals from naturally occurring compounds and the subsequent refinement to a purity suitable for commercial use. These operations, known as winning and refining of metals, follow mining and beneficiation of the ore. They precede the fabricating processes. Selection and design of the extractive processes depend on the raw materials available, and conditions for the refining steps are related to the ultimate use of the metal. Thus mining, extraction, and fabrication are closely interrelated (see also MINERALS RECOVERY AND PROCESSING).

Production of a metal is usually achieved by a sequence of chemical processes represented as a flow sheet. A limited number of unit processes are commonly used in extractive metallurgy. The combination of these steps and the precise conditions of operations vary significantly from metal to metal, and even for the same metal these steps vary with the type of ore or raw material. The technology of extraction processes was developed in an empirical way, and technical innovations often preceded scientific understanding of the processes.

The scientific basis of extractive metallurgy is inorganic physical chemistry, mainly chemical thermodynamics and kinetics (see THERMODYNAMICS). Metallurgical engineering relies on basic chemical engineering science, material and energy balances, and heat and mass transport. Metallurgical systems, however, are often complex. Scale-up from the bench to the commercial plant is more difficult than for other chemical processes.

Extractive metallurgy is usually divided into three principal areas: (*1*) pyrometallurgy which consists of high temperatures processes to carry out smelting and refining reactions; (*2*) hydrometallurgy which is characterized by the use of aqueous solutions and inorganic solvents to achieve the desired reactions; and (*3*) electrometallurgy in which electrical energy is used to extract and refine metals by electrolytic processes. Electrometallurgy may be carried out either at high temperature or in aqueous solution. An integrated metallurgical flow sheet may include pyrometallurgical, hydrometallurgical, and/or electrometallurgical steps.

## 2. History

Of the seven metals known and widely used in antiquity, copper, gold, silver, tin, lead, iron, and mercury, only the first three occur naturally in the metallic state. The first extractive metallurgy process was probably used in the mountains of western Asia, in the areas that are now Iraq and Iran. There is tangible evidence of the smelting of copper (qv) by the Summerians and Egyptians as early as ca 4000 BC. Whereas discovery of the reduction of copper ore by fire was certainly accidental, the observation of the relationship between the blue azurite [1319-45-5], $Cu(OH)_2 \cdot 2CuCO_3$, or the green malachite [1319-53-5], $Cu(OH)_2 \cdot CuCO_3$, and the red copper metal was a truly remarkable scientific discovery. Ancient peoples also knew how to treat copper sulfide ores.

Gold was used extensively in antiquity and the operation of gold mines and mills by the Egyptians is well documented (see GOLD AND GOLD COMPOUNDS). Mercury (qv) also was known to the ancients. Preparation from cinnabar [19122-79-3], HgS, and use in the amalgamation process for the recovery of gold were discovered in prehistory. Silver was found associated with gold, and the gold–silver alloy called electrum was commonly used by the ancients (see SILVER AND SILVER ALLOYS). Silver also was obtained from argentiferrous lead ores, and the cupellation process for the separation of precious metals from base metals was another early metallurgical achievement.

The production of metallic lead (qv) from galena, PbS, is a simple metallurgical operation, and both this metal and its compounds were used in antiquity. Tin, used mainly in bronze, was probably obtained by mixing the tin ore cassiterite [1317-45-9], $SnO_2$, and copper ore. Some iron (qv) of meteoric origin was found by the ancients, but use of wrought iron was also widespread. Iron was obtained easily by reduction of iron ore by carbon, followed by hammering of the sponge iron, and forging.

During the Middle Ages an active mining industry developed in central Europe, but it produced few technological breakthroughs. Several books on mining and metallurgy were written. The extensive treatise by Agricola (1) illustrates the state of the art of the industry in the mid-sixteenth century.

Further progress was made in the eighteenth and early nineteenth centuries. Many metals were discovered upon the development of experimental chemistry. The modern metallurgical industry was born with the invention of steelmaking in 1856 (see STEEL). Industrial processes for making zinc (see ZINC AND ZINC ALLOYS), aluminum (see ALUMINUM AND ALUMINUM ALLOYS), and copper followed before the end of the nineteenth century. These processes made possible the industrial revolution and the development of an industrial society relying heavily on the use of metals.

## 3. Sources of Metals and Ore Preparation

All metals come originally from natural deposits present in the earth's crust. These ore deposits result from a geological concentration process, and consist mainly of metallic oxides and sulfides from which metals can be extracted. Seawater and brines are another natural source of metals, eg, magnesium (see CHEMICALS FROM BRINE; MAGNESIUM AND MAGNESIUM ALLOYS; OCEAN RAW MATERIALS). Metal extracted from a natural source is called primary metal.

Scrap is also an important raw material for the metallurgical industry. The metal produced by a recycling (qv) process is called secondary metal.

The concentration of most metals in the earth's crust is very low, and even for abundant elements such as aluminum and iron, extraction from common rock is not economically feasible. An ore is a metallic deposit from which the metal can be economically extracted. The amount of valuable metal in the ore is the tenor, or ore grade, usually given as the wt% of metal or oxide. For precious metals, the tenor is given in grams per metric ton or troy ounces per avoirdupois short ton (2000 pounds). The tenor and the type of metallic compounds are the main characteristics of an ore. The economic feasibility of ore processing, however, depends also on the nature, location, and size of the deposit; the availability and cost of a suitable extraction process; and the market price of the metal.

Valuable metal is present in the ore in a form called the ore mineral, an inorganic substance of given composition. The ore mineral may be native metal or a compound of the metal. Most ores contain several ore minerals. The minerals without economic value are called the gangue minerals. Because designation as ore minerals or gangue minerals depends on the economics of processing the ore, the same mineral may be classified in either group. In particular, silica, alumina, and iron oxides are usually gangue minerals except when the concentration is high enough to warrant extraction.

The direct treatment of an ore by a chemical extraction process is usually not economically feasible. Instead the first step after mining is the ore preparation, also called ore dressing, milling, mineral processing, or beneficiation. The purpose of ore dressing is to separate the ore minerals from the gangue minerals by physical methods. Milling yields a concentrate containing most of the valuable metals to be recovered and a tailing containing most of the gangue minerals to be discarded.

The first step in ore processing is the liberation of finely disseminated minerals. This is accomplished by comminution, or crushing and grinding the ore (see SIZE REDUCTION). It is followed by screening and/or classification. The main type of mineral beneficiation is concentration, achieved by making use of different physical properties of the mineral particles: magnetic and electrostatic separation (see SEPARATIONS, MAGNETIC), gravity concentration, and flotation (qv).

Table 1 gives the average metal content of the earth's crust, ore deposits, and concentrates. With the exceptions of the recovery of magnesium from seawater and alkali metals from brines, and the solution mining and dump or

Table 1. **Metal Content of Igneous Rocks, Ore Deposits, and Concentrates, wt%**

| Metal | Igneous rocks | Ore deposits | Concentrates |
|---|---|---|---|
| aluminum | 8.13 | 27–29 | |
| iron | 5.01 | 30–60 | 55 |
| magnesium | 2.09 | | |
| titanium | 0.63 | 2.5–25 | |
| manganese | 0.10 | 45–55 | |
| nickel | 0.020 | 1.5–3 | 10 |
| vanadium | 0.017 | 1.6–4.5 | |
| copper | 0.010 | 0.5–5 | 30 |
| uranium | 0.008 | 0.1–0.9 | |
| tungsten | 0.005 | | 50 |
| zinc | 0.004 | 10–30 | 50 |
| lead | 0.002 | 5–10 | 70 |
| cobalt | 0.001 | 1–11 | |
| beryllium | 0.001 | | 3–4 |
| molybdenum | $2 \times 10^{-4}$ | 0.6–1.8 | 50 |
| tin | $4 \times 10^{-4}$ | 1.5 | 40–75 |
| mercury | $5 \times 10^{-5}$ | 0.1–0.5 | |
| silver | $2 \times 10^{-6}$ | 0.04–0.08 | |
| platinum | $5 \times 10^{-7}$ | 0.001 | |
| gold | $10^{-7}$ | 0.001 | |

heap leaching of some copper, gold, and uranium (see URANIUM AND URANIUM COMPOUNDS), most ores are processed through mills. Concentrates are the raw materials for the extraction of primary metals.

The successive stages of mining, mineral beneficiation, smelting, and refining usually require large energy inputs in the form of fuels, electrical energy, and energy-intensive reagents and supplies. Some metals are energy intensive because their ores are low grade; other metals are energy intensive because the reduction process is difficult. Among the commonly used metals, steel is the least energy intensive because of high grade ore and ease of reduction. Titanium is the most energy intensive because of low grade ore and complex processing chemistry. Although recovering metals from common rocks is technologically feasible, the energy requirements are prohibitive. Production of secondary metals from metal scrap, on the other hand, requires much less energy than the production of primary metals. Secondary metal production conserves metallic resources and reduces the net cost of waste disposal.

## 4. Pyrometallurgy

The essential operations of an extractive metallurgy flow sheet are the decomposition of a metallic compound to yield the metal followed by the physical separation of the reduced metal from the residue. This is usually achieved by a simple reduction or by controlled oxidation of the nonmetal and simultaneous reduction of the metal. This may be accomplished by the matte smelting and converting processes.

In a simple pyrometallurgical reduction, the reducing agent, R, combines with the nonmetal, X, in the metallic compound, MX, according to a substitution reaction of the following type:

$$\mathrm{MX} + \mathrm{R} \longrightarrow \mathrm{M}^0 + \mathrm{RX} \tag{1}$$

In order to achieve a spontaneous process, the Gibbs energy change for equation 1 must be negative. This condition is obtained not merely by the choice of the appropriate reducing agent, but also by adjusting the chemical activities of the reactants and products and by selecting the optimum temperature and pressure for a suitable thermodynamic driving force and acceptable reaction rates.

Often the starting raw material to be reduced is an oxide. The standard Gibbs energies of formation, under a pressure of 100 kPa (1 bar) of a few oxides of metals along with those of water, carbon monoxide, and carbon dioxide are represented in Figure 1. A metal oxide is reduced by another metal, or C, $H_2$, or CO, if the Gibbs energy of formation at the given temperature is less negative than that of the oxide of the reductor. Similar diagrams are available for sulfides and halides (2,3). These diagrams provide a simple way of estimating the value of standard Gibbs energy changes for reactions such as that shown in equation 1.

The selection of a particular type of reduction depends on technical feasibility and the economics of the process as well as on physicochemical considerations. In particular, the reducing agent should be inexpensive relative to the

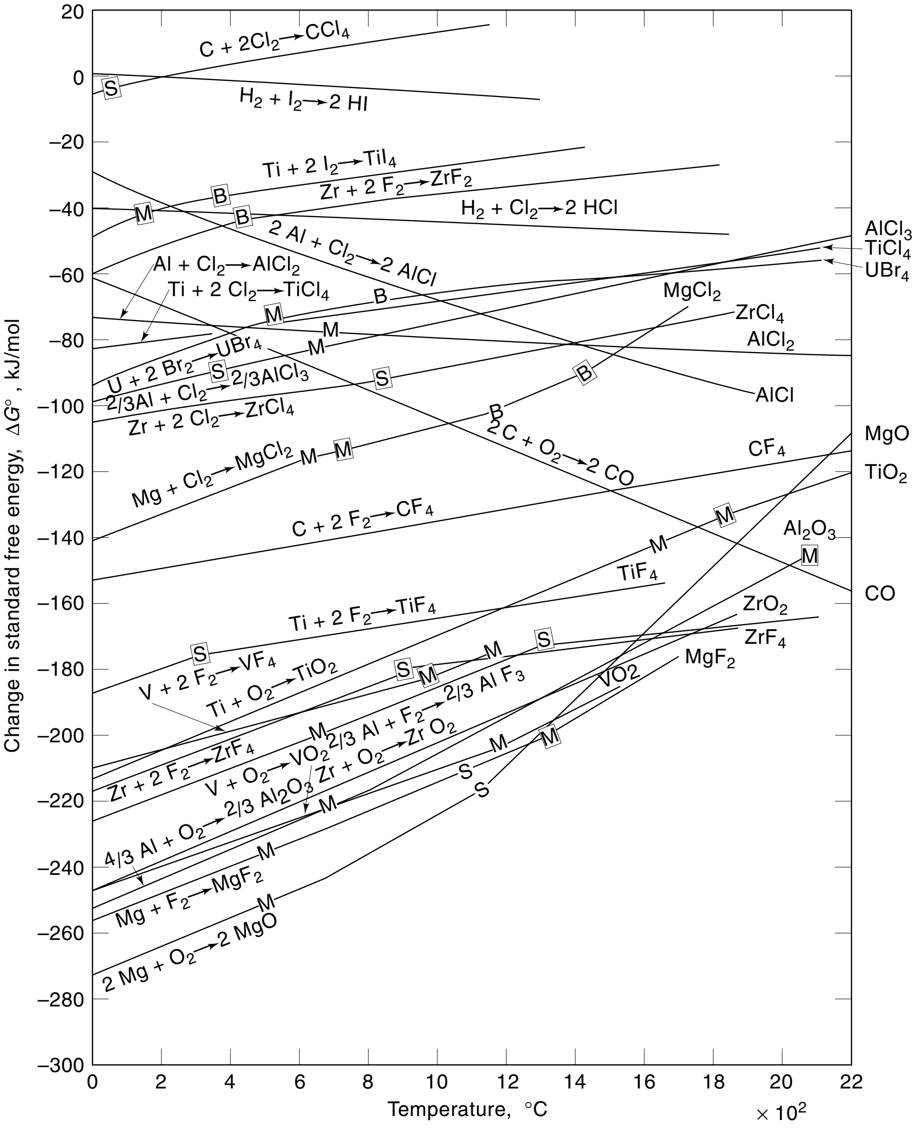

**Fig. 1.** Standard Gibbs energy of formation vs temperature where changes in state are denoted as M, B, and S for melting, boiling, and sublimation points, respectively, for elements, and for oxides or halides. To convert kJ to kcal, divide by 4.184.

value of the metal to be reduced. The product of the reaction, RX, should be easily separated from the metal, easily contained, and safely recycled or disposed of. Furthermore, the physical conditions for the reaction should be such that a suitable reactor can be designed and operated economically.

Reduction processes are characterized either by the reducing agent selected or by the physical state of the metallic product. The separation of reaction products determines the choice and design of the furnace. Reduction processes are classified according to the physical state of the reduced metal.

Usually, the ore or concentrate cannot be reduced to the metal in a single operation. An additional preparation process is needed to modify the physical or chemical properties of the raw material prior to its reduction. Furthermore, most pyrometallurgical reductions do not yield a pure metal and an additional step, refining, is needed to achieve the chemical purity that is specified for the commercial use of the metal.

The preparation, reduction, and refining operations are very much interdependent, and for a given metal must be considered as parts of a single flow sheet. To illustrate the principles of extractive metallurgy, however, it is convenient to discuss the various operations separately.

**4.1. Preparatory Processes.** Several pyrometallurgical operations are used to change the chemical and physical properties of the ore or concentrate in order to make it more suitable for the main extraction process. The chemistry of these preparatory processes, which involve mainly gas–solid reactions, is relatively simple.

*Drying and Calcination.* The simplest pyrometallurgical operation is the evaporation of free water and the decomposition of hydrates and carbonates. A typical reaction is the decomposition of pure limestone [1317-65-3], $CaCO_3$, to calcium oxide [1305-78-8] and carbon dioxide:

$$CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g) \tag{2}$$

This reaction is strongly endothermic, and the equilibrium pressure of $CO_2$, equal to the equilibrium constant of the reaction, increases exponentially with temperature (see LIME AND LIMESTONE).

Lime [1305-78-8] is an important raw material for the metallurgical industry. It is used primarily as a flux in smelting and converting, but it is also a neutralizing agent for hydrometallurgical processes. The calcination of magnesite, $MgCO_3$, yields magnesia, MgO, which is an essential raw material for furnace refractories. The calcination of dolomite, $CaCO_3 \cdot MgCO_3$, also yields a calcine used as a feed for the preparation of magnesium metal.

Examples of similar processes are the decomposition of precipitated aluminum trihydroxide to alumina, which is the feed for the electrolytic production of aluminum metal, and the drying of wet sulfide concentrates in preparation for flash roasting (see ALUMINUM AND ALUMINUM ALLOYS).

*Roasting of Sulfides.* Most nonferrous metals occur in nature mainly as sulfides. These cannot be easily reduced directly to the metal. Burning metallic sulfides in air transforms them into oxides or sulfates which are more easily reduced. The sulfur is released as sulfur dioxide, as shown by the following typical reaction for a divalent metal, M:

$$MS\ (s) + 3/2\ O_2\ (g) \rightleftharpoons MO\ (s) + SO_2\ (g) \tag{3}$$

This reaction is strongly exothermic and proceeds spontaneously from left to right for most common metallic sulfides under normal roasting conditions, ie, in air, because $P_{SO_2} + P_{O_2} = {\sim}20$ kPa (0.2 atm) at temperatures ranging from 650 to 1000°C. The physical chemistry of the roasting process is more complex than indicated by equation 3 alone. Sulfur trioxide is also formed,

$$SO_2\,(g) + 1/2\,O_2\,(g) \rightleftharpoons SO_3\,(g) \tag{4}$$

and the oxide–sulfate equilibrium must be considered:

$$MO\,(s) + SO_3\,(g) \rightleftharpoons MSO_4\,(s) \tag{5}$$

Very little $SO_3$ is produced at 1000°C, but the equilibrium of equation 4 shifts to the right at lower temperatures favoring the formation of sulfates according to equation 5. This behavior is illustrated by the schematic diagram in Figure 2.

Most roasting is carried out to obtain an oxide for reduction by carbon or carbon monoxide (qv), or for leaching in sulfuric acid solution followed by electrowinning. This roasting to completion, which eliminates all the sulfur and produces the metal oxide, is called dead roast or sweet roast. Incomplete roasting is used to remove excess sulfur in preparation of copper and nickel sulfides for the matte smelting process. A sulfating roast yields water-soluble sulfates in preparation for leaching.

The sulfur dioxide produced by the process is usually converted to sulfuric acid, or sometimes liquified, and the design of modern roasting facilities takes into account the need for an efficient and environmentally clean operation of the acid plant (see SULFURIC ACID AND SULFUR TRIOXIDE).

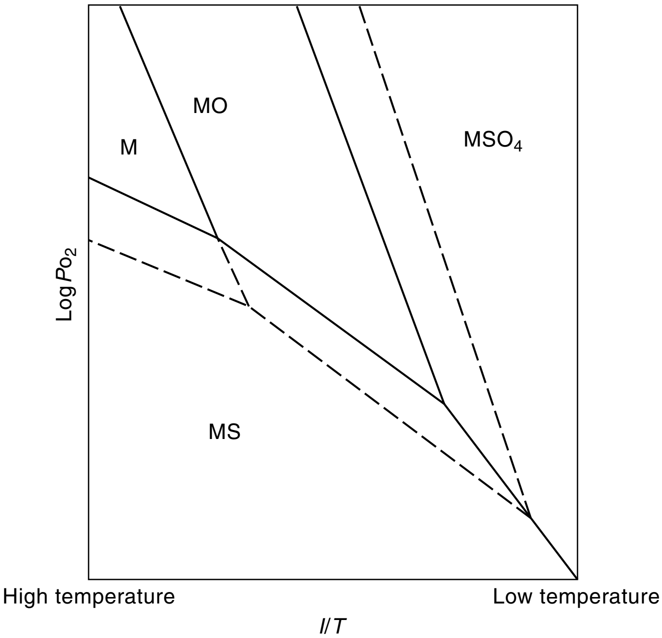

**Fig. 2.** Equilibria and predominance areas at constant $SO_2$ pressure as a function of temperature for the system M–S–O where (—) represents $P_{SO_2} = 101\,kPa$ (1 atm), and (–), $P_{SO_2} = 10\,kPa$ (0.1 atm) (2).

*Chlorination.* In some instances, the extraction of a pure metal is more easily achieved from the chloride than from the oxide. Oxide ores and concentrates react at high temperature with chlorine gas to produce volatile chlorides of the metal. This reaction can be used for common nonferrous metals, but it is particularly useful for refractory metals like titanium (see TITANIUM AND TITANIUM ALLOYS) and zirconium (see ZIRCONIUM AND ZIRCONIUM COMPOUNDS), and for reactive metals like aluminum.

The chlorination of titanium requires a reducing agent such as carbon,

$$\mathrm{TiO_2\ (s)C^0\ (s) + 2\ Cl_2\ (g) \longrightarrow TiCl_4\ (g) + CO_2\ (g)} \tag{6}$$

This reaction is slightly exothermic, but additional heat is required to maintain the operating temperature at 800–900°C.

*Sintering and Pelletizing.* The beneficiation of ores by physical techniques requires the liberation of metal-bearing minerals. This is usually achieved by reducing the raw material to a very fine size. The high throughput reduction processes, such as the iron blast furnace, however, cannot handle a finely divided feed. Sintering and pelletizing are techniques for agglomerating finely divided solid particles into a coarse material suitable for charging a blast furnace.

Sintering consists of heating a mixture of fine materials to an elevated temperature without complete fusion. Surface diffusion and some incipient fusion cause the solid particles in contact with one another to adhere and form larger aggregates. In the processing of hematite, $Fe_2O_3$, or magnetite, $Fe_3O_4$, fines to prepare a suitable feed for the iron blast furnace, the oxide ore is mixed with 5–8% of coal (qv) or coke to supply the fuel requirement. Often limestone is added to produce the self-fluxing sinter, and it is calcined during the sintering process. In the processing of sulfide ores, such as the treatment of lead sulfide concentrates, the contained sulfur acts as the fuel after ignition of the charge, and a single process achieves both roasting and sintering of the feed.

Pelletizing was developed for treating low grade iron ores. In particular, taconite ores consist of finely divided magnetite or hematite mixed with the gangue. The agglomeration of this material after fine comminution and separation is accomplished by balling in a rotating device such as a disk, drum, or cone followed by heating to a final temperature of $\sim$1300°C; this process is called induration. The induration achieves not only the agglomeration of the fines, but also the vaporization of free or combined water, the calcination of limestone, and the oxidation of magnetite to hematite. The pelletizing process has many advantages over sintering, and it is applied to high grade ores. The use of computers has made possible the automatic control of operations in modern pelletizing plants (see PROCESS CONTROL). The induration process can also be carried out under reducing conditions to yield partially reduced pellets for the blast furnace or fully reduced pellets for direct charging to steelmaking furnaces.

*Equipment.* Drying and calcination are usually carried out in various types of kilns such as rotary kilns, shaft furnaces, and rotary hearths. The induration step in a pelletizing plant requires similar equipment, but sometimes the charge passes through successive stages, ie, traveling grates for drying, a rotary hearth for preheating, and a shaft furnace for the chemical reactions and sintering (see also DRYING; FURNACES ELECTRIC).

The Dwight-Lloyd continuous sintering machine is commonly used. It consists of a series of grates mounted as an endless traveling belt. The feed is spread as a bed (10–20-cm deep), and the top is ignited as it passes through a fuel-fired ignition box. Air passes through the bed into a suction box and fan below the grate, and the combustion zone progresses through the bed as material moves to the discharge end of the belt. Downdraft machines are used for sintering iron ores, and updraft machines are preferred for sinter-roasting of lead and zinc concentrates.

The older roasting furnace is the multiple-hearth roaster consisting of 8–12 hearths enclosed in a cylindrical shell. The ore or concentrate fed at the top drops from hearth to hearth by the moving action of a rotating rabble attached to a central shaft. The sulfide particles are roasted by contact with the rising gases and are discharged at the bottom as calcine. In a suspension roaster, the pulverized concentrate is dried on the top hearths, drops through a combustion chamber, and is collected at the bottom. If the roasting process occurs while a very fine concentrate is mixed with the gas stream in the hot chamber, it is called flash roasting.

Fluid-bed roasters are well suited for gas–solid reactions. Usage in metallurgical operations started in 1950 and developed rapidly thereafter. Fluid-bed roasters have no moving parts in the hot zone, and the temperature and gas composition can be easily controlled. Air is pumped upward through a perforated hearth at a rate sufficient to expand the bed of sulfide particles, and the gas–solid reaction proceeds very fast. Circulating fluidized beds, elutriation reactors, and cyclones are commonly used for treating fine feed materials (see FLUIDIZATION).

### 4.2. Reduction to Liquid Metal.

Reduction to liquid metal is the most common metal reduction process. It is preferred for metals of moderate melting point and low vapor pressure. Because most metallic compounds are fairly insoluble in molten metals, the separation of the liquified metal from a solid residue or from another liquid phase of different density is usually complete and relatively simple. Because the product is in condensed form, the throughput per unit volume of reactor is high, and the number and size of the units is minimized. The common furnaces for production of liquid metals are the blast furnace, the reverberatory furnace, the converter, the flash smelting furnace, and the electric-arc furnace (see FURNACES, ELECTRIC).

*The Iron Blast Furnace.* The reduction of iron oxides by carbon in the iron (qv) blast furnace is the most important of all extractive processes, and the cornerstone of all industrial economies. Better understanding of the reactions taking place within the furnace has made possible a more efficient operation through better preparation of the burden, higher blast temperature, and sometimes increased pressure. Furnace capacity has doubled since the 1800s, whereas coke consumption has been reduced by about half. The ratio of coke to iron produced on a per weight basis is ca 0.5 to 1.

The iron blast furnace (Fig. 3) is a circular shaft furnace ca 30-m high having a maximum internal diameter of ca 9 m. It is a steel shell lined with refractory bricks (see REFRACTORIES). The furnace is charged at the top and preheated

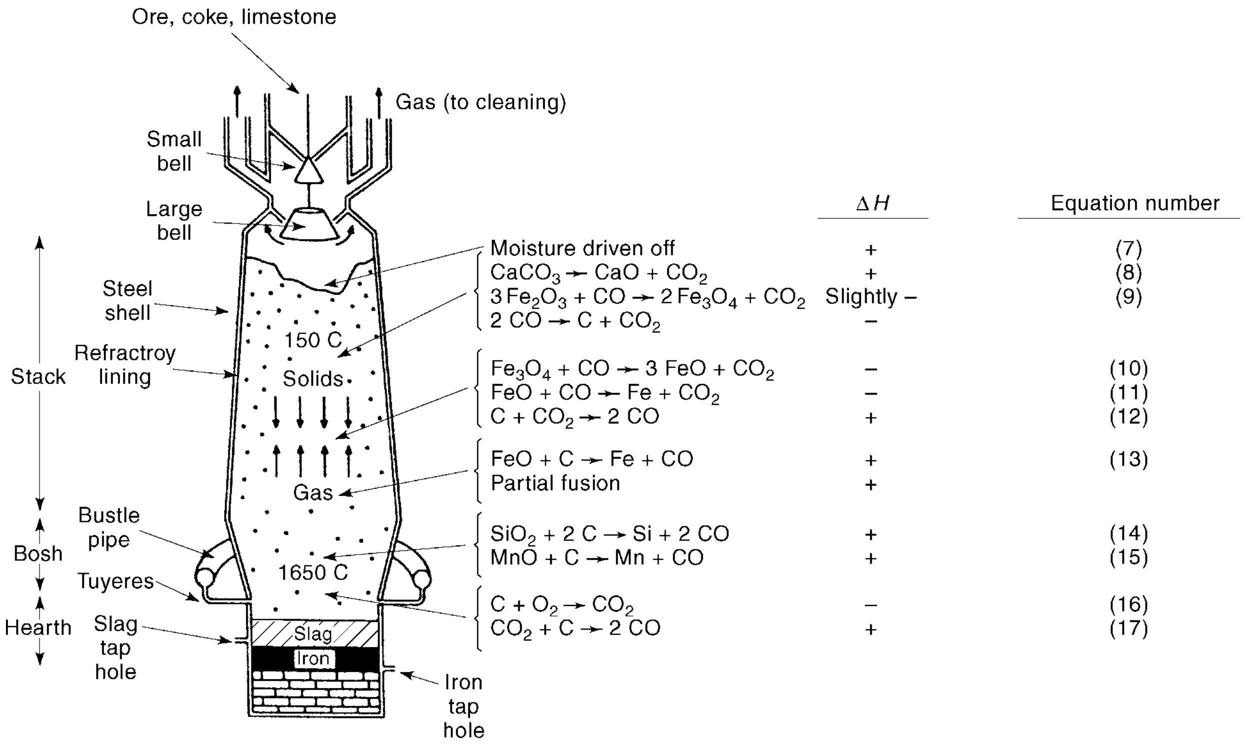

**Fig. 3.** Schematic diagram of the iron blast furnace indicating some of the chemical reactions (3).

air is introduced through the tuyeres above the hearth. At the tuyere level, the coke burns in the air. This strongly exothermic reaction (eq. 13) is the main source of heat for the process. Equation 13, the Boudouard reaction, supplies the reducing gas, carbon monoxide. This reaction is endothermic, and the value of its equilibrium constant determines the composition of the gas phase in the furnace. This furnace is a countercurrent reactor in which the iron oxides descending through the upper part of the stack are heated and reduced in stages as shown (Fig. 3). In the lower part of the stack, where the temperature is >1000°C, the Boudouard reaction (eq. 13) is shifted to the right and proceeds simultaneously with equation 13, yielding

$$\mathrm{FeO\ (s) + C^0\ (s) \longrightarrow Fe^0\ (s) + CO\ (g)} \tag{13}$$

referred to as the direct reduction of wustite, FeO. The fluxes consisting mainly of limestone, or sometimes dolomite, are heated and calcined on the way down the shaft. In the lower part of the furnace, called the bosh, these melt with the gangue material to form the slag. The iron blast furnace slag consists mainly of lime, alumina, and silica and has smaller amounts of magnesia, manganese oxide, iron oxide, and calcium sulfide. The lime is added as a flux to produce a slag having a melting point of 1300–1400°C and a relatively low viscosity. The reduced iron is also molten at the tuyere level. It drops as globules through the slag and settles at the bottom of the furnace.

The dissolution of carbon in molten iron in the lower part of the furnace, leads to the reduction of manganese oxide (eq. 13) and some silica (eq. 13), both in the slag, whereby the subsequent dissolution of these metals occurs in the molten iron.

$$\mathrm{C^0\ (s) \longrightarrow C^0_{Fe}\ (l)} \tag{18}$$

The molten slag and the molten iron, called hot metal or pig iron, are tapped from the hearth of the blast furnace. A modern blast furnace yields 5000–9000 t/d of iron. The compositions of the pig iron and the slag are determined by the furnace temperature, the composition of the ore, and the added flux. Pig iron always contains 3.5–4.5 wt% carbon, variable amounts of silicon, manganese, sulfur, and phosphorus.

The main technique for regulating the operating temperature of the blast furnace is the preheating of the blast. Progress in regulation has been made with the addition of natural gas, pulverized coal, or oil to the blast, oxygen enrichment, and addition of steam. Preheating and prereduction of the ore is also considered.

*Reduction Smelting of Nonferrous Metals.* The traditional method of lead (qv) smelting is reduction of an oxide in a blast furnace similar in principle to that used for iron, but very different in design and operation. The lead furnace consists of a shaft of rectangular cross section, 9-m high, 7-m long, and tapering in width from ca 2.5 m at the top to ca 1.5 m at the bottom. The feed, added at the top, consists mainly of roasted and sintered lead concentrates, coke, and fluxes to form a slag with the gangue material. Air is blown through tuyeres near the bottom, and coke burns according to equations 13 and 17 (Fig. 3). The reduction proceeds by contact between the hot reducing gas and the lump charge.

$$PbO\ (s) + CO\ (g) \longrightarrow Pb^0\ (l) + CO_2\ (g) \qquad (19)$$

The lead is molten (mp = 327°C) and trickles down to the crucible below the tuyeres. The slag melts when it reaches the high temperature zone of the tuyeres and floats on top of the lead. The slag consists mainly of $SiO_2$, CaO, FeO, with lesser amounts of $Al_2O_3$, MgO, ZnO, and other oxides. Most lead ores contain zinc because zinc-plant residues are often charged into lead blast furnaces. The amount of zinc in the slag is generally sufficient to justify recovery by treatment in a separate fuming furnace. Molten lead, ie, lead bullion, is alloyed with other easily reducible metals, mainly copper, tin, antimony, arsenic, gold, and silver present in the charge. The capacity of furnaces ranges from 100 to 400 t/d.

Many nonferrous metals can be extracted by reduction smelting, eg, copper, tin, nickel, cobalt, silver, antimony, and bismuth. Blast furnaces are sometimes used for the smelting of copper or tin, but flash and reverberatory furnaces are more common for metals other than lead.

The reverberatory furnace consists of a shallow, usually rectangular, hearth, side-walls, end-walls, and a roof or arch. The charge rests on the hearth and the furnace is fired using gas, oil, or pulverized coal which burns in the space between the charge and the roof. Heat transfer is achieved mainly by radiation directly from the flame and by reflection from the arched refractory roof. There is little or no reaction between the charge and the waste gases which leave the furnace at very high temperature. The feed often consists of fine-particle concentrates, and the reducing agent is usually coke. Both are added through ports on the side or the top of the furnace. Slag and metals are removed through tap holes, and the smelting can be carried out either continuously or as a batch process. Reverberatory furnaces are made in many sizes. Small furnaces hold only about one metric ton of metal; large ones such as those employed in copper smelting hold several hundred tons.

Electric heat provided by a resistance or by an electric arc can be substituted for the burning of a fuel. Electric furnaces can be designed in a variety of shapes and are more versatile than fuel-heated furnaces. The furnace atmosphere can be controlled independently of the chemistry of the combustion (see FURNACES, ELECTRIC).

*Matte Smelting and Converting.* Rich oxide ores of copper or roasted sulfide concentrates can be treated by reduction smelting in a blast or reverberatory furnace to yield an impure copper (qv) known as black copper. Except for a few plants treating mainly copper scrap, this process is obsolete. Most primary copper is produced by matte smelting, an operation yielding a molten sulfide of copper and iron, called matte, which is further oxidized in the converting step to yield metallic copper. A similar process is used for the extraction of nickel (see NICKEL AND NICKEL ALLOYS).

Copper is easily reduced from its compounds. The most important copper mineral is chalcopyrite [1308-56-1], $CuFeS_2$, and the separation of copper from iron is one of the objectives of the smelting operation. The sulfur in the ore has value as a fuel as well as a reducing agent. The traditional matte smelting is carried out in a reverberatory furnace in which a solid charge consisting of concentrates, calcines, converter slags, and fluxes is heated to 1150–1250°C. This melting produces two separate immiscible liquid phases, ie, a slag floating on top of a copper-rich matte. Matte consists mainly of $Cu_2S$ and FeS and ranges from 30 to 60 wt% Cu. The smelting slag is a mixture of iron oxides and silica having smaller amounts of alumina and lime. This slag is usually discarded. It should contain as little copper as possible.

The electric furnace is an alternative to the reverberatory furnace in environmentally sensitive areas where electricity costs are not too high. The electric furnace is versatile, produces small volumes of effluent gases, and the $SO_2$ concentration can be easily controlled. Operating costs, however, are high.

Since the mid-1960s most matte smelting capacity has been provided by flash smelting furnaces. In flash smelting, dry concentrates are blown with oxygen, hot air, or a mixture of both, into a hearth-type furnace. Inside the furnace, the sulfide particles react rapidly with the gases, causing a large evolution of heat and controlled partial oxidation of the concentrates. The main reactions, which are exothermic, can be summarized by the following:

$$2\ \mathrm{CuFeS_2}\ (\mathrm{s}) + 5/2\ \mathrm{O_2}\ (\mathrm{g}) \longrightarrow \mathrm{Cu_2S}\cdot\mathrm{FeS}\ (\mathrm{l}) + \mathrm{FeO}\ (\mathrm{l}) + 2\ \mathrm{SO_2}\ (\mathrm{g}) \tag{20}$$

$$\mathrm{FeS}\ (\mathrm{s}) + 3/2\ \mathrm{O_2}\ (\mathrm{s}) \longrightarrow \mathrm{FeO}\ (\mathrm{l}) + \mathrm{SO_2}\ (\mathrm{g}) \tag{21}$$

$$2\ \mathrm{FeO}\ (\mathrm{l}) + 2\ \mathrm{SiO_2}\ (\mathrm{s}) \longrightarrow 2\ \mathrm{FeO{\cdot}SiO_2}\ (\mathrm{l, slag}) \tag{22}$$

The reacting particles melt rapidly, and the droplets fall to the slag layer. The sulfide drops settle through it to form the matte phase. Any oxidized copper is reduced to the matte by the following reaction:

$$\mathrm{Cu_2O}\ (\mathrm{l,slag}) + \mathrm{FeS}\ (\mathrm{l}) \longrightarrow \mathrm{FeO}\ (\mathrm{l,slag}) + \mathrm{Cu_2S}\ (\mathrm{l}) \tag{23}$$

Flash smelting is efficient because the fuel value of the sulfur and iron in the charge is fully used, and the productivity (8–12 t/d of charge processed per square meter of hearth) is higher than that of the reverberatory or electric furnace.

In addition to copper, iron, and sulfur, the matte produced by smelting contains oxygen and various impurities, eg, As, Bi, Ni, Pb, Sb, Zn, Au, and Ag, depending on the composition of the concentrate. The converting operation removes the iron and the sulfur along with some of the other impurities. The molten matte is charged to a converter where it is oxidized by blowing air. This is universally done in a Pierce-Smith converter, or a similar reactor consisting of a cylindrical steel shell lined with magnesite refractory bricks. The shell is placed horizontally and rotates to achieve the different positions for charging, blowing through submerged tuyeres, and pouring. Typical inside dimensions are 4 m dia and 9 m in length for an output of 100–200 t/d.

The converting operation takes place in two successive stages. In the slag-forming stage, the main reaction is the oxidation of FeS to FeO and $Fe_2O_3$ which combine with a silica flux to form a silicate slag by reactions similar to those of equations 21 and 22. The matte is added in several batches, each addition followed by oxidation and discharge of the slag. In the copper making stage, the remaining sulfur is oxidized to sulfur dioxide.

$$Cu_2S\ (l) + O_2\ (g) \longrightarrow 2\ Cu^0\ (l) + SO_2\ (g) \qquad (24)$$

Some copper oxide is formed which then reacts with the remaining sulfide to form metallic copper:

$$2\ Cu_2O\ (l) + Cu_2S\ (l) \longrightarrow 6\,Cu^0\ (l) + SO_2\ (g) \qquad (25)$$

The equilibrium constants for these reactions are such that copper is not appreciably oxidized by oxygen until most sulfur has been removed. This makes possible the production of blister copper, 98.6–99.5% Cu that is low in both sulfur (0.02–0.1%) and oxygen (0.5–0.8%). The converter slag, however, contains a significant amount of copper and must be recycled to the smelting stage.

All the operations in the winning of copper from sulfide ores are controlled oxidations using air or oxygen. An important effort has been made to carry out the operation as a continuous single-step process. The Noranda submerged tuyere process, carried out in a long cylindrical vessel, produced copper for several years. In order to improve impurity elimination and to increase capacity, it is used to produce a high grade copper matte (70% Cu). The Outokumpu flash smelting (see COPPER) is the only single-furnace direct-to-blister process. Blister copper can be obtained by precise control of the input rate of oxygen relative to that of the concentrate. The advantage is a single source of $SO_2$ emission and potentially lower costs. The significant drawback is the high copper content of the slag (15–35% of the copper input) which has to be reduced in an electric slag cleaning furnace. The Mitsubishi process uses three furnaces interconnected by a continuous flow of matte and slag, ie, a smelting furnace, an electric slag cleaning furnace, and a converting furnace. Its advantages are a high productivity achieved by $O_2$-enrichment and an efficient recovery and use of high strength $SO_2$ streams.

Two processes, developed for the direct processing of lead sulfide concentrates to metallic lead (qv), have reached commercial scale. The Kivcet process combines flash smelting features and carbon reduction. The QSL process is a bath-smelting reactor having an oxidation zone and a reduction zone. Both processes use industrial oxygen. The chemistry can be shown as follows:

$$PbS\ (s) + 2\ C^0\ (s) + 5/2\ O_2 \longrightarrow Pb^0\ (l) + SO_2\ (g) + CO\ (g) + CO_2\ (g) \qquad (26)$$

### 4.3. Reduction to Gaseous Metal.

Volatile metals can be reduced and easily and completely separated from the residue before being condensed to a liquid or a solid product in a container physically separated from the reduction reactor. Reduction to gaseous metal is possible for zinc, mercury, cadmium, and the alkali and alkaline-earth metals, but industrial practice is significant only for zinc, mercury, magnesium, and calcium.

Zinc is produced by reduction of zinc oxide, usually a calcine obtained by roasting zinc sulfide concentrates. Carbon is used in the absence of air at

1200–1300°C, well above the boiling point of the metal (906°C).

$$\mathrm{ZnO\ (s) + C^0\ (s) \longrightarrow Zn^0\ (g) + CO\ (g)} \qquad (27)$$

The original process, patented in 1810 and known as the Belgian retort process, was the main process for winning zinc for more than a century. This process, now obsolete, is historically significant. The reaction was carried out in small retorts, each producing daily batches of 25–50 kg of zinc. The gases produced (eq. 27) exited through a condenser, the liquid zinc was collected, and carbon monoxide vented and burned in air. The retorts and condensers, made of fireclay, were placed horizontally in a fuel-fired furnace. This process was labor intensive and had a poor metallurgical efficiency.

The development in the 1950s of a zinc–lead blast furnace (Imperial smelting process) is the most recent breakthrough in zinc smelting as of this writing. Both lead bullion and zinc metal are recovered by roasting and reducing mixed lead and zinc concentrates. The main feature of the process is the rapid cooling of zinc vapor from 1100 to 550°C in a spray of molten lead in a specially designed condenser. This prevents reoxidation of the zinc vapor by carbon dioxide in the furnace gases.

A vacuum-retort process (Pidgeon process) was used during World War II for the production of magnesium and calcium. Silicon, in the form of ferrosilicon, was used as the reducing agent instead of carbon to avoid the problem of cooling magnesium vapor in the presence of carbon dioxide:

$$\mathrm{2\,CaO \cdot MgO\ (s) + Fe_{\mathit{x}}Si\,(s) \longrightarrow 2\,Mg^0\ (g) + (CaO)_2 \cdot SiO_2\ (s) + \mathit{x}\,Fe^0\ (s)} \qquad (28)$$

At 1200°C, the equilibrium pressure of magnesium vapor for this reaction was well below atmospheric pressure, and a high vacuum had to be maintained in the condenser. The reduction was carried out in small retorts made from Cr–Ni–Fe alloys and placed horizontally in a furnace. A newer process using a vertical electric-arc furnace (Magnetherm process) has been developed, but most magnesium is produced by electrolysis (see MAGNESIUM AND MAGNESIUM ALLOYS).

**4.4. Reduction to Solid Metal.** Metals having very high melting points cannot be reduced in the liquid state. Because the separation of a solid metallic product from a residue is usually difficult, the raw material must be purified before reduction. Tungsten and molybdenum, for instance, are prepared by reduction of a purified oxide ($WO_3$, $MoO_3$) or a salt, eg, $(NH_4)_2MO_4$, using hydrogen. A reaction such as

$$\mathrm{WO_3\ (s) + 3\,H_2\ (g) \longrightarrow 3\,H_2O\,(g) + W^0\ (s)} \qquad (29)$$

is used. The metallic product consists of fine particles fabricated into various shapes by the techniques of powder metallurgy (see METALLURGY; MOLYBDENUM AND MOLYBDENUM ALLOYS; POWDER METALLURGY; TUNGSTEN AND TUNGSTEN ALLOYS).

Very reactive metals, eg, titanium or zirconium, which in the liquid state react with all the refractory materials available to contain them, also require reduction to solid metal. Titanium is produced by metallothermic reduction of its chloride using liquid magnesium at 750°C (Kroll process).

$$\mathrm{TiCl_4\ (g) + 2\,Mg_0\ (l) \longrightarrow Ti^0\ (s) + 2\,MgCl_2\ (l)} \tag{30}$$

A steel reaction vessel is partly filled with solid magnesium, sealed, and flushed with helium or argon. The reactor is placed in a furnace and heated to melt the magnesium. Pure liquid titanium tetrachloride is slowly fed to the vessel, where it vaporizes and is reduced by molten magnesium. The reaction (eq. 30) is exothermic and proceeds to completion. Some of the liquid magnesium chloride is drained, and the vessel is cooled to room temperature. The reaction mass, interlocking crystals of metallic titanium, magnesium chloride, and some magnesium metal, is removed by boring. The magnesium chloride and the magnesium are separated from the titanium by vacuum distillation or by leaching with dilute acid. About 700–1400 kg of titanium is produced in one batch. This process is summarized in Figure 4 (see TITANIUM AND TITANIUM ALLOYS).

Less reactive metals can also be produced by reduction below their melting point. Several processes, referred to as direct reduction, have been developed for the reduction of iron oxides to solid iron. The reducing agents used commercially are hydrogen, carbon monoxide, natural gas, carbon, and carbonaceous fuels. The reaction can be carried out in a rotary kiln, a shaft furnace, or in the case of gaseous reduction, in a fluidized-bed reactor. These processes require a

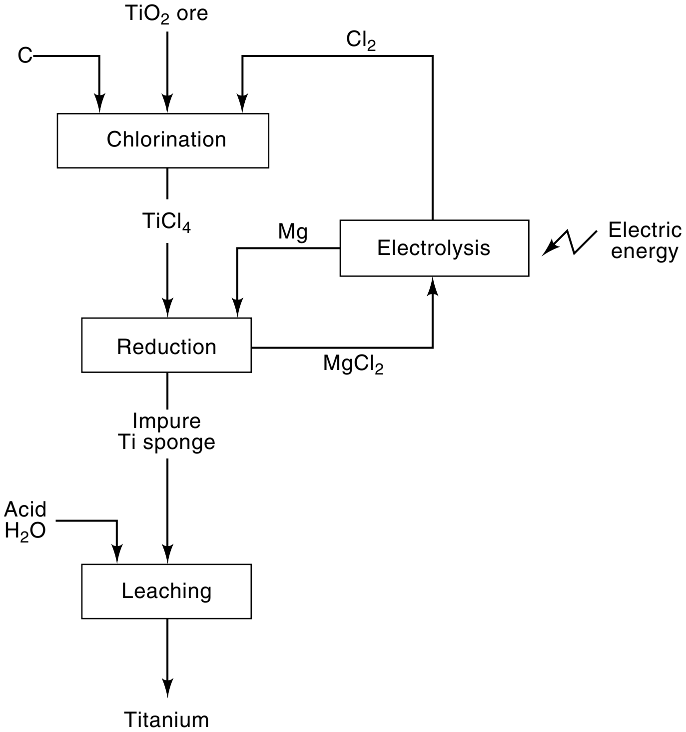

**Fig. 4.** Flow sheet for the processing of titanium ore by chlorination followed by reduction with magnesium.

relatively pure iron ore. The metallic product is impure metal (90–95 wt% Fe), usually charged to a steelmaking furnace. The advantage of the direct reduction process is that it can be operated on a small scale and the capital investment is much lower than that of a blast-furnace plant (see IRON BY DIRECT REDUCTION).

**4.5. Refining Processes.** All the reduction processes yield an impure metal containing some of the minor elements present in the concentrate, eg, cadmium in zinc, or some elements introduced during the smelting process, eg, carbon in pig iron. These impurities must be removed from the crude metal in order to meet specifications for use. Refining operations may be classified according to the kind of phases involved in the process, ie, separation of a vapor from a liquid or solid, separation of a solid from a liquid, or transfer between two liquid phases. In addition, they may be characterized by whether or not they involve oxidation–reduction reactions.

*Volatilization.* In this simplest separation process, the impurity or the base metal is removed as a gas. Lead containing small amounts of zinc is refined by batch vacuum distillation of the zinc. Most of the zinc produced by smelting processes contains lead and cadmium. Crude zinc is refined by a two-step fractional distillation. In the first column, zinc and cadmium are volatilized from the lead residue, and in the second column cadmium is removed from the zinc (see ZINC AND ZINC ALLOYS).

Impurities can be removed by formation of a gaseous compound, as in the fire-refining of copper (qv). Sulfur is removed from the molten metal by oxidation with air and evolution of sulfur dioxide. Oxygen is then removed by reduction with C, CO, $H_2$, or $CH_4$ in the form of natural gas, reformed natural gas, or wood. Final impurity contents of ca 0.001 wt% sulfur and 0.05–0.2 wt% oxygen are usually achieved.

The iodide or van Arkel-de Boer process is a volatilization process involving transfer of an involatile metal as its volatile compound. It is used for the purification of titanium. The reaction of iodine gas with impure titanium metal at 175°C yields gaseous titanium iodide and leaves the impurities in the solid residue.

$$\mathrm{Ti}^0\ (\mathrm{s}) + 2\ \mathrm{I}_2\ (\mathrm{g}) \rightleftarrows \mathrm{TiI}_4\ (\mathrm{g}) \tag{31}$$

The equilibrium is reversed at high temperature. The iodide is decomposed by passing the vapor over an electrically heated wire (1300–1400°C), yielding purified solid titanium and iodine gas which is recycled. The iodide process also applies to the purification of zirconium, hafnium, and silicon.

The vapometallurgical refining of nickel is based on the reaction of the metal with carbon monoxide to form gaseous nickel tetracarbonyl [13463-39-3], $Ni(CO)_4$, at 50°C. Decomposition occurs at ca 230°C.

*Precipitation.* In the simplest case, the solubility of an impurity in the liquid metal changes with temperature. Thus the impurity may precipitate as a solid phase upon cooling. For instance, the removal of iron from tin and of copper from lead are achieved by precipitation. When the solid is lighter than the liquid, it floats as a dross on the surface of the melt where it is easily removed by scraping. The process is called drossing.

Precipitation can also occur upon chemical reaction between the impurity and a precipitating agent to form a compound insoluble in the molten metal.

The refining of crude lead is an example of this process. Most copper is removed as a copper dross upon cooling of the molten metal, but the removal of the residual copper is achieved by adding sulfur to precipitate copper sulfide. The precious metals are separated by adding zinc to liquid lead to form solid intermetallic compounds of zinc with gold and silver (Parkes process). The precious metals can then be recovered by further treatment (see LEAD).

*Slag Refining.* Unwanted constituents can be removed by transfer into a slag phase. Slag refining is also used for operations in which the liquid metal is maintained in contact with a slag or a molten salt. This second immiscible liquid is usually more oxidizing than the metallic phase and selective oxidation of the impurities renders them soluble in the slag or molten salt. Impurities that are less easily oxidized remain in the liquid metal.

Slag refining is effective for the purification of the less reactive nonferrous metals, eg, gold, silver, copper, lead, and others. In the recovery of precious metals from anode slimes, one of the steps is a fusion, usually in a small reverberatory furnace, where impurities are removed by oxidation with air and dissolution into successive slags: an oxide slag, a sodium carbonate slag, and a sodium nitrate slag. The product of this operation is a silver–gold alloy, ca 90% Ag and 9% Au, called doré metal, which is further refined by electrolysis. In the refining of lead, one of the steps is the removal of arsenic, antimony, and tin in a molten mixture of sodium hydroxide and sodium nitrate (Harris process). Slag refining of copper is effective in removing impurities less noble than copper, but has been replaced by electrorefining for the production of primary copper.

*Steelmaking.* Steelmaking is the most economically important slag refining process (see STEEL). Pig iron contains up to 4% carbon, 1% manganese, 1% silicon, and variable amounts of phosphorus and sulfur. The removal of these impurities is based on preferential oxidation and control of the slag metal equilibrium. Modern steelmaking started with the invention of the Bessemer process in 1856. Blowing air through the bottom of a converter containing pig iron oxidizes silicon first, then manganese, and finally carbon. The reactions are exothermic, and the heat released is sufficient to maintain the final product, a low carbon steel, molten at ~1600°C. The original Bessemer process uses an acid slag high in silica, in which silicon oxide and manganese oxide are soluble. Carbon escapes as carbon monoxide. Phosphorus is also oxidized, but it does not transfer into an acid slag. The Thomas or Basic Bessemer process uses a basic slag high in lime which removes phosphorus and sulfur by the following reactions:

$$2\ \mathrm{P}^{0}_{\mathrm{Fe}}\ (\mathrm{l}) + 3\ \mathrm{CaO}\ (\mathrm{l, slag}) + 5\ \mathrm{FeO}\ (\mathrm{l, slag}) \longrightarrow \mathrm{P_2O_5} \cdot 3\ \mathrm{CaO}\ (\mathrm{l, slag}) + 5\ \mathrm{Fe}_0\ (\mathrm{l}) \tag{32}$$

$$\mathrm{S}^{0}_{\mathrm{Fe}}\ (\mathrm{l}) + \mathrm{Ca\ O(l, slag)} \longrightarrow \mathrm{CaS}\ (\mathrm{l, slag}) + \mathrm{O}^{0}_{\mathrm{Fe}}\ (\mathrm{l}) \tag{33}$$

Steel produced by the converter process contains dissolved nitrogen and oxygen. The steel is usually deoxidized by small additions of elements like aluminum, manganese, and silicon. Vacuum degassing is used to remove residual oxygen, nitrogen, and hydrogen. The Siemens-Martin or open-hearth process, developed ca 1880, used a reverberatory furnace which is charged with solid steel scrap, limestone, iron ore, and molten pig iron. As of the 1990s, electric-arc furnaces are used. These provide the higher temperatures and flexibility of operation required for the production of alloy steels.

Shortly after World War II, the top-blown converter was invented in Austria (L-D process), and oxygen lancing was applied to the open-hearth process. Top-blown oxygen steelmaking, common practice in the 1990s, reduces the time for processing of high carbon iron into steel from hours to minutes. The process is autogeneous. Larger (250–300 t capacity) converters can handle 25–35% scrap. Rotating converters like the Kaldo and Rotor processes have also been developed (4). The invention of the Savard/Lee gas-shielded tuyere made possible the injection of oxygen through tuyeres in the bottom of a steel converter. The bottom injection of argon is another improvement in the production of stainless steel by the argon–oxygen decarburization process.

## 5. Hydrometallurgy

The treatment of ores by dissolution in aqueous solutions is a fairly simple operation which imitates natural leaching processes. The development of hydrometallurgy started when aqueous physical chemistry became better understood in the late nineteenth and early twentieth centuries. Hydrometallurgical processes are preferred when the pyrometallurgical route is impossible or impractical. If the metal to be extracted is more reactive than the impurities to be removed, eg, aluminum, or if the grade of the ore is very low and cannot be upgraded by physical beneficiation, eg, gold and uranium, hydrometallurgy becomes important.

In some respects, hydrometallurgy can be described as wet analytical chemistry carried out on a large scale. Many different flow sheets can be designed with various types of unit operations and most metals can be extracted from a complex ore and recovered at the desired level of purity. A viable hydrometallurgical process, however, must achieve that goal at an economically acceptable cost.

The continuing decrease in grade, the increasingly complex nature of available ores, and the need for high purity metallic products has favored the development of hydrometallurgy which has found applications for advanced materials, including ceramics (qv), composites (see COMPOSITE MATERIALS), and nanostructure materials. Concern for air pollution (qv) caused by pyrometallurgical plants and the cost of preventive devices are incentives to consider hydrometallurgy in cases where water pollution can be controlled.

The three main steps are leaching or dissolution of the metal in a suitable aqueous solvent, purification or removal of impurities and/or concentration of the solution, and recovery or precipitation of the reduced metal or its compound from solution. In exceptional cases such as the treatment of seawater or brines for metal values, the first step has been taken by nature (see CHEMICALS FROM BRINES; OCEAN RAW MATERIALS). Most hydrometallurgical processes, however, involve several steps for the purification and/or concentration of the solution before the recovery of a pure product becomes feasible. In addition, steps are required for the physical separation of the solid phases from the liquid, ie, washing, clarification, thickening, filtering, drying (qv), evaporation (qv), etc. Last but not least, the solvent is usually too valuable to be discarded, and must be regenerated and recycled (see Solvent recovery). Hydrometallurgical plants operate most efficiently in a closed circuit which limits water pollution.

### 5.1. Leaching Chemistry.

The purpose of the leaching operation is to dissolve the desired mineral and separate it from the gangue material. The reaction should be selective and fast, the solvent inexpensive or easily regenerated. Several leaching agents are commonly used.

*Water.* Because most metallic chlorides and sulfates are fairly soluble in water, water can be used to leach calcines from chloridizing or sulfating roasts.

*Acid Solutions.* Dilute sulfuric acid is the most important solvent for oxide ore and for dead roasted sulfide concentrates. For instance, the leaching of zinc oxide, described by the following equation, can be written as follows:

$$\mathrm{ZnO\ (s) + 2\ H^{+}\ (aq) \longrightarrow Zn^{2+}\ (aq) + H_2O\ (l)} \tag{34}$$

Other acids, eg, hydrochloric or nitric acid, are more seldom used because of higher costs and corrosion problems.

*Alkaline Solutions.* The most important example of alkaline leach is the digestion of hydrated alumina from bauxite by a sodium hydroxide solution at 160–170°C, ie, the Bayer process (see Aluminum and aluminum alloys).

$$\mathrm{Al_2O_3{\cdot}3\ H_2O\ (s) + 2\ OH^{-}\ (aq) \longrightarrow 2\ AlO_2^{-}\ (aq) + 4\ H_2O\ (l)} \tag{35}$$

*Complex-Forming Solutions.* The solubility of a metal can be enhanced by complexation using a suitable ligand. The dissolution of copper oxide in ammoniacal solutions is an example:

$$\mathrm{CuO\ (s) + 4\ NH_4^{+}\ (aq) + 2\ OH^{-}\ (aq) \longrightarrow Cu(NH_3)_4^{2+}(aq) + 3\ H_2O\ (l)} \tag{36}$$

The alkalinity of the solution prevents the attack of a carbonate gangue which would be soluble in an acid medium.

*Oxidizing Solutions.* In many leaching processes the mineral must be oxidized, as for instance, in the leaching of copper sulfides by ferric sulfate or ferric chloride solutions.

$$\mathrm{Cu_2S\ (s) + 2\ Fe^{3+}\ (aq) \longrightarrow CuS\ (s) + Cu^{2+}\ (aq) + 2\ Fe^{2+}\ (aq)} \tag{37}$$

$$\mathrm{CuS\ (s) + 2\ Fe^{3+}\ (aq) \longrightarrow S\ (s) + Cu^{2+}\ (aq) + Fe^{2+}\ (aq)} \tag{38}$$

Bacterial leaching is another example of oxidizing dissolution whereby specific bacteria either directly attack the sulfide mineral or indirectly enhance the regeneration of the oxidant.

*Oxidizing and Complex-Forming Solutions.* The leaching of gold or silver can be achieved only by oxidation of the metal by air followed by formation of a stable cyanide complex.

$$\mathrm{2\ Au_0\ (s) + 4\ CN^{-}(aq) + 1/2\ O_2\ (g) + H_2O\ (l) \longrightarrow 2\ \left[Au(CN)_2\right]^{-}(aq) + 2\ OH^{-}(aq)} \tag{39}$$

Another important example is the leaching of nickel sulfide under ammonia and oxygen pressure to form hexaammine nickel (Sherritt-Gordon process).

$$\mathrm{NiS\ (s) + 2\,O_2\ (g) + 6\,NH_3\ (g) \longrightarrow \left[Ni(NH_3)_6\right]^{2+}\ (aq) + SO_4^{2-}\ (aq)} \qquad (40)$$

*Leaching Techniques.* Leaching techniques vary depending on the type of reaction and the characteristics of the ore. Dissolution occurs at the interface between the solid and the solution. The rate depends on the rate of transport of the leaching agent from the solution to the solid and on the rate of chemical reaction. These rates are enhanced by increasing the surface area of the solid, usually by fine grinding of the ore or concentrate. For some low grade material, however, little preparation is justified beyond fracture and rubblization of the rock.

*In Situ Leaching.* Copper and uranium ores are sometimes leached in place by circulating acidified mine water through the underground deposit. This process is known as solution mining.

*Heap and Dump Leaching.* Heap leaching is practiced mainly for oxide copper ores, and for gold and silver. The crushed ore is placed in large heaps and sprayed with the leaching solution. Mine wastes containing copper values as sulfides are also leached in a similar way known as dump leaching. *In situ* and dump leaching of copper sulfide values rely on the presence of iron in natural waters. The source of this iron and the acidity of the solution results from the aqueous oxidation of pyrite. The iron is oxidized by contact with the atmosphere, and the ferric ions act as oxidant for the dissolution of sulfides by reactions similar to equations 37 and 38. Bacterial activity in the bed has been found to enhance reaction rates. This type of leaching, however, is a slow process carried out over periods of several years.

*Percolation Leaching.* Ground material coarse enough to permit circulation of a solution through a bed of particles can be leached by percolation of the solvent through the material placed in a tank or vat. The process usually takes several days.

*Agitation Leaching.* Very fine ore products, slimes, are treated by agitation of a pulp, which is a suspension of the ore particles in the solution. The process is carried out in a tank with mechanical or air agitation. In a leaching process for which oxygen is needed, eg, gold leaching, air agitation is preferred. Residence time is several hours.

*Pressure Leaching.* Leaching at elevated (90–250°C) temperature is carried out in autoclaves under pressure. In some instances the purpose is to modify equilibrium conditions and to increase the solubility of the ore, eg, digestion of bauxite. In cases requiring a gaseous reagent, eg, oxygen or ammonia, the higher pressure increases the solubility of the gas and enhances the reaction rates. The increased temperature also increases reaction rates, and residence times are one or two hours. This process has been applied successfully to oxidation of sulfidic refractory gold ores prior to cyanidation.

*Liquid–Solid Separation.* The separation of the solution containing the dissolved metal, ie, the pregnant solution, from the leach residue is the final leaching step. Most leaching operations are carried out in several tanks in series to permit countercurrent flow. The pregnant solution leaves at one end after contacting fresh ore, and the depleted solids exit at the other end after contacting the fresh solvent. Additional steps such as washing the residue, clarification of the solution, and filtering are required.

### 5.2. Recovery of Metal from Solution.

The same chemical principles govern the recovery of an element or compound from solution, whether it is the main metal to be processed or an impurity to be removed.

*Electrowinning.* When it is possible, electrolytic deposition is the most efficient way of recovering a valuable metal from solution. It is quite selective and usually yields a pure product which can be marketed directly as cathodes, or after casting into commercial shapes. It is, however, the most expensive method.

*Precipitation.* The precipitation of aluminum trihydroxide in the recovery step of the Bayer process is achieved either by lowering the temperature or by diluting the pregnant liquor and reducing its pH. Both methods reverse the direction of equation 35, but seeding with previously precipitated crystals is required in order to initiate nucleation.

The removal of copper from the pregnant nickel solution in the Sherritt-Gordon process is an example of purification by precipitation of a fairly insoluble compound. First, in the copper boil step, ammonia is driven off by heating the solution, and some copper sulfide precipitates. The residual copper is removed by adding hydrogen sulfide for the chemical precipitation of more copper sulfide.

$$\mathrm{Cu^{2+}\ (aq) + H_2S\ (g) \longrightarrow CuS\ (s) + 2\ H^+\ (aq)} \qquad (41)$$

*Cementation.* A metal can be removed from solution by displacing it with a more active metal. This simple, inexpensive method has been commonly used to recover copper from dilute (1–3 kg/m$^3$) solution using shredded iron and detinned iron cans as reducing agent.

$$\mathrm{Cu^{2+}\ (aq) + Fe^0\ (s) \longrightarrow Cu^0\ (s) + Fe^{2+}\ (aq)} \qquad (42)$$

A similar reaction leads to the precipitation of gold or silver from cyanide solution using zinc powder.

$$\mathrm{2\ Au(CN)_2^-\ (aq) + Zn^0\ (s) \longrightarrow 2\ Au^0\ (s) + Zn(CN)_4^{2-}\ (aq)} \qquad (43)$$

Cementation is also an efficient way of purifying a pregnant solution by removing impurities that are more noble than the metal being processed. An example is the cementation of copper, cadmium, cobalt, and nickel from zinc solutions prior to electrowinning.

The cementation of gold and the purification of the zinc electrolyte are usually carried out in cylindrical vessels using mechanical agitation. The cementation of copper is carried out in long narrow tanks called launders, in rotating drums, or in an inverted cone precipitator (see COPPER).

*Gas Reduction.* The use of a gaseous reducing agent is attractive because the metal is produced as a powder that can easily be separated from the solution. Carbon dioxide, sulfur dioxide, and hydrogen can be used to precipitate copper, nickel, and cobalt, but only hydrogen reduction is applied on an industrial scale. In the Sherritt-Gordon process, the excess ammonia is removed during the purification to achieve a 2:1 ratio of $NH_3$:Ni in solution. Nickel powder is then precipitated by

$$\mathrm{Ni(NH_3)_2^{2+}\ (aq) + H_2\ (g) \longrightarrow Ni^0\ (s) + 2\ NH_4^+\ (aq)} \qquad (44)$$

The reaction proceeds in an autoclave at 200°C under ca 3 MPa (30 atm) of hydrogen pressure.

*Ion Exchange.* Metallic ions can be removed from an aqueous solution by ion exchange (qv) at the surface of an organic resin. Both anionic and cationic exchangers are available. Anionic ion-exchange resins are used for concentration and purification of the dilute pregnant solutions obtained by leaching uranium ores with sulfuric acid. The ion-exchange reaction is represented by

$$\mathrm{UO_2(SO_4)_3^{4-}\ (aq) + 4\ RX\ (s) \longrightarrow R_4UO_2(SO_4)_3\ (s) + 4\ X^-\ (aq)} \qquad (45)$$

where $X^-$ is an anion, usually $NO^-{}_3$ or $Cl^-$, and R represents the organic resin. After the resin is loaded, it is eluted with a strong solution of the $X^-$ ion. This reverses the equilibrium conditions for equation 45, transfers the complex uranyl ion back to an aqueous phase, and regenerates the resin. The technology for this process, borrowed from the water-treatment industry, uses mainly packed columns (see WATER). The resin-in-pulp process is typical of uranium hydrometallurgy. The leaching pulp and ion-exchange resin are agitated together and both reactions proceed in the same reactor. The residue and the loaded resin are then separated.

*Solvent Extraction.* Liquid–liquid extraction, well known in the chemical industry, was first used in extractive metallurgy for the processing of uranium. When a dilute solution of uranium is contacted with an extractant such as di(2-ethylhexyl) phosphoric acid (D2EHPA) or $R_2HPO_4$, dissolved in kerosene, the uranyl ion is transferred to the organic phase.

$$\mathrm{2\ R_2HPO_4\ (org) + UO_2^{2+}\ (aq) \longrightarrow UO_2(R_2PO_4)_2\ (org) + 2\ H^+\ (aq)} \qquad (46)$$

The pregnant organic solvent is stripped by agitation with a strong carbonate solution which removes uranium as the stable $UO_2(CO_3)_3^{4-}$ aqueous complex.

The development of selective extractants for copper has made extraction from dilute solutions (1–5 kg/m$^3$) economically feasible. Transfer of the copper by stripping to a more concentrated sulfuric acid solution, ie, 30–40 kg/m$^3$ for $Cu^{2+}$ and 150–170 kg/m$^3$ for $H_2SO_4$, from which the copper is recovered by electrowinning. The simplified reaction,

$$\mathrm{Cu^{2+}\ (aq) + 2\ HR\ (org) \longrightarrow CuR_2\ (org) + 2\ H^+\ (aq)} \qquad (47)$$

is carried out in two or three extraction mixer-settlers followed by one or two stripping mixer-settlers. The organic extractants are hydroxyphenyl oximes, typically 5–10 vol% of salicylaldoximes and ketoximes in purified kerosene (4).

In addition, solvent extraction is applied to the processing of other metals for the nuclear industry and to the reprocessing of spent fuels (see NUCLEAR REACTORS). It is commercially used for the cobalt–nickel separation prior to electrowinning in chloride electrolyte. Both extraction columns and mixer-settlers are in use.

**5.3. Hydrometallurgical Flow Sheets.** The various hydrometallurgy operations can be combined in many ways to design processes appropriate for specific metals.

*Aluminum.* All primary aluminum as of 1995 is produced by molten salt electrolysis, which requires a feed of high purity alumina to the reduction cell. The Bayer process is a chemical purification of the bauxite ore by selective leaching of aluminum according to equation 35. Other oxide constituents of the ore, namely silica, iron oxide, and titanium oxide remain in the residue, known as red mud. No solution purification is required and pure aluminum hydroxide is obtained by precipitation after reversing reaction 35 through a change in temperature or hydroxide concentration; the precipitate is calcined to yield pure alumina.

*Uranium.* The hydrometallurgical treatment of uranium ores is a concentration and purification process. Typical ore grade is 0.1–0.5% $U_3O_8$, and pregnant solutions contain ca 1 kg/m$^3$ of $U_3O_8$. The dissolution requires the presence of an oxidant, either oxygen or a ferric salt.

$$U_3O_8\ (s) + 6\ H^+\ (aq) + 1/2\ O_2\ (g) \longrightarrow 3\ UO_2^{2+}\ (aq) + 3\ H_2O\ (l) \qquad (48)$$

The solvent, a solution of either sulfuric acid or sodium carbonate, forms the stable complex uranyl ions $UO_2(SO_4)_2^{2-}$, $UO_2(SO^4)_3^{4-}$, and $UO_2(CO_3)_3^{4-}$. The pregnant solution is concentrated and purified by ion exchange or solvent extraction, yielding a stripping solution of ca 50 kg/m$^3$ $U_3O_8$. Uranium is then precipitated chemically. Pure $U_3O_8$ is obtained by calcination (see URANIUM AND URANIUM COMPOUNDS).

*Gold.* Gold is produced exclusively by hydrometallurgy. The traditional steps are leaching in alkaline cyanide solution (eq. 39) and cementation on zinc powder (eq. 43). In modern plants, the dissolved gold in the pregnant solution is adsorbed on carbon from which it can be transferred into a more concentrated solution suitable for electrowinning. The need to process refractory ores, so-called because these contain organic carbon or metal sulfides which make direct leaching less efficient, has led to the development of preparatory steps including aqueous chlorine oxidation of carbon, bacterial leaching, oxidizing autoclave leach, and roasting of sulfides.

*Nickel.* Most nickel is produced by smelting sulfide ores. Several hydrometallurgical processes have been developed. Among them the Sherritt-Gordon process stands out as the first successful commercial application of pressure hydrometallurgy to a complex feed. The raw material is a pentlandite, $NiS \cdot FeS$ concentrate. The flow sheet in Figure 5 illustrates how several hydrometallurgical operations are integrated into a complex process. Nickel is leached selectively in an ammoniacal solution according to equation 40, iron remains in the residue as $Fe_2O_3$. Copper is removed from solution by the purification steps mentioned earlier with equation 41. Cobalt remains in solution and nickel is recovered by hydrogen reduction following equation 44. Similar flow sheets are quite appropriate for the treatment of complex raw materials containing several different metal values.

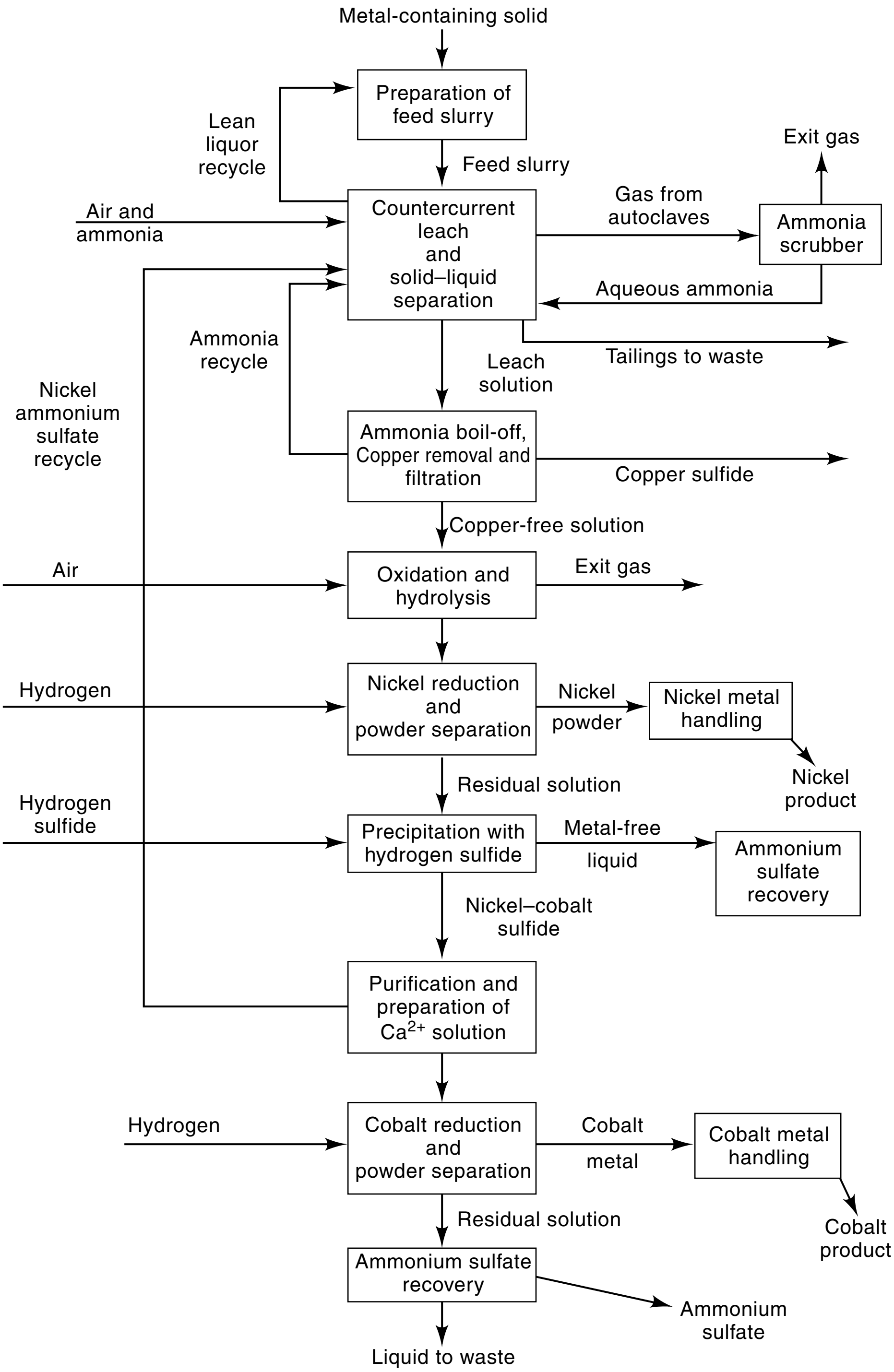

**Fig. 5.** Flow sheet for Sherritt-Gordon process for production of nickel and cobalt metals from sulfide ore.

## 6. Electrometallurgy

The use of electricity for winning and refining metals could not have been developed without an understanding of the basic principles of electrochemistry and the availability of cheap industrial electric power. Electrometallurgy is a more powerful tool than the other extractive processes. It supplies energy to the system in a way that enables a reaction to proceed against its chemical affinity and in the direction of its electrochemical affinity. Chemically reactive metals are more easily recovered by electrometallurgy than by chemical reduction, and can be obtained in high purity. Electrometallurgy, however, has practical limitations. First, is expense. Second, the electrochemical process occurs at an electrolyte–metal interface so that the output of an electrochemical reactor is directly proportional to the area of that interface. Improving the energy efficiency and increasing the electrode area per unit volume of reactor remain a challenge.

The theoretical energy requirement for an electrochemical process is given by

$$nFE = -\Delta G \tag{49}$$

where $E$ is the reversible electromotive force (emf), $\Delta G$ is the Gibbs free energy change, $n$ is the number of electrons involved in the process, and $F$ is Faraday′s constant $= 96,485$ C/eq. For an electrolytic process, $\Delta G$ is positive and $E$ is negative, ie, energy must be supplied to the system. The actual voltage to be applied to the cell, $V$, is larger than the reversible emf because of the irreversibility of the process, namely electrochemical overpotentials, $\eta$, and ohmic losses owing to the resistance of the circuit, $R$:

$$V = -E + \sum_i \eta_i + RI \tag{50}$$

where $I$ is the current. The voltage efficiency, $\varepsilon_V$, is defined as the ratio between the arithmetic value of the emf and the applied voltage:

$$\epsilon_V = \frac{-E}{V} \tag{51}$$

The theoretical amount of metal produced by electrolysis is directly proportional to the amount of electricity according to Faraday’s law. Because of losses by chemical or electrochemical processes, the actual amount is less. It is characterized by the current efficiency, $\varepsilon_I$ defined by the following:

$$\epsilon_I = \frac{nF}{It} \tag{52}$$

where $t$ is the time required to produce one mole of metal. Combining equations 51 and 52 leads to the relationship between $\Delta G$ and the energy actually used, $W$, and the definition of the energy efficiency, $\varepsilon_w$:

$$W = VIt = \frac{\Delta G}{\epsilon_I \epsilon_V} = \frac{\Delta G}{\epsilon_w} \tag{53}$$

Usually the specific energy consumption, $w$, is reported in kWh/kg of product:

$$w = \frac{VnF}{\epsilon_I M} \tag{54}$$

where $M$ is the atomic weight of the metal in kg.

**6.1. Electrowinning from Aqueous Solutions.** Electrowinning is the recovery of a metal by electrochemical reduction of one of its compounds dissolved in a suitable electrolyte. Various types of solutions can be used, but sulfuric acid and sulfate solutions are preferred because these are less corrosive than others and the reagents are fairly cheap. From an electrochemical viewpoint, the high mobility of the hydrogen ion leads to high conductivity and low ohmic losses, and the sulfate ion is electrochemically inert under normal conditions.

The generalized flow sheet of an aqueous electrowinning process consists of at least three main steps. (*1*) The metal is put into solution by leaching of a calcine, ie, a roasted concentrate of sulfide ore, or by direct leaching of low grade ores containing oxidized minerals or weathered sulfides. (*2*) The pregnant solution is purified to remove metallic impurities more noble than the metal to be electrowon, and impurities that could reduce the current efficiency. Sometimes, the pregnant solution is treated by solvent extraction to produce a more concentrated electrolyte. (*3*) The purified solution is fed to the electrolysis tanks where the metal is plated on a cathode and oxygen is evolved at an inert anode, usually made of lead or one of its alloys. The sulfuric acid is regenerated by the anodic process and is recycled to leaching.

*Zinc.* The electrowinning of zinc on a commercial scale started in 1915. Most newer facilities are electrolytic plants. The success of the process results from the ability to handle complex ores and to produce, after purification of the electrolyte, high purity zinc cathodes at an acceptable cost. Over the years, there have been only minor changes in the chemistry of the process to improve zinc recovery and solution purification. Improvements have been made in the areas of process instrumentation and control, automation, and prevention of water pollution.

Zinc sulfide ores are concentrated by flotation, roasted, and then leached in sulfuric acid. The leaching involves at least two stages. In a neutral leach, an excess of calcine maintains a pH of ca 5. Using aeration and sometimes addition of manganese dioxide, iron is removed by precipitation of ferric hydroxide. The solid residue undergoes further dissolution of the zinc in one or several stages of cold or hot acid leach, and the final residue goes to a lead smelter. Improvements have resulted in the precipitation of iron as goethite, FeOOH, or jarosite, $NaFe_3(SO_4)_2(OH)_6$. Impurities such as arsenic, antimony, and germanium coprecipitate with iron. Copper, cadmium, cobalt, and nickel are removed by cementation on zinc powder. A simplified flow sheet of the process is shown in Figure 6.

The standard electrode potential for zinc reduction ($-0.763$ V) is much more cathodic than the potential for hydrogen evolution, and the two reactions proceed simultaneously, thereby reducing the electrochemical yield of zinc. Current efficiencies slightly above 90% are achieved in modern plants by careful purification of the electrolyte to bring the concentration of the most harmful impurities, eg, germanium, arsenic, and antimony, down to ca 0.01 mg/L. Addition of organic

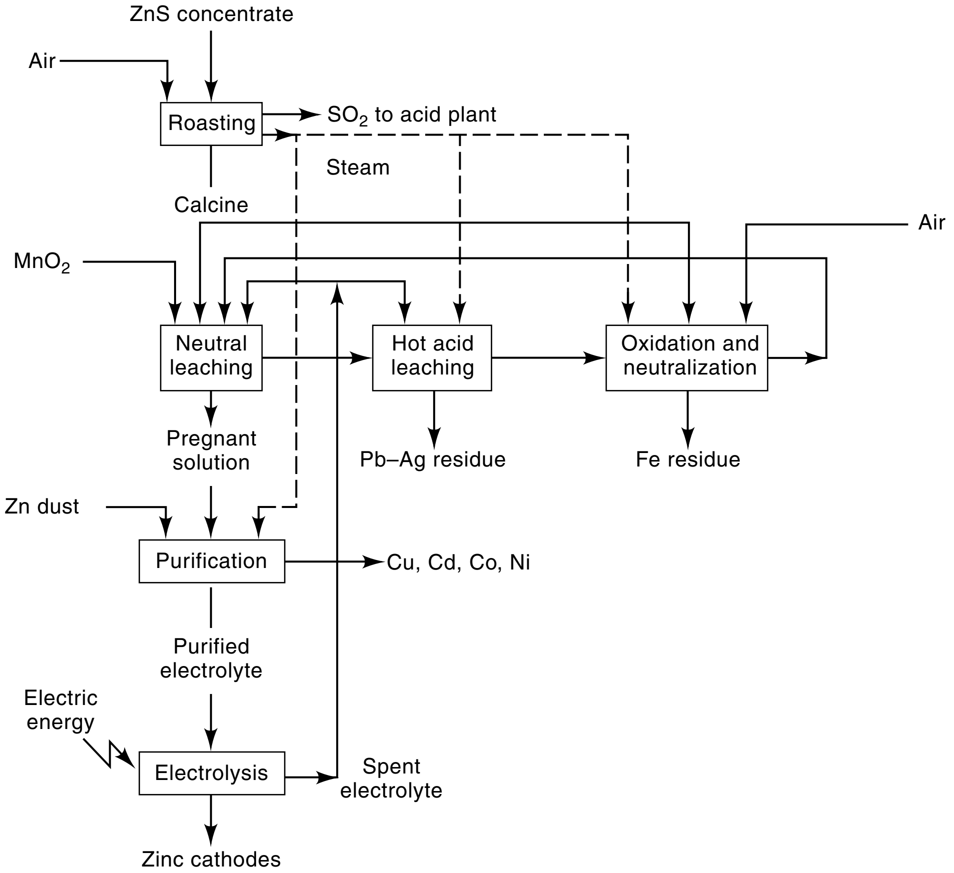

**Fig. 6.** Roast-Leach electrowinning process for the production of zinc metal from a sulfide concentrate.

surfactants (qv) like glue, improves the quality of the deposit and the current efficiency.

The zinc electrolyte contains ca 60 kg/m$^3$ zinc as sulfate and ca 100 kg/m$^3$ free sulfuric acid. It is electrolyzed between electrodes suspended vertically in lead or plastic-lined, eg, poly(vinyl chloride), concrete tanks. The insoluble anodes are made of lead with small amounts of silver. The anodic reaction produces oxygen and regenerates sulfuric acid which is recycled to the acid leach. The cathodes are aluminum sheets, from which the zinc deposits are stripped every 24–48 hours. The effective cathode area varies from about 1.5 m$^2$ in traditional plants to 3.2 m$^2$ for the newer jumbo cathodes. The current density is usually 300–600 A/m$^2$. The electrodes are in parallel in each cell and the cells are connected in series. The average voltage across a cell is ca 3.5 V. The reversible emf calculated for the cell reaction,

$$\mathrm{Zn^{2+}\ (aq) + H_2O\ (l) \longrightarrow Zn^0\ (s) + 1/2\ O_2\ (g) + 2\ H^+\ (aq)} \qquad (55)$$

is ca 2 V; the remaining 1.5 V is accounted for by the anodic overvoltage (about

0.9 V), the cathodic overvoltage, and the ohmic drop in the electrolyte and at the electrode contacts. The voltage efficiency is ca 57% and the energy efficiency is usually slightly above 50%. The energy consumption is 3.3 kWh/kg zinc. The relatively high energy cost of the process is acceptable in view of the special high grade zinc produced (99.995% zinc).

*Copper.* Copper is economically extracted by smelting of a chalcopyrite concentrate. A copper electrowinning process was developed commercially in 1912 for the treatment of lean ores. It is also suitable for treatment of copper oxide or sulfate obtained by roasting of the concentrate. Most electrowon copper comes from the direct leaching of low grade oxidized copper ores. It accounted for approximately one-tenth of the world output of copper-from-ore in 1994 (4). Dilute copper solutions from dump leaching or solution mining are concentrated by solvent extraction to a level suitable for electrolysis. In the United States in 1994, ca 35% of the primary copper was produced by electrowinning. The electrowinning of copper is carried out in sulfate solutions containing 25–35 kg/m$^3$ Cu$^{2+}$ and ca 160 kg/m$^3$ free $H_2SO_4$ at current densities equal to ca 200 A/m$^2$. The anodes are made of lead alloyed with antimony, and copper is deposited on copper starting sheets.

*Other Nonferrous Metals.* Cadmium, and in much smaller quantities thallium and indium, are by-products of zinc and are recovered by electrolysis in sulfate solutions. When associated with copper, cobalt is also electrowon by a similar process. About 10% of the primary nickel output is produced by electrolysis in chloride and sulfate solutions. Some cobalt is electrowon from chloride electrolytes. Metallic chromium and manganese, as distinct from the ferroalloys, are electrowon from ammonium sulfate solutions. These metals are more difficult to electroplate because of the more negative electrode potential and complex chemistry. The required close control of the process variables is achieved by separating the anolyte and catholyte by a diaphragm. Gallium is produced in the liquid state or as an amalgam by electrolysis of a caustic solution.

### 6.2. Electrolysis of Molten Salts.

Metals more active than zinc and manganese cannot be recovered by electrodeposition from aqueous solutions. Most of them, however, can be electrowon from a molten electrolyte. A compound of the metal to be electrodeposited is dissolved in a mixture of salts of more active metals in order to achieve a low melting point, a suitable viscosity and density, and a high conductivity. Solid electrodeposits obtained from molten salts are mostly dendritic or powdery, and are difficult to separate from the melt. Reduction of the metal as a separate liquid phase having a density different from that of the electrolyte is preferable. The recombination of reaction products is the most common cause of faradaic inefficiency. Because recombination is often related to the solubility of the reduced metal in the molten electrolyte, the cells must be designed to protect the reduced metal from contact with the anodic reaction products and with air. The cell electrolyte cannot be recycled through leaching and purification as in aqueous electrowinning, and the feed must be carefully purified and dehydrated.

*Aluminum.* The electrowinning of aluminum, developed in 1886 by Hall in the United States and by Héroult in France, is the single most important electrometallurgical process and remains the only commercial process for the production of aluminum. The purified alumina, obtained by the Bayer process, is dissolved in an electrolyte consisting mainly of cryolite, $AlF_3 \cdot 3NaF$, and other fluorides in smaller amounts, eg, $CaF_2$ and LiF. The electrolysis cells, called pots or furnaces, are made of steel lined with insulating material and carbon bricks that make electrical contact to the molten aluminum cathode. The fused salt electrolyte floats on top of the molten metal and carbon anodes dip into the bath from above, leaving a spacing of ca 5 cm to the cathode. Two types of anodes, prebaked blocks and self-baking Soderberg anodes, are used, but the prebaked anodes are preferred in modern plants.

The electrolytic decomposition of alumina yields oxygen which reacts with the carbon anode for an overall cell reaction:

$$\mathrm{Al_2O_3\ (melt) + 3/2\ C^0\ (s) \longrightarrow 2\ Al^0\ (l) + 3/2\ CO_2\ (g)} \qquad (56)$$

The theoretical value of the reversible electromotive force for this reaction is 1.5 V, but the cell operates under a total voltage from ca 4 to 4.5 V. The difference is accounted for by the overvoltage at the electrodes, including the anode effect, and the ohmic drop through the electrolyte and the electrode contacts. The heat generated by irreversible electrode processes and by ohmic losses keeps the operating temperature of the cell at the desired level of ca 960°C. Current densities range from 6 to 12 $kA/m^2$, and the total current of modern pots is ca 100–300 kA. Alumina is periodically added to the melt to maintain its concentration between 2 and 5%. The current efficiency of modern plants is ca 90%; the main losses are due to the reoxidation of aluminum by carbon dioxide, yielding alumina and carbon monoxide. The energy consumption is ca 14 kWh/kg of aluminum.

The chemistry of the process has not changed significantly since its invention. Improvements in the energy efficiency and operation of modern plants have been achieved mainly by improved cell design and better control of the electrolysis through the use of computers to monitor the pot conditions. The electrolysis of an all-chloride mixture in a cell of a new bipolar design has been tested successfully on a small commercial scale with an energy consumption below that of the Hall-Héroult cell, but problems encountered in the production of the aluminum chloride feed from bauxite have prevented further development as of this writing (see ALUMINUM AND ALUMINUM ALLOYS).

*Magnesium.* The electrowinning of magnesium, another well-established process, accounts for ca 80% of the metal output. The electrolyte is a mixture of chlorides of potassium, sodium, calcium, and magnesium. Because the liquid metal has a lower density than the electrolyte, it floats to the surface. The cells are designed so that the reduced metal does not come into contact with air or with the chlorine gas produced at the anode. The temperature of the cells is kept between 700 and 750°C by external heating. The cell voltage ranges from 5 to 8 V, and the energy consumption is ca 17–22 kWh/h of magnesium (see MAGNESIUM AND MAGNESIUM ALLOYS).

*Other Metals.* All the sodium metal produced comes from electrolysis of sodium chloride melts in Downs cells. The cell consists of a cylindrical steel cathode separated from the graphite anode by a perforated steel diaphragm. Lithium is also produced by electrolysis of the chloride in a process similar to that used for sodium. The other alkali and alkaline-earth metals can be electrowon from molten chlorides, but thermochemical reduction is preferred commercially. The rare earths can also be electrowon but only the mixture known as mischmetal is prepared in tonnage quantity by electrochemical means. In addition, beryllium and boron are produced by electrolysis on a commercial scale in the order of a few hundred t/yr. Processes have been developed for electrowinning titanium, tantalum, and niobium from molten salts. These metals, however, are obtained as a powdery deposit which is not easily separated from the electrolyte so that further purification is required.

**6.3. Electrorefining.** Electrolytic refining is a purification process in which an impure metal anode is dissolved electrochemically in a solution of a salt of the metal to be refined, and then recovered as a pure cathodic deposit. Electrorefining is a more efficient purification process than other chemical methods because of its selectivity. In particular, for metals such as copper, silver, gold, and lead, which exhibit little irreversibility, the operating electrode potential is close to the reversible potential, and a sharp separation can be accomplished, both at the anode where more noble metals do not dissolve and at the cathode where more active metals do not deposit.

Because the same electrochemical reaction proceeds in opposite directions at the anode and the cathode, the overall chemical changes is small change in the activity of the metal at the two electrodes. Therefore, the reversible emf is practically zero. There is some polarization of the electrodes during electrolysis, but the main component of the voltage across the operating cell is the ohmic drop through the electrolyte and at the electrode contacts. Normal cell voltages are ca 0.2 V. The power consumption is correspondingly very small, and electrorefining is much less sensitive to the cost of electric power than other electrometallurgical processes. When a diaphragm is used to separate the anodic and cathodic solutions, the cell voltage increases up to ca 1.2 V, and the power consumption rises accordingly.

*Copper.* The first electrolytic copper refinery was started in 1871, making electrorefining the oldest commercial electrometallurgical process (see COPPER). Most copper is electrorefined. The refining process ensures that the metal meets the specifications of the electrical industry which are stringent because minor quantities of some impurities lower the electrical conductivity of copper markedly. Furthermore, silver and gold, common constituents of copper ores, follow along through all the pyrometallurgical steps. Removal by the electrolytic refining is an important economic asset of the process.

Impure copper is cast in the shape of anodes ~0.9 by 1.0 m and 3.5–4.5-cm thick, weighing 300–400 kg. These anodes are cast with lugs that support them from the walls of the cell or from bus bars and make electrical contact. The starting cathodes used to be pure copper sheets, made by electrodeposition on smooth starting blanks of copper or titanium. The copper starting sheets have been replaced by permanent stainless steel cathodes. The electrode spacing from anode center to anode center is ca 10 cm. The current density is usually 200–250 A/m$^2$. The anodes are consumed and replaced at regular intervals of 20–28 days, and two successive cathodes are produced during the same period. The solution contains ca 45 kg/m$^3$ of copper as copper sulfate and ca 200 kg/m$^3$ of sulfuric acid. The temperature is maintained at 55°C to lower the resistance of the electrolyte which is circulated through the cell. The lead or plastic-lined tanks of wood or concrete used hold ~30 – 35 anodes and one more cathode than anode.

Metals less noble than copper, such as iron, nickel, and lead, dissolve from the anode. The lead precipitates as lead sulfate in the slimes. Other impurities such as arsenic, antimony, and bismuth remain partly as insoluble compounds in the slimes and partly as soluble complexes in the electrolyte. Precious metals, such as gold and silver, remain as metals in the anode slimes. The bulk of the slimes consist of particles of copper falling from the anode, and insoluble sulfides, selenides, or tellurides. These slimes are processed further for the recovery of the various constituents. Metals less noble than copper do not deposit but accumulate in solution. This requires periodic purification of the electrolyte to remove nickel sulfate, arsenic, and other impurities.

*Nickel.* Most nickel is also refined by electrolysis. Both copper and nickel dissolve at the potential required for anodic dissolution. To prevent plating of the dissolved copper at the cathode, a diaphragm cell is used, and the anolyte is circulated through a purification circuit before entering the cathodic compartment (see NICKEL AND NICKEL ALLOYS).

*Other Metals.* Although most cobalt is refined by chemical methods, some is electrorefined. Lead and tin are fire refined, but a better removal of impurities is achieved by electrorefining. Very high purity lead is produced by an electrochemical process using a fluosilicate electrolyte. A sulfate bath is used for purifying tin. Silver is produced mainly by electrorefining in a nitrate electrolyte, and gold is refined by chemical methods or by electrolysis in a chloride bath.

The electrorefining of many metals can be carried out using molten salt electrolytes, but these processes are usually expensive and have found little commercial use in spite of possible technical advantages. The only application on an industrial scale is the electrorefining of aluminum by the three-layer process. The density of the molten salt electrolyte is adjusted so that a pure molten aluminum cathode floats on the electrolyte, which in turn floats on the impure anode consisting of a molten copper–aluminum alloy. The process is used to manufacture high purity aluminum.

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