# **Extractive Metallurgy 3**

# **Processing Operations and Routes**

**Alain Vignes** 







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# **Extractive Metallurgy 3**

Processing Operations and Routes

Alain Vignes





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## <u>Preface</u>

Extractive metallurgy is the art of extracting metals from their ores and refining them.

This book deals with the processes, operations, technologies and processing routes of extractive metallurgy, i.e. the (production) extraction of metals from ores, concentrates (enriched ores), scraps and other sources and their refining to liquid metals before casting or to solid metals.

In many books dealing with metallurgy, the introduction starts by recalling the steps of the progress of metallurgy. These steps, according to and since Lucrèce, are identical to those of human progress: the copper age, the bronze age, the iron age, the silicon age<sup>1</sup>. According to Mohen<sup>2</sup>, the considerable role attributed to the three principal metals in the development of human societies must not be overstressed or overvalued. It is nonetheless true that "metallurgy is the most advanced prehistoric manifestation of the mastery of natural resources" (Mohen). Extracting copper from its ore dates back to the middle of the fifth millennium before our age and extracting iron from its ore dates from the beginning of the second millennium before our age.

The winning (production) of metals and alloys today is still one of the basic industries of the transformation of matter. Metals and alloys still are essential resources for metallic, mechanic, electromagnetic, electric and even electronic industries (silicon is treated as a metal).

This industry is characterized by:

- Production (of primary metal) ranging from 1,345 million tons (Mt) of steel a year to 138,000 tons of titanium, in  $2007\frac{3}{2}$ .

Table 1. World metal production in	า 2007
------------------------------------	--------

Steel	Aluminum	Copper	Zinc	Lead	Nickel	Magnesium	Titanium
1,345	38	15.6	10.6	7.0	1.66	0.79	0.138

- Very high growth rates in the years 1950 to 1973, and again since 2000. The production of steel was 200 million tons in 1950. The production of aluminum increased from 2 million tons in 1950 to 10 million tons in 1973, reaching 38 million tons in 2007. If in developed countries the growth in terms of tonnage has strongly slowed in recent decades, this is due to a smaller consumption of these products owing to the increase in mechanical and physical properties of the materials and parts forged from these materials, thus requiring less material for the same usage. However the annual production of steel in China increased from 182 million tons in 2002 to 489 million tons in 2007<sup>4</sup>.

- Production costs varying by a factor of 20 to 25 between steel and titanium. The three principal costs in metal production are investment, ore and energy consumption. The energy consumption is about 20 GJ/ton of steel, 80 GJ/ton of aluminum and 160 GJ/ton of titanium. Hence the permanent research into improvements of the processes or operations and/or the development of new processes.

- Very high recycling rates. Recycled steel represents 46% of iron sources in worldwide steel production. The "electric furnace processing route" produces 35% of steel. It uses 75% less energy than the integrated route. The recycling rate of aluminum represents 25% of total production and the energy consumption from recycled aluminum represents 5% (energy reflow) of energy consumption from the ore. The production of primary zinc is 7.4 million tons and from

recycled zinc is 2.1 million tons. In the case of lead, the production from recycled lead is greater than 50%.

- Very high quality products with degrees of purity (i.e. contents of harmful impurities) for the finished products, comparable to the purity of materials for electronics and with very narrow concentration ranges of the alloying elements, to obtain physical or mechanical properties with very small dispersions. For metal castings reaching 300 tons, steel grades with carbon content of less than 25 ppm, and sulfur and phosphorus content of less than 20 ppm or even 10 ppm can be guaranteed. The impurities in liquid aluminum after electrolysis and refining are <3 ppm for Li, <1 ppm for Ni and <1/10 ppm for H. The contents of each impurity in copper for electric wire must be <1 ppm. Achieving these chemical performances coupled to research into the lowest energy consumption requires perfect mastery of the process and thus a profound knowledge of its technology.

- The energy consumption and reduction of pollution (rejected  $CO_2$ ,  $SO_2$  and dust) from the production of metals have become major objectives, leading to the development of new processes or product lines.

- Non-ferrous metal ores often have very low contents of many rare or noble metals, whose extraction and recuperation often constitutes essential steps for the global production economy. Such extraction requires very complex processing routes for recovering rare or precious metals.

Often the metal can or could be produced via several processing routes. The industrial processing routes for a given metal are to a large extent dependent on economic considerations, i.e. the cost of raw materials, cost of energy, cost of equipment and market conditions.

The raw materials for the production of metals and alloys are the ores on one hand and recovered and recycled products on the other: - the ores. The ores of Sn, Fe, Mn, Cr, Al, Ni are oxides. The ores of many non-ferrous metals, e.g. Cu, Ni, Pb, Zn, Cd, Mo, are sulfides;

- the recycled metals (Fe, Al, Cu, Zn, Pb);

the steel plant dust containing metals or oxides (Zn, Cd, Pb);

- the residues from leaching operations, e.g. the red muds, a residue containing titanium, vanadium, gallium produced by bauxite leaching during the Bayer process, the gold cyanide sludge;

- the drosses, slags and scoria treated to recover rare metals or to eliminate harmful components.

The operations of mineralogy are known as ore-dressing. In the general case, the ore must be concentrated to free it from minerals of no value, called the gangue, whose main components are oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO, MgO). This is done using physical operations: grinding (comminution) or fragmentation of the ore to small sizes to allow easy separation, then separation by sedimentation and enrichment by flotation, magnetic sorting etc., leading to a raw material enriched in components.

The operations of extractive metallurgy treat ores, concentrates and recycled metals. These are mixtures of oxides or sulfides. The processing routes of the ore's treatment, raw or enriched, together with the technologies used in these routes depend first of all on the ore's nature and its metal content.

Thus iron ore is practically pure iron oxide (hematite or magnetite), with a content of iron of the order of 65% and several percent of silica (SiO<sub>2</sub>). The basic treatment will be the direct reduction of the iron oxide.

Alternatively, the ores can be treated to give an essentially pure chemical compound of the metal and this compound may be converted to give the metal. For example, aluminum's ore (bauxite), is composed of alumina (Al<sub>2</sub>O<sub>3</sub>, 30–60%), iron oxide (Fe<sub>2</sub>O<sub>3</sub>, 1–30%) and silica (1–10%). The first phase of the ore's treatment will be the separation of these oxides to obtain the pure alumina, which will be reduced in a second phase by electrolysis in molten salts.

The copper sulfide ores, whose copper content is very low, exceptionally reaching 5%, undergo processes of mineralogy (flotation) to obtain concentrates containing Cu (20–25%), Fe (30%) and S (30%). The separation of copper sulfide from iron sulfide via a selective roasting constitutes the first step of the treatment. The second step is a copper converting.

Zirconium ore, zircon (silicate of zirconium and hafnium, i.e. ZrSiO<sub>4</sub> and HfSiO<sub>4</sub>), is converted into gas chlorides whose separation is possible before the reduction of zirconium chloride to very pure zirconium.

Extraction and refining operations may be carried out by pyrometallurgical, hydrometallurgical, halide and electrometallurgical processes:

- *pyrometallurgy* involves processes carried out at high temperatures divided into:

- primary pyrometallurgy, which converts the ore or concentrate to impure metal generally in liquid form. The main operations are oxide reduction, sulfide roasting, smelting and converting;

- secondary pyrometallurgy is the treatment of the liquid metal, obtained either directly in the first step or by remelting metallic recycled products. It consists of several refining operations, mainly the removal of harmful elements left in the liquid metal (deoxidation, dehydrogenation, etc.) and addition of the alloying elements;

- hydrometallurgy consists of operations of primary metallurgy performed in aqueous solutions, at relatively low

temperatures and often under high pressure, such as leaching, precipitation and solvent extraction;

- hydroelectrometallurgy consists of salt electrolysis in an aqueous solution, yielding the metal in a solid state. Electrorefining constitutes a refining process of the metal obtained in a first electrolysis;

- *pyroelectrometallurgy* consists of processes employing electrolysis (reduction), either of mattes or oxides (e.g. Al<sub>2</sub>O<sub>3</sub>) or chlorides (e.g. MgCl<sub>2</sub>) into molten salts, yielding the metal in a liquid state;

- *chlorometallurgy* consists of the following processes:

- *chlorination* of a highly reactive metal oxide, such as titanium or zirconium,

- *separation* of the chlorides via physical processes: distillation and extractive distillation,

- *reduction* of chlorides by metallothermic reduction.

The upholding into operation of an existing processing unit, the improvement of an industrial operation, the implementation of a new technology (not formerly used in the unit) and the development of a new process all fall within technical considerations, as well as economic considerations. In this series, economical considerations will not be discussed, for obvious reasons, but sound economic decisions rest on in-depth technical analyses of the processes and operations. Such in-depth analyses are based on process engineering principles. These methods use mathematical models allowing us to simultaneously take into account the elementary processes and their couplings<sup>2</sup>. These mathematical models are sets of fundamentallybased differential equations derived from thermodynamics, kinetics, heat flow, fluid flow, mass transfer and electromagnetic phenomena. Modeling will thus be at the heart of all the analyses here. The solutions to these differential equations, via analytical or numerical methods,

allow us to achieve sound quantitative previsions. Analytical solutions of these equations of partial derivatives have been established in numerous instances, but only for specific cases. They are nonetheless interesting as they reveal the influence of certain factors or parameters on the processes. This leads to very useful dimensionless numbers. These analytical solutions and the dimensionless equations are presented and used in these volumes. For the numerical methods of the solution of equation systems, the reader is referred to specialized publications.

The subject of extractive metallurgy is also addressed in two other publications written by myself and published by ISTE. The first volume, *Basic Thermodynamics and Kinetics* deals with the fundamentals of thermodynamics and kinetics of the extraction processes. The second volume, *Metallurgical Reaction Processes*, deals with the extraction and refining unit processes. This final volume, *Processing Operations and Routes*, deals with the operations and technologies used in industrial production and industrial processing routes, i.e. the combination of steps or operations used to convert the available ore to metal, illustrated by flowsheets.

This book is intended not only for students of metallurgical and mechanical engineering who want to acquire the bases of this technology, decreasingly taught in universities and engineering schools, but also for engineers confronted with a new production problem, either directly (management of a industrial operation or development of a new process) or indirectly (in the definition of a materials' specification).

It is conceived to be accessible to any student or engineer general chemistry and physics training. It only with elementary knowledge necessitates in chemistry. thermodynamics chemical of the and kinetics. One objectives of this book is to allow the easy consultation of books and technical publications dealing with this field.

This book is the result of my chemical engineering training, courses taught in the Écoles des Mines of Nancy and Paris (France), visits to industrial plants, research performed in collaboration with industry, studies and common work as a consultant and as an industrialist in direct contact with numerous producers of metallic parts. I would like to thank, more particularly, engineers from the research centers of Arcelor-Mittal (IRSID), Alcan (ex-Péchiney), Cezus and Eramet for their advice and authorized opinions.

I would most particularly like to thank Professors Jean Philibert and André Pineau. Finally this book is dedicated to Professors Pierre Le Goff and Pierre-Marie Fourt.

> Alain VIGNES February 2011

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<u>3</u> US Geological Survey, *Minerals Commodity Summaries and Minerals Yearbook*, 2007.

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<u>5</u> J. SZEKELY, "The mathematical modeling revolution in extractive metallurgy", *Metallurgical Transactions B*, Vol. 19B, p. 525–540, 1988, and H.Y. SOHN, "The coming-of-age of process engineering in extractive metallurgy", *Metallurgical Transactions B*, Vol. 22B, p. 737–754, 1991.

# **Chapter 1**

# **Physical Extraction Operations**

This chapter presents the unit operations of separation of the components of a mixture. These physical operations do not involve a chemical reaction. Only the bases of these processes are presented.

# **<u>1.1. Solid-solid and solid-</u>** <u>fluid separation</u> <u>operations</u>

## 1.1.1. Flotation

Flotation ("froth flotation") is one of the primary mineral processing operations that is a beneficiation process. Flotation is a sorting (separation) process of chemically different solid particles by using surfactants and wetting agents [FUE 07]. The principle of froth flotation is as follows: after grinding into a fine powder, the solid particles to be separated are mixed with water. A water slurry (called a pulp) is then made. This pulp is treated with reactants (surfactants) that, by being selectively absorbed at the surface of certain particles, make them hydrophobic (having a greater affinity for air than for water).

This pulp of hydrophobic and hydrophilic particles is placed in a flotation cell with impellers (see Figure 1.1.1) and air bubbles are blown through it. Air bubbles attach themselves to the hydrophobic particles and carry them to the surface if the result of the surface tension, mass and buoyancy forces is negative. They are floated out in a stable froth (concentrates) that is skimmed off and discharged of its burden.

**Figure 1.1.1.** *Diagram of a froth flotation cell: showing pulp from the previous flotation cell; and pulp to the next flotation cell* 



Collectors are ions of organic molecules that belong to the family of alkyldithiocarbonates or xanthates and dithiophosphates [RAO 04].

Flotation is one of the processes used for concentrating (beneficiating) complex ores, such as sulfide and carbonate ores of nonferrous metals (lead, copper, zinc, nickel). Sulfide ores can always be concentrated by flotation with good yields. Flotation is the most commonly used technique for separating minerals from their gangue (silicates are wetted by water, sulfides are non-wetted). The ore has to be subjected to a grinding until particles with a size lower than 150  $\mu$ m are obtained. This operation has a major economical importance (units have a treatment capacity of more than 100,000 tons of ore per day).

Flotation also allows the separation of sulfides: in the treatment of zinc-lead sulfide ores, nickel-copper sulfide concentrates and nickel-copper mattes (see <u>Chapter 10</u>, <u>Figure 10.5.2</u>) leading to a concentrate rich in one sulfide and a concentrate rich in the other.

In the refining operations of steel and aluminum, flotation is used to remove from the liquid phase oxide inclusions formed during the deoxidation of steel (see [VIG 11b], <u>Chapter 7</u>, <u>section 7.2.3</u>) or present in [MIR 09]. This operation is performed by injection of argon bubbles that attach themselves to the inclusions.

The removal of sulfur S°, which forms in the leaching of zinc sulfides, is performed by flotation (see [VIG 11b], <u>Chapter 1</u>, section 1.5.2.2).

# **1.1.2.** *Settling under gravity*

Settling under gravity is the natural separation of solids that are suspended in a liquid. Settling can be accelerated by coagulation of the particles with flocculating agents.

# 1.1.3. Centrifugation

The gas-solid separation is carried out in cyclones (see <u>Figure 1.1.2</u>). The solid particles carried along by a gas

flowing at a high rate, due to the centrifugal force, end up on the walls of the cyclone during a downward helical journey and fall to the lower conical part, whereas the gas escapes from the higher part.

For liquid-solid suspensions, the separation by centrifugation is obtained by rotating the suspension.

Figure 1.1.2. Gas-solid separation in a cyclone



## 1.1.4. Filtration

Ordinary filtration is used in hydrometallurgical operations. For aqueous suspensions, the separation of the particles resulting from a precipitation is obtained by filtration, which is carried out by passing the slurry through a natural or synthetic cloth that will not permit passage of solids. The cloth should offer minimal resistance to water flow and act mainly as a support for the deposited solids that form the effective filter bed. The water may be forced through the filter under pressure or drawn through by suction.

The presence of non-metallic inclusions in cast iron, steels and aluminum alloys is very detrimental to product quality. These very fine oxide inclusions (of 1–3  $\mu$ m) are formed when the steel is deoxidized with various deoxididizers, such as aluminum, silicon, etc. They do not separate into the slag phase during these refining operations in spite of their low

density. Filtration of liquid metals prior to casting is used to remove inclusions (see [VIG 11b], <u>Chapter 7</u>, <u>section 7.2.3</u>).

The ceramic (alumina) filters are made either of a bed of spherical particles or of a monolith bearing parallel cylindrical pores with a diameter of about 1 mm. The pore diameter in a deep bed filter can be 100 times as large as the filtered particle diameter. The particles are captured by adsorption on the pore walls throughout the entire depth of the filter. The flow rate of the liquid metal in these pores is thus a significant parameter for the efficiency of these filters. The ceramic (alumina) used allows the filtration of aluminum alloys (see Figure 1.1.3), copper alloys, cast iron (see Figure 1.1.4) and of super-alloys.

Figure 1.1.3. Pechiney deep-bed filter [CLE 95]



**Figure 1.1.4.** *Ceramic filter for cast iron (Daussan Group document)* 



A filter, such as the one presented in Figure 1.1.3, with a height of 1.5 m and a global surface of 2.7 m<sup>2</sup> can treat 25 tons of aluminum per hour. It contains 2.5 tons of liquid metal [BRE 95].

# **1.2. Separation operations** of the components of a fluid phase

# 1.2.1. Condensation

Condensation allows separation of components of a gaseous phase by cooling. Condensation is carried out in zirconium and titanium metallurgy in order to separate the gaseous chlorides obtained by carbochlorination of the ores (see <u>Chapter 10</u>, Figure 10.10.1).

# 1.2.2. Vacuum distillation

In zirconium metallurgy, after the Kroll reduction that produces a pseudo Zr-Mg alloy, vacuum distillation

producing a vaporization of magnesium allows the separation of magnesium and magnesium chloride from titanium or zirconium, leaving a sponge (see <u>Chapter 10</u> Figure 10.10.1).

Lead bullion is refined (see <u>Chapter 10 Figure 10.7.1</u>) using a vacuum distillation operation, to remove zinc whose content reaches  $\approx 0.55\%$ . At 600°C, under a vacuum of 0.05 mbar, the volatilized metallic zinc condenses on the higher part of a tank cooled down by water (see <u>Figure 1.2.1</u>). A mechanical vacuum pump produces a residual pressure of about 0.05 mbar. A temperature of 600°C, a stirring time of five hours reduces the zinc content in lead from 0.50% to 0.05%.

**Figure 1.2.1.** *Lead bullion refining in a batch vacuum dezincing plant. The distance between the evaporating and condensing surfaces is about 30 cm [DAV 00]* 



# 1.2.3. Liquation

After cooling, a two-component liquid phase is separated into two liquid phases. This is liquation. One of the phases is rich in component A and the other is rich in component B when the phase diagram of the A-B binary solution presents a miscibility gap.

Liquation is also an operation in which impurities in a metal are removed by cooling the mixture to just above the melting point of the pure metal. Where the solubility of the impurity decreases and precipitation of this impurity or a compound occurs.

operation is used in zinc metallurgy, in the This pyrometallurgical processing route based on the Imperial smelting process, after zinc condensation by lead to separate lead from zinc (see Chapter 4, Figure 4.4.1 and <u>Chapter 10</u> <u>Figure 10.6.1</u>). The zinc-lead equilibrium diagram (see [VIG 11a], Chapter 3) presents a miscibility gap. By lowering the temperature of the liquid phase down to 430-440°C, two liquid phases form; one of the phases is rich in zinc and contains 0.9% lead and the other is rich in lead and contains 2% zinc. The phase rich in zinc contains some iron and the solubility of iron in zinc significantly decreases when the temperature is reduced from 800°C to 419°C. By cooling, we obtain a liquid very rich in zinc and a solid component: phase  $\zeta$  (whose formula is FeZn<sub>13</sub>). This operation is carried out by keeping zinc in a reverberatory furnace with a sloping hearth for 24 to 48 hours at a temperature of 430-440°C. Lead settles down, as do the FeZn<sub>13</sub> crystals, called "zinc matte". Three products are thus obtained:

- refined zinc with 0.9% lead;
- lead with 5-6% zinc;

- the "matte".

This operation is carried out for many other metals. In the extraction of tin by smelting-reduction, we obtain tin with 2% iron (see [VIG 11b], <u>Chapter 7</u>, <u>section 7.6</u> and <u>Chapter 10</u>, <u>Figure 10.3.1</u> of this volume). Refined tin is obtained by liquation. By cooling down the tin bath, precipitation of FeSn2 compounds occurs. The solid precipitates, having a density close to that of tin, form a dross whose separation from liquid tin is performed by filtration or centrifugation. During this operation, other impurities (Cu, As, Sb) that also form inter-metallic components are also partly removed.

In lead refining, copper is the first impurity to be removed from lead bullion. The "decoppering" is performed by liquation (see [VIG 11b], <u>Chapter 7</u>, section 7.5.1 and

<u>Chapter 10</u>, <u>Figure 10.7.1</u> of this volume). The lead bullion is melted and held just above its melting point. The solid copper precipitates and rises to the surface, forming a dross that is skimmed off.

The recovery of silver and gold from lead bullion, known as "lead desilverizing" involves liquation by the Parkes process (see [VIG 11b], <u>Chapter 7</u>, section 7.5.4 and <u>Chapter 10</u>, <u>section 10.7</u>, <u>Figure 10.7.1</u> of this volume). This is performed by addition of zinc to the (Pb + Ag + Au) solution at 480°C. The phase diagram of the Pb-Zn-Ag system (see <u>Figure 1.2.2</u>) shows that the system is split into two phases, with silver being concentrated in liquid zinc. The temperature of the melt is gradually lowered to below 419.5°C, at which point the zinc (now containing all the silver and gold) begins to solidify as a crust on the surface of the lead and can be skimmed off.

**Figure 1.2.2.** *Lead-zinc-silver ternary phase diagram [WIL 80]* 



# 1.2.4. Distillation

Distillation is a separation operation of the components of a liquid phase whose boiling points are not too close to each other. The simplest equilibrium diagram for two-component system is composed of a liquid-phase region, a gas-phase region and two-phase liquid + gas region. The а temperature-composition curves for each phase in twophase equilibrium are the two curves that separate the single phase from the two-phase region (see Figure 1.2.3). At temperature  $T_2$ , for instance, the liquid phase is richer in component B and the gas phase is richer in component A. The principle of distillation relies upon this fact.

Separation is carried out in a distillation column with trays above each other, along which a temperature gradient is imposed (see Figure 1.2.4). A layer of liquid is held on each tray and bubbles of the gas phase pass through. At each tray, the liquid phase and vapor phase in equilibrium have different compositions. There is then extraction from the liquid phase of one or two of the most volatile components, which are carried out by the gas bubbles and absorbed by the liquid phase of one or two components of the gaseous phase with the highest boiling points [PET 04].

**Figure 1.2.3.** *Liquid-vapor phase diagram of a binary system* 



In this operation, the liquid mixture to be distilled is introduced to the column at an intermediate level. The vapor phase circulates upwards in the column as bubbles through the liquid layer of each tray; it carries away the most volatile component(s). The liquid phase circulates downwards due to gravity and becomes richer in the components whose boiling points are the highest. A fraction of the liquid at the bottom of the column is removed, as residue; another part is vaporized in the boiler. This fraction forms the vapor phase required for distillation. The vapor at the head of the column is condensed; some of the condensates are carried back to the head of the column and form the liquid phase that passes goes down the column.

This operation is carried out in the INCO pressure carbonyl process of nickel production, where nickel is converted into nickel carbonyl, Ni(CO)<sub>4</sub> (see [VIG 11b], <u>Chapter 7</u>, section 7.9 and Figure 7.9.1). Distillation is used to separate nickel carbonyl Ni(CO)<sub>4</sub> (TE: 43°C) from iron carbonyl Fe(CO)<sub>5</sub> (TE: 102.8°C). Ni(CO)<sub>4</sub> is released at the head of the column.

Zinc, obtained by pyrometallurgy, contains always lead, cadmium, (see [VIG 11b], Chapter 7, section 7.7). Zinc refining is performed by "fractional distillation", in a unit consisting of four parallel working columns (see Figure 1.2.5). Each column has between 56 and 58 silicon carbide (SiC) trays with holes that allow vertical counter-current flows of rising vapor and descending molten metal zinc between the trays [HAN 00]. Crude zinc is inserted at 580°C into the middle of the *lead column* where the less volatile elements, such as iron, copper and lead, are removed along with half the zinc at the bottom of the column. This metal feeds a liguation furnace where the Zn-Pb separation is carried out. The zinc thus recovered is reheated to 600°C and feeds a second re-boiling column (not represented in the figure) where zinc vapor with a purity of 99.995% collects at the top of the column. The vapor passing out of the top of the lead column containing about 0.3-0.9% cadmium, is condensed and fed into the *cadmium column*.

After condensation, the vapor passing out of the top of the cadmium column, enriched in cadmium (20% Cd-80% Zn) is fed into a second cadmium column (not represented in the figure), at the top of which cadmium, with a purity of