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Chapter 15

Primary Production and Recycling of Critical Metals

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Metals are important engineering materials, and are produced from nonrenewable natural resources. This chapter starts with the criticality and scarcity issue of metals and metal resources. Then various available extraction and refining technologies and processes are introduced for primary production and recycling of metals. The principles of pyrometallurgy, hydrometallurgy and electro-metallurgy (electrowinning and electro-refining) are described for primary production of metals. The applications of metallurgical technologies to metals recovery from secondary resources (metal scrap and waste residues), i.e. recycling of metals, are discussed. As the last part, the extraction and recycling of cobalt, one of the most critical metals, is given as an example to illustrate how different metallurgical technologies are used and combined to extract a metal from different types of raw materials.

15.1 Introduction

The definition of critical metals or materials is a dynamic process. The list of critical materials depends on the region of end use or consumption and will change with time. Globally there are four countries and regions where critical materials have been defined in recent years: EU, USA, Japan, and China. Table 15.1 lists the critical materials (including metals) defined by different countries and regions. There are big overlaps and also many differences.

As the definitions of critical metals and materials have been discussed in the previous chapters of this monograph, this chapter focuses on the extraction and recycling technologies for "critical metals". Because of the dynamic nature of critical materials selection, this chapter will try to provide a

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Country or region	Critical materials list	Remarks
European Union		
(2010)	REEs, PGM, Ge, Ga, In, Ta, Nb, Co, W, Be, Sb, Mg, graphite.	$EU \ 2010^1$
	fluorspar	
(2014)	REEs (HREEs, LREEs), PGM, Ge,	EU 2014 update ²
	Ga, In, Nb, Co, W, Be, Sb,	
	Mg, Li, Cr, Si, magnesite, borates,	
	coking coal, natural graphite,	
(9017)	fluorspar, phosphate rock	EU 0017 l.+.3
(2017)	REES (LREES, HREES), SC,	EU 2017 update ^o
	T_{2} Nb Hf Co W V Mg Si	
	He barvte borates natural	
	graphite, natural rubber, fluorspar.	
	phosphate rock	
United States (DOE)	Critical: REEs (Dy , Eu , Nd , Tb , Y)	US DOE 2011^4
(2010-2011)	Near Critical: Li, Te, In, Ce, La	
China (2014)	17 REEs , Rare metals: 4 light metals	Recommendations
	(Li, Rb, Cs, Be), 6 PGMs, 15	only. No official
	heavy and refractory metals (W,	list. ⁵
	Mo, Cr, Sn, Sb, Co, Ni, V, Ti,	
	$\mathbf{Zr}, \mathbf{Hf}, \mathbf{Nb}, \mathbf{Ta}, \mathbf{Sr}, \mathbf{Be}$), 8 scare	
	metals (Ga, In, Ge, Se, Te, Re,	
I_{2222} (2008-2000)	31 types of metals (47 elements in	Ceneral coverage
Japan (2008–2009)	total): 17 BEEs , 30 rare metals (Li	of all rare and
	Rb. Cs. Be. Sr. Ba. Ti. V. Zr.	$REEs^6$
	Hf, Nb, Ta, Cr, Mo, W, Re,	
	Mn, Co, Ni, Pt, Pd, B, Ga, In,	
	Tl, Ge, Sb, Bi, Se, Te)	
UNEP (2009)	In, Ge, Ga, Ta, PGM, Sb, Co, Li,	UNEP report,
	REEs	$2009.^{7}$

Table 15.1: List of Critical Metals and Materials Defined by EU, U.S.A., Japan, China.

broader coverage of the metals which have been selected as "critical" or could become "critical" in the future. The description of their primary production and recycling will be based on the similar properties shared by each group of metals.

Although different countries or regions have their own critical materials agenda from a geopolitical perspective, materials "criticality" or "scarcity" is also a global issue. It should be addressed globally, and a more healthy and sustainable solution is required. The ideal solution would be joint efforts which are binding on all the parties in the production and consumption world. Therefore the following actions are strongly recommended:

- (1) Curbed/reduced consumption (austerity): However, this is one of the most difficult actions. People face all kind of attractive new products in modern society, and it is very challenging or difficult to reduce the living standard once people have enjoyed a better life. The austerity measures imposed during or after the financial crisis in 2008–2009 encountered huge problems, e.g. in southern Europe. There is quite often a conflict of interest between material/metal producers and societal needs due to financial benefits/profits.
- (2) Increasing the "recycling" rate: From both the production waste/scrap and from end-of-life (EOL) products. This is the most relevant option, and has been taking place at different levels. However, there is still a large potential to improve. It is both a short-term and a long-term solution. Furthermore, recycling should be promoted all the time for both resource saving, under the conditions that it is technologically and economically feasible, and has less environmental footprint. Recycling is part of the circular economy, and takes place at various steps in the whole life cycle of materials, from material production and product manufacturing, to the end-of-life phase.
- (3) Development of "substitutional" materials: Using a more abundant and less critical material/metal to replace a more critical material or element. In fact, material substitution has been happening all the time in human civilization. However, this normally takes a very long time, and sometimes not all materials can be replaced with another material with the same functionality and performance.
- (4) *Increase resource efficiency of materials*: This should be practiced by both materials producers and product manufacturers.

In practice, a harmonic development among the three pillars of materials/metals supply is highly recommended: primary production, recycling, and substitution, in order to balance the increased demand and consumption with limited and reduced resource availability. Quite often, the primary production of critical metals involves the use of secondary raw materials from the recycled source, and thus this chapter will address both the primary production and recycled production for critical metals.

15.2 Metallurgical Processes for Metals Extraction & Refining

Metals are primarily produced from concentrates, after mining and mineral processing, through various metallurgical processes. Primary metallurgical production is the starting point of the whole life cycle of metals, and together with recycling, it closes the metals cycle from both ends, as is illustrated in Fig. 15.1.

During primary production of metals, also called "Extractive Metallurgy", minerals or compounds of the targeted metals are converted to pure metals or alloys through various chemical reactions, using many different steps. Different technologies are used: pyrometallurgy, hydrometallurgy, quite often in combination with electrowinning or electrorefining. These technologies are also used to separate and refine metals from secondary resources such as scrap or production wastes of various forms.

At present, primary production and secondary production (recycling) have many overlapping issues. Many secondary raw materials or solid residues are processed as part of raw materials in primary smelters. For example, copper scrap of different quality is refined in a copper smelter at the converting or fire refining stages. At a primary zinc smelter, secondary zinc oxide from electric arc furnace (EAF) flue dust or zinc-bearing residues from other industrial processes can be treated together with primary zinc sulfide concentrates during or after roasting. However, for some metals such as aluminum, the metallurgical recycling takes place exclusively at secondary smelters. It does not make sense to melt Al scrap (pure or contaminated) in the primary Al smelter which relies exclusively on molten salt



Fig. 15.1. Primary production (extractive metallurgy) and recycling of metals close the metals cycle.

electrolysis technology. Steel scrap is refined exclusively in primary steelmaking, either in the integrated BOF (basic oxygen furnace) or EAF processes. The latter utilizes 100% steel scrap as the raw material. When the raw material is from secondary sources, such as scrap or production waste, the separation and refining of metals is called "secondary metallurgy" or "recycling metallurgy". However, in steelmaking, "secondary metallurgy" means the refining of steel after BOF or EAF crude steel production.

15.2.1 General introduction of metallurgical processes

Metal extraction takes place either at near room temperature or at very high temperatures. We can divide these metallurgical operations into two different categories: (1) hydrometallurgy (low or near room temperature in aqueous media), and (2) pyrometallurgy (at high temperatures of a few hundred degrees or well above 1000°C), depending on the temperatures and state of the materials involved (feed and products).

In addition, there is the 3^{rd} type of operation, *electrometallurgy*, (we often call it *electrolysis*), in which the metallurgical reactions (deposition of metals) take place under the application of an electric potential difference. *Electrolysis* can take place in aqueous solutions at lower temperatures, but it can also take place in molten salts at higher temperatures, which is normally regarded as part of *pyrometallurgy*. There are two types of electrolysis: (1) "*electrowinning*" for metal deposition from dissociated species (compounds), (2) "*electrorefining*" for converting impure metals to pure metals (this can be applied to aqueous solutions and also to molten salt systems).

Pyrometallurgy is the science and technology of extracting metals from minerals or refining metals at high temperatures. It is a general term for all metallurgical operations at high temperature above a few hundred degrees Celsius. Pyrometallurgy consists mainly of the following 3 steps or unit operations:

- (1) Feed preparation
- (2) Smelting
- (3) Fire-refining or pyro-refining

The products of pyrometallurgical operations include *metals* (crude or refined) and *metal alloys* as the main products, various *metal compounds* as intermediate products (e.g. copper or nickel matte for converting, TiCl₄ for sponge titanium production, or MgCl₂ for molten salt electrolysis of Mg), and *slags* and *off-gases* as wastes or by-products. Off-gases consist

of high temperature gases, smoke and flue-dusts. Off-gases normally go through cleaning processes to recover thermal energy via heat exchangers or waste-heat boilers (as steam, or electricity), de-dusting through wasteheat boilers, cyclones, electrostatic precipitators, and other gas purification units such as acid or basic scrubbers (e.g. Venturi scrubbers). For sulfide smelting–extraction of metals from sulfidic ores–the off-gas is basically SO_2 arising from oxidation of metal sulfides, and is used to produce sulfuric acid (H₂SO₄). Therefore, many pyrometallurgical smelters also include a chemical plant. A good example is ironmaking and steelmaking, and all iron and steel of more than 1.6 billion tons in the world are produced by pyrometallurgical technologies.

Hydrometallurgy is the science and technology for metal extraction through dissolution of metal ions from the minerals, crude metal or metal scrap and precipitation of the metals from the purified and concentrated solutions. Hydrometallurgical processes are conducted mostly in aqueous solutions at lower temperatures below the boiling point of water. Some operations take place at higher temperature in pressurized vessels (autoclaves) or using organic solvents (e.g. solvent extraction).

Hydrometallurgical processes normally consists of the following unit operations:

- (1) Leaching
- (2) Liquid–solid separation
- (3) Solution purification
- (4) Metal precipitation

The hydrometallurgical unit operations also generate some solid residues and waste water or effluent which need proper processing and final disposal. Some of the solid residuals contain valuable metals and compounds, and are often used for further processing to recover the remaining valuable products. Waste water could be easily purified and used internally in the process. Nowadays, hydrometallurgical processes are often operated as a closed system, and if electrowinning is used for metal precipitation, leaching agents are also regenerated during electrolysis. A good example is the hydrometallurgical production of zinc, which accounts for 80% of total zinc production (over 13.5 million tons per year).

Electrometallurgy or electrolysis is quite often the last step in hydrometallurgical or pyrometallurgical processes. For example, zinc electrowinning is the last part of the hydrometallurgical production of zinc; copper electrorefining is the last step of the pyrometallurgical production of copper. Molten salt electrolysis is conducted at high temperatures and can also be viewed as a pyrometallurgical operation; quite often the feed materials (oxides or chlorides) require purification from ore minerals with hydrometallurgical and/or pyrometallurgical processing. For molten salt electrolysis of aluminum, the raw materials of pure aluminum oxide (Al₂O₃) are produced through refining bauxite ore using hydrometallurgical processes (Bayer process). Due to the limited scope, electrometallurgy will not be discussed separately in this chapter.

In industrial practice, different types of metallurgical technologies are used in combination to produce one or more metals from primary ore concentrates or scrap metals and waste residues. Figure 15.2 shows a typical flowsheet from Umicore's multi-metal production (a) and rechargeable battery recycling (b) in Hoboken (Belgium), processing both primary concentrates and secondary raw materials (electronic waste, and spent rechargeable batteries).⁸

15.2.2 Pyrometallurgy

In general pyrometallurgical processes include 3 types of unit operations: (1) feed preparation such as roasting, sintering, (2) smelting such as sulfide smelting of copper concentrates and reduction smelting of iron ore, and (3) fire-refining e.g. copper fire-refining, and steelmaking.

Feed preparation: The following operations are used to upgrade and transform the nature or characteristics of the feed materials so as to make the metals extraction easier and more effective. They normally include *feed drying, feed mixing, granulating and pelletizing, calcinations, roasting and sintering.* The first 3 operations are more physical processes, and last 3 operations are chemical processes.

For certain smelting operations such as flash smelting of copper, the water content in the concentrates (originally $\sim 8\%$) must be very low (<1%, normally 0.1–0.2%) before feeding to the flash furnace. The drying of the concentrates is normally arranged in rotary and flash dryers by burning natural gases or using waste off-gases. Pelletizing and sintering are common pre-steps for reduction smelting. Examples include ironmaking and lead-producing blast furnaces. Grate sintering is the dominant technique. For the bath-type of sulfide smelting, the furnace can take the feed with 6–8% H₂O content, and normally pelletizing is needed. Roasting is the oxidation



Fig. 15.2. (a) Flowsheet of Umicore's multi-metal extraction, refining and recycling plant,⁸ with permission from Elsevier. (b) Flowsheet of Umicore's battery recycling plant,⁸ with permission from Elsevier.

Yongxiang Yang

of metals sulfides to oxides/sulfates, and is needed for hydrometallurgical production of metals from their sulfide concentrates such as zinc, or for reduction of metal oxides from their sulfide minerals (e.g. pyrometallurgical production of zinc). Roasting can take place in fluidized-bed roasters or multi-hearth furnaces, and normally the process is autogenous (energy selfsufficient).

Smelting: In the smelting process, minerals (usually metal sulfides and oxides) are heated beyond their melting point, and are chemically processed to purify them while in the liquid phase. Smelting operations in pyrometallurgical processes include the oxidation and reduction processes in a molten state, to further concentrate or upgrade the metal content or extract as crude metals. The smelting processes include matte smelting of sulfide concentrates, reduction smelting of oxidic ores or oxide materials converted from sulfide ores. Applications of smelting technologies are numerous. A few examples are given below in Table 15.2.

The metals produced through smelting operations normally contain various impurities, and the purity is normally around 99%, and the products are called crude metals (each metal may have its own name: pig iron or hot metal, blister copper, lead bullion etc.). They need to be refined by either pyro-refining (fire-refining) or electrorefining (at low temperatures), or by both such as for copper.

Process examples for smelting	Process characteristics
Matte smelting of copper and nickel	Transforming sulfide concentrates to copper matte or nickel matte or Cu-Ni matte, and molten slag by using oxygen. The matte can be converted to crude metal such as copper
Lead or lead-zinc blast furnace smelting	Producing lead or lead and zinc metals, and molten slag after roasting from their sulfide ores, using coke as reductant
Reductive smelting of tin concentrates	Producing crude tin metal and slag from the oxide concentrates using coke as reductant
Reductive smelting of laterite concentrates	Production of ferronickel using carbonaceous reductant
Blast furnace ironmaking	Reduction of iron oxides to crude iron — called "hot metal" using coke and pulverized coal as reductants
Ferroalloy production by submerged arc furnaces (SAF)	Reduction of iron and another metal from their oxide ores using coke

Table 15.2: Example of Smelting Technologies and their Applications.

Fire-refining, also called pyro-refining: The fire-refining operation is carried out at high temperatures to remove impurities according to the property differences among the metallic elements. Examples are the fire-refining of crude lead to remove Cu, As, Sb, Sn, Au, Ag and Bi; the fire-refining of crude tin to remove Cu, Fe and Pb; the fire-refining of copper to remove O and S, As, Sb and Pb; the ladle-refining of crude steel; the vacuum degassing of liquid steel to remove hydrogen and nitrogen; the vacuum refining of niobium and tantalum; the re-melting and fire-refining of secondary metal scraps such as aluminum and copper. Steelmaking is generally classified as a refining operation. After fire-refining, the metal purity can generally reach from 99% up to 99.999% to meet the market requirements. Sometimes, electrorefining is needed to obtain the required purity. Copper is a typical example where high purity of at least 99.99% is needed, which cannot be provided by fire-refining operation and electrorefining must be used.

Metallurgical furnaces: Pyrometallurgical operations require high temperatures and are carried out at various reactors heated with various fuels or other energy sources. These types of reactors are normally lined with refractory materials and are called metallurgical furnaces, to keep the high temperature environment and to prevent significant heat losses. Table 15.3 below lists the main types of metallurgical furnaces and their typical applications.

Furnace type	Example of applications
Fluidised-bed roaster	roasting of zinc concentrates
Rotary kiln	roasting and drying of concentrates, zinc fuming
Multi-hearth furnace:	roasting of molybdenum concentrates
Reverberatory furnace:	copper smelting, tin smelting
Blast furnace	ironmaking, lead & zinc smelting
Electric arc furnace (EAF)	steelmaking, stainless steelmaking
Submerged arc furnace (SAF)	copper and nickel smelting
Flash smelting furnace	copper and nickel smelting
Bath smelting furnaces	Noranda and Mitsubishi for copper smelting, QSL,
	Kivcet etc. for lead smelting, TSL (Ausmelt or
	Isasmelt) for copper, lead and tin smelting
P-S converter	copper and nickel converting
BOS converter (BOF or LD)	steelmaking (also called LD converter)
Fuming furnace	zinc fuming

Table 15.3: Main Furnace Types and their Typical Applications.

15.2.3 Hydrometallurgy

Hydrometallurgical processes consist of 4 types of unit operations: (1) leaching of minerals and ores or scrap metals, (2) liquid-solid separation, (3) solution purification, and (4) metal precipitation from solutions.

Leaching: Leaching is a dissolution process of minerals in an ore or scrap metals through use of a leaching agent such as an acid or alkaline solution. After leaching, the remaining non-dissolvable gangue materials will be separated from the metal containing ionic solutions. In another word, leaching is also a separation process for the targeted metals from the impurities and the gangue materials. Thus, leaching selectivity is very important for the targeted metals over the gangue minerals or impurities (unwanted species).

Leaching can be operated with various leaching agents: mineral acid (such as H_2SO_4 and HCl), alkaline (such as NaOH and NH₄OH), or salt solutions (such as NH₄Cl and NaCl). The leaching system can be arranged at atmospheric pressure (below the boiling point of water), or in pressurized vessels (autoclaves) to accelerate the leaching process at higher temperatures above the boiling point of water. Sometimes bacteria could also be used to help dissolve certain metals from ores or scrap (bio-leaching).

Liquid-solid separation: During the leaching process, not all minerals will be dissolved into solution, and in fact it is only the targeted metals that are preferred to dissolve. The rest of the minerals will remain as solids, which need to be separated from the leach solution. Liquid-solid separation can be performed with thickeners, vacuum filters, and press filters. The liquid-solid separation process requires that the solid residues have a large particle size and a good crystallization structure.

Solution purification: The objective of the solution purification is to remove the co-dissolved impurities from the leach solution which will otherwise pollute the main metal product or make the precipitation of the targeted metals difficult or less efficient. In addition, the impurities co-dissolved in the solution may be of great market value, and the solution purification will also separate the impurities into a valuable secondary resource for other metals production. The typical solution purification technologies include: crystallization, distillation, precipitation such as hydrolysis, cementation, solvent extraction, ion-exchange, etc.

Metals precipitation: The last step in the hydrometallurgical process is to reduce the metallic ions in the purified solution to elemental form. To do this, one can use "cementation", in which a more electro-negative metal is used or sacrificed as the reducing agent to precipitate the targeted metal from the solution. For large scale production, electrowinning is used where a DC current is passed through the purified solution and the targeted metal will be precipitated on the cathode if the electrode potential is properly controlled. However, only relatively electro-positive metals could be electrodeposited in aqueous solutions. For more electro-negative metals such as aluminum and magnesium, a non-aqueous molten salt electrolyte has to be used. Furthermore, a gaseous reductant can be used to reduce the metal in the solution. For instance hydrogen reduction in aqueous solutions is used to produce metallic powders of copper, nickel and cobalt.

15.2.4 Waste treatment and utilization of secondary resources

During pyro- and hydrometallurgical operations, there are also various byproducts and wastes generated together with the metal production. These by-products and wastes have to be effectively recovered and processed to increase the value of production and to control the environmental pollution.

Off-gas treatment: The off-gases handling is an important part of the pyrometallurgical operation and involves the removal and recycling of the flue dust, the recovery of the thermal energy, and the removal of environmentally hazardous compounds such as SO_x , NO_x etc. From the flue gases other chemical products can be produced e.g. production of H_2SO_4 or liquid SO_2 from sulfide smelting processes. Energy recovery as high pressure steam and thus electricity is not uncommon in pyrometallurgical smelters. Many sulfide smelters are also small power plants, and they often can partly provide the power required to operate the whole smelter. They produce also steam, which can be used for various heating purposes.

The main equipment used in an off-gas treatment system include: cyclones, bag filters, electrostatic precipitators (ESPs) for dust removal, and the total dust removal efficiency can reach $95\% \sim 98\%$. The energy recovery is through various heat exchangers, e.g. hot stove for blast furnace ironmaking, and waste-heat boilers (WHBs) for sulfide smelting. In addition, wet scrubbers (e.g. Venturi scrubbers) are used to remove gaseous compounds such as SOx and fine dust. It is worth noting that the off-gas treatment system often is larger than the smelting furnace, and the total investment of the off-gas handling system accounts for 25% to 50% of the total plant investment. **Treatment of metallurgical slags:** Slag formation plays a critical role in pyrometallurgical metal production. Metallurgists often say that if you can make a good slag, then you will automatically make a good metal. Slags are more often complex silicates (similar to glass in structure) formed from various metal oxides of the gangue materials in the ores together with the added fluxing agents such as silica (SiO₂) and lime (CaO). Ironmaking slags are basically CaO-SiO₂-Al₂O₃-MgO, and slags from non-ferrous smelting are generally SiO₂-CaO-FeO-Al₂O₃. Slags in steelmaking systems contain mainly CaO-SiO₂-FeO. The relative amounts or concentrations of different components depend on the process selection and operating conditions.

The amount of generated slag can be very high in comparison with the produced metal, depending on the main metal grade in the ores. Production of 1 ton of pig iron generates 300–600 kg of slag, and production of 1 ton of steel generates 120–150 kg of slag. However, production of 1 ton of copper will generate 1 to 3 tons of slag; for lead smelting this figure is 1 to 1. On one hand, the slag production rate depends on the metal grade in the concentrates. On the other hand, it also depends on how much fluxing agent such as silica or quartz, lime, dolomite, and fluorspar (CaF₂) is added.

Metallurgical slags have found various applications, but the main application is their use as construction materials. Sometimes, the smelting slag contains relatively high valued metals. In this case, the metal needs to be recovered before the final disposal of the slag, and thus there are slag leaning operations. For instance, copper smelting slags containing higher than 0.5% Cu must be cleaned, and this is carried out in electric furnaces such as in copper flash smelting. Another example is the lead smelting slag, and it normally contains 10% or more zinc which is recovered through slag fuming. In some special cases, the slag is the intermediate product but not a waste, e.g. the production of titanium slag through reduction smelting of titanium-bearing iron ore. The titanium slag is further used to extract titanium dioxide or titanium metal.

Waste water treatment: In hydrometallurgical processes, water is an important diluent for the leaching agents: acid, alkaline, or salt. Water is also used to wash the leach residues and capture the solid particles during gas–solid separation in off-gas treatment. Water is also used in pyrometallurgical processes for cooling the furnace systems in the forms of water jackets or simply water spray. The waste water may contain heavy metals, arsenic or mercury. Various waste-water treatment technologies are

available, and have been successfully applied in waste water purification from metallurgical smelters.

Recovery of minor but valued elements: It is very common during the extraction of non-ferrous metals, particularly for heavy metals (such as copper, lead and nickel), that various precious and rare metals are recovered. Those precious metals come from the concentrates together with the bulk metal, and get enriched during smelting and refining. They are then further recovered after refining operations. These metals include silver (Ag), gold (Au), platinum group metals (PGM), and the scarce metals of selenium (Se), tellurium (Te), indium (In) and germanium (Ge). Many sulfide smelters also treat low-grade gold and silver ores together with bulk metal concentrates. For example, approximately 60% of the silver in the world is produced from lead smelters. In the non-ferrous smelters, the recovery of the precious metals can reach 95% to 99%.

Figure 15.3 shows a modern copper smelter using flash smelting and converting technologies.⁹ As can be seen, flue dust, slags, and hot off-gases are generated, but most of them are internally circulated first and exit the process at a single point. The off-gases from smelting and converting are firstly cleaned at waste heat boilers (WHBs) to remove coarse dust and recover waste heat as high-pressure steam for power generation. The



Fig. 15.3. Illustration of a modern copper smelter with Outokumpu/Outotec Flash smelting and Flash converting technologies,⁹ with permission from TMS.

cleaned SO₂-bearing off-gas is further cooled and cleaned in electrostatic precipitators (ESPs) and after that the cleaned off-gas is sent for H_2SO_4 acid production before discharge to the ambient air. Converter slag with high copper content is circulated back to the smelting furnace for copper recovery, and the smelter slag is cleaned in a slag cleaning furnace before exiting the process.

15.2.5 Current status and future perspective

Pyrometallurgy versus hydrometallurgy: Worldwide, iron and steel are produced exclusively via the pyrometallurgical route, and almost all lead (Pb), tin (Sn), antimony (Sb), titanium (Ti), and the majority of nickel (Ni) are also produced by pyrometallurgical processes. In addition, 85% copper and 20% of zinc are produced by way of pyrometallurgy. On the other hand, various hydrometallurgical processes involve also pyrometallurgical unit operations, such as the roasting of sulfidic zinc and cobalt concentrates for the hydrometallurgical recovery of zinc and cobalt. In the same way, the pyrometallurgical production of various metals such as copper, nickel and lead involves electrorefining as hydrometallurgical or electrometallurgical operation.

Hydrometallurgy is the main technology to produce zinc metal (80%) through leaching and electrowinning process. However, sulfide roasting as unit operation of pyrometallurgy is almost always used to prepare the raw materials (calcine) for the leaching operation, although direct pressure leaching is also available for sulfide zinc concentrates. Hydrometallurgical processes are used to produce gold and silver through leaching, cementation or electrowinning. Hydrometallurgical processes are particularly suitable for recovery of metals from low grade ores and solid wastes and residues. The recovery of copper from low grade copper concentrates or oxidic copper ores occurs mainly through hydrometallurgical processes (15% total copper production). Recently, the full hydrometallurgical production of copper has been practiced by direct pressure leaching of normal sulfide copper concentrates in the Phelps Dodge copper smelter (Bagdad, USA),¹⁰ now part of Freeport-McMoRan.

Main characteristics of pyrometallurgical operations: the following lists some main features of pyrometallurgical processes, both advantages and disadvantages.

• Fast reaction rate at high temperatures, and thus with high productivity and low investment and operating cost.

- Possible utilization of the chemical energy contained in the sulfide concentrates, and thus with relatively low energy consumption.
- Good ability to capture precious metals by matte and heavy metals, and thus with high recovery of valued metals coming from the concentrates.
- Slags as the by-product with relatively stable compositions and properties, and thus with less environmental impact.
- Large volume of high temperature off-gases, requiring expensive treatment before final disposal to the air.
- Relatively poor working environment due to the presence of thermal radiation and emissions, which need to be improved.

Main characteristics of hydrometallurgical operations:

- Efficient technology for the treatment of low grade and complex ores.
- Better utilization of all valuable contents of the ore due to high selectivity over different metal species in the raw materials.
- Better environmental conditions (absence of waste off-gases).
- Lower productivity and larger facilities and higher investment cost in land use.
- Generation of larger amount of waste water and solid residues.
- Higher energy consumption in particular for sulfide concentrates, compared to pyrometallurgical processes.

Perspectives and future developments: The following lists a number of points which show the further needs in process improvement and development.

For pyrometallurgical processes:

- Process intensification through more use of oxygen and oxygen-enriched air: this can significantly reduce the off-gas volume, and reduce the off-gas processing cost.
- Process intensification through more use of fluidization and injection techniques.
- Expanding use of suspension smelting and bath smelting for sulfide smelting processes, for more efficient utilization of the energy content in the sulfide ores.
- Development of more efficient oxygen production techniques and new refractories to serve the needs of the process intensification.
- Development of more advanced reactors and furnaces, and improvement of process automation and process control, as well as working environment.

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For hydrometallurgical processes:

- Increasing the metal recovery and selective extraction, for lower grade and multi-metal complex concentrates.
- Intensification of the leaching rate, in particular more use of pressure leaching as an efficient leaching technology.
- Efficient use of metal separation technologies
- Development of more efficient separation technologies for multi-species and low concentration solutions.
- Innovation in new technologies for more effective extraction of minor metals and scarce metals from EOL products.

The development of new energy-efficient technologies for the electrowinning of metals is needed. New anode materials and new electrolyte systems for low cell voltage deserve more investigation.

15.3 Metallurgical Processes for Metals Recycling

The former discussion in section 18.2 focuses mainly on the introduction of metallurgical processes for the extraction of metals from primary raw materials, i.e. ores or concentrates. For metals recycling, the raw materials are different in nature in comparison with the primary ores. Generally speaking, there are two types of secondary resources for metals recycling: (1) metal scrap, and (2) wastes of residues and sludge or solutions. To convert metallic scrap and waste residues into pure metals or alloys, different processing routes are taken. Comparing metallurgical recycling to primary extraction and refining technologies, there are a lot of similarities and many extraction and refining technologies can be used more or less directly apart from some fine tuning. There are also distinctive differences where different technologies are used particularly for scrap metals. Figure 15.4 illustrates different processing routes to transform metal scrap or the waste of residues back into pure metals or alloys.

15.3.1 Metallurgical recycling of metal scrap

Metal scrap is already in metallic form, and it can take relatively pure form arising from product manufacturing (new and production scrap), or it can be in a very contaminated and complex form from EOL products (old scrap).

New scrap generated from product manufacturing is often specifically collected and re-melted in the plant or sold to the re-melters for production



Fig. 15.4. Overview of processing routes for metals recovery from secondary resources.

of the same type and quality of metals or alloys. This is a common practice for aluminum and copper. Re-melting is a simple physical process of heating – melting – casting operation. What's important is to keep the metals from oxidation loss during re-melting. The main operating cost is the energy which can be electrical or fossil fuels (oil or gas). Since no refining is required, the consumption and operational cost is very low. It has to be kept in mind that recycling of new scrap does not generate new metals, and it is one of the internal material loops or circles, as considered from a circular economy perspective. However, for steelmaking, new and old scrap are both recycled through the primary production of steel via either the integrated steelmaking route (BOF) or mini mills of the EAF route. Heat treatment is always required after steel re-melting or refining, and casting.

Production scrap from within the smelters are normally rejects or offspecs. The quality is not high enough for remelting to produce the end quality of metals. In this case, the scrap is refined at different stages and comes out together with the primary production process. Internal scrap from smelters is normally treated together with old scrap together at a proper refining stage. This is a typical operational strategy for copper smelters. The copper anode rejects due to physical defects or incorrect mass (2-3%), and the undissolved remaining anodes from electrorefining (12-20%) are normally remelted in the anode refining furnace and cast again into fresh anodes for electro-refining.

Scrap from EOL product recycling (old scrap) is contaminated at different levels. It needs refining using different refining technologies: pyrometallurgical, hydrometallurgical, and electrometallurgical methods. During pyrometallurgical refining, the targeted metal for recycling will normally not be oxidized, and only impurity metals or nonmetallic contaminations are removed through e.g. oxidation or salt treatment. For aluminum, the recycling of old scrap is completely organized in separate aluminum recycling plants (aluminum refineries). Normally a refining is conducted at ca. 800° C in a rotary furnace or box furnace by use of molten salt of NaCl + KCl in the presence of a small amount of fluoride such as in cryolite (Na₃AlF₆).

Old scrap of copper is partially recycled and refined within primary copper smelters. Depending on the contamination level of the scrap, it could be smelted during the matte smelting and converting stage such as for electronic scrap. Then the scrap goes through the smelting and two stage refining steps (fire-refining and electro-refining) for a final quality of at least 99.99%. Old copper scrap is also refined to new copper of virgin quality in secondary copper smelters. In the secondary copper smelter, the contaminated old copper scrap first goes through smelting to produce "black copper" (Cu contaminated with iron). Then the black copper (70–90% Cu) is converted to blister copper (96–98% Cu) in a Peirce– Smith (P-S) converter or a Top-Blown Rotary Converter (TBRC) through oxidation and slagging of iron and other impurities. The blister copper is further fire-refined and electro-refined to produce the final quality of electrolytic copper of 99.99%, quite similar to the quality achieved by the operations of the primary smelter. Copper scrap from cables, wires, automotive parts or motors, and electronic waste, are typical EOL scrap and are recycled and refined either in primary smelters or secondary smelters. Good examples in Europe are Umicore, New Boliden, and Aurubis, which are large scale metal producers of copper and precious metals from both primary and secondary copper resources.

If metal scrap is very complex and heavily contaminated, hydrometallurgical recycling or electro-chemical processing could be used. However, during hydrometallurgical recycling, the metals are chemically or electrochemically dissolved or oxidized into solutions (acid or alkaline), and the purification and separation of metal species in the solutions are required. The purified metal-containing solutions (containing metal cations) need to be processed though electrowinning or other precipitation reduction operations such as cementation or hydrogen reduction to produce pure metals. Hydrometallurgically recycling can be flexible and robust, however, it involves re-oxidation and reduction of the targeted metals and from energy consumption perspectives it is not always favorable. If the scrap metal is not heavily contaminated, electrorefining could be used. For example, high quality copper could be electro-refined without converting and fire-refining. Furthermore, anodic dissolution can be used to selectively dissolve the targeted metals (less noble compared to the impurities or precious metals) in the scrap. However, on the cathode no metal is precipitated except for H_2 evolution for more electro-negative metals. Following the solution purification the targeted metals can be produced through electrowinning or cementation, or a metal compound is produced for further reduction. Printed circuit boards (PCBs) from WEEE or e-waste can be treated hydrometallurgically through acid (or alkaline) leaching, in this case an oxidizing agent may be needed e.g. oxygen for acidic dissolution of copper, depending on their relative redox potential compared to H₂. Leached copper using e.g. H_2SO_4 will be purified to remove other impurities e.g. through solvent extraction, and finally copper will be reduced to pure metallic metal through electro-winning, similar to the hydrometallurgical production of copper from low grade primary copper ores.

15.3.2 Metal recovery from wastes of residues

Another type of secondary resource for metal recovery comes from waste residues, sludge and solutions containing metallic elements in the oxidation state in the form of various compounds. They include the following categories:

- (1) Tailings from mining and mineral processing operations.
- (2) Metallurgical slags and residues, as well as flue dust.
- (3) Solid residues from waste processing and energy production such as bottom ashes and fly ashes from municipal solid waste (MSW) incineration and pyro-power plants.
- (4) Waste sludge and residues from chemical and other process industries.

Metal-containing solid waste and residues as well as sludge and solutions are normally smelted together with ore and concentrates in primary smelters for recovery of valuable metals. However, separate processing in secondary smelters is also possible. This will depend on which metals are to be recovered.

Spent lead-acid batteries are smelted mostly in secondary lead smelters e.g. by using lead blast furnaces. Zinc-bearing neutral leach residues and electric arc furnace (EAF) steelmaking dust are normally processed through Waelz kilns or bath fuming to produce higher grade ZnO raw materials, which are then fed into primary zinc smelters for Zn recovery. The modern hydrometallurgical zinc smelters can treat up to 30% secondary zinc raw materials in the form of ZnO.

Furthermore, primary metals smelters recycle their flue-dust and slags within their plant to different processing stages. In primary copper smelters, converter slag contains often high copper (2-15%), and it is normally recycled back to the matte smelting stage. Anode furnace slag will return to the converter. The only slag which is discarded is the matter smelting slag, containing less than 1% copper (normal range: 0.3-0.5% Cu). In comparing the copper grade in the copper ore, which is at 0.5% level nowadays, to the discarded copper slag, it becomes clear that the copper grade of discarded copper slag is comparable to the copper ore. Therefore, the discarded copper slag could become a future copper resource, which is at present limited by the processing cost and economics. The flue dust in smelters contain normally high toxic compounds as volatiles such as arsenic in copper smelters. Internal treatment without removing toxic compounds will cause accumulation of the toxic elements. They are often cleaned externally and returned to primary smelters or treated in secondary smelters for metal recovery. When the economics of doing this is not feasible, they have to be landfilled with fees.

Ironmaking and steelmaking flue dust are internally recycled to certain extent to recover ferrous materials, fluxing agents and/or carbon. However, the internal recycling is limited by the accumulated zinc content of up to 4–5% which causes operational problems in the blast furnace ironmaking system. Therefore, these types of dusts may have to be landfilled at a certain cost. Different technologies have been developed to remove zinc in the dust, however, they are also limited by the economic feasibility of the operation. For instance, rotary hearth technology can be used to remove zinc and the iron oxide is also reduced to crude iron from the steelmaking dust. Nevertheless it has not yet gained wide application due to some remaining technology issues and relatively high investment and operational costs.

15.4 Production of Critical Metals: Example of Cobalt

The critical metals (in a broader perspective) referred to in this chapter cover mainly those from the EU definition plus selections from the US, Japan and China. However, some other metals which fall into the same type or group may also become critical such as Mo, Zr, and Re together with W, V, Hf, Nb and Ta as the refractory metals group, and Se, Te together with Sb, Bi, In, Ge, and Ga as the scarce metal group. REEs both heavy and light are among the most critical metals, as are introduced in a separate chapter of this book, and the same accounts for PGMs. Chromium and silicon are two important metals in the critical metal family, and both of them are mainly produced and used in steelmaking as alloying elements in the form of ferroalloys (FeCr, FeSi). But they are also produced as pure metals of chromium and silicon for special applications such as solar grade and electronic grade silicon for photovoltaic and electronic applications.

A description of the production technologies and processes for all these critical or near critical metals is not possible in a chapter within this book. Instead, cobalt as an example from the critical metal list is used to illustrate briefly how various metallurgical processes and technologies are applied in the production and recycling of typical metals, in particular critical metals.

15.4.1 Primary production of cobalt

Cobalt is a critical metal used in rechargeable battery electrodes, superalloys for gas turbine engines, cemented carbides and diamond tools, and more. Cobalt is mostly produced as a by-product or co-product with nickel (50%) and copper (44%).³ Only less than 6% of Co total primary production is mined as a main product (in Morocco). The Democratic Republic of Congo has the largest reserves of cobalt in the world accounting for 48.5% (3.4 million tons out of 7 million tons), and the second largest reserve comes from Australia with 15% of the world total, according to USGS.¹¹ World mine production reached a record level of 126,000 tons in 2015. Congo (Kinshasa) remained the leading producer of mined cobalt, supplying 50% of world mine production, followed by China (6%), Canada (5.5%), Russia (5%), and Australia (5%).¹¹ In 2015, world production of refined cobalt reached a record level of 97,400 tons according to USGS,¹² contributed mainly by China (50%), Finland (10%), Belgium (6.5%), Australia (5%) and Japan (4%).

Cobalt is mainly extracted from nickel-cobalt and copper-cobalt concentrates and occasionally directly from the ore itself, by hydrometallurgical, pyrometallurgical, and electrometallurgical processes.¹³ Although most methods of extraction are based on hydrometallurgy, cobalt concentrates, mattes, and alloys have been reduced to metal by pyrometallurgical methods. The hydrometallurgical processes involve (1) the leaching of concentrates to generate a cobalt-containing solution, (2) the separation of cobalt from the other metal ions in solution, and (3) the reduction of cobalt ions to cobalt metal. Electrolysis is used in the electrowinning of the metal from leach solutions and in refining the cobalt that has been extracted by hydrometallurgical or pyrometallurgical methods.

Figure 15.5 illustrates the nickel and cobalt extraction from Ni-Co sulfide concentrates at Harjavalta smelters (Norilsk and Boliden), Finland, using well known Outokumpu/Outotec DON process.^{14,15}



Fig. 15.5. DON-process flowsheet for nickel and cobalt production at Harjavalta smelter, Finland, 14 adapted from Grundwell *et al.*

Pyrometallurgical matter smelting is the first step to produce Co-bearing Ni-Cu matte using both flash smelting (having low Fe content) and electric smelting (high Fe content) at Boliden smelter, and both mattes produced at Boliden smelter are treated at Norilsk smelter in the neighborhood by the atmospheric and pressure leaching of nickel and copper. Flash smelting furnace (FSF) matte is dissolved in 4 steps: copper removal with atmospheric Ni-Co leaching, atmospheric and pressure leaching of remaining nickel, and copper pressure leaching. Cobalt is produced by hydrogen reduction as cobalt powder from all leach solutions after the separation of nickel with solvent extraction. After the solvent extraction of cobalt, nickel is produced as a cathode by electrowinning and briquette by hydrogen reduction. The electric furnace (EF) matte is leached in a combined atmospheric-autoclave leach step in the acidic solution coming from the nickel pressure leach step. The leach solution is returned to the atmospheric FSF matte leach step after separation of the iron residue in the form of goethite (FeOOH). The filtered residue containing copper sulfides and PGMs coming from the nickel pressure leach step is fed to the adjacent copper smelter of Boliden for further processing. Alternatively the copper leach residue can be pressure leached followed by PGM separation and copper electrowinning.¹⁵

Figure 15.6 shows the cobalt extraction from Cu-Co sulfide concentrates.¹⁴ The extraction and separation of cobalt involve sulfate roasting, atmospheric H_2SO_4 acid leaching, solvent extraction to separate copper from cobalt, the precipitation of cobalt hydroxide and the re-dissolution of the cobalt hydroxide followed by cobalt electro-winning. Copper extracted to the organic solvent is stripped to aqueous solution for copper production by electro-winning.

15.4.2 Cobalt recycling

Cobalt scrap generated from product manufacturing is well recycled. Major EOL cobalt scrap is also recyclable and recycled. Cobalt used in the main applications of super-alloys, hard metals, batteries and even spent catalysts (80–85% of total cobalt) can be collected and either reused or recycled. However, dissipative use of cobalt as pigment in glass, ceramics and paints are not recycled. There are no reliable global statistics on the recycling rates of cobalt. However, if using the U.S. as a reference or benchmark, the end-of-life recycling rate for the U.S. is about 68%, and the recycled content or recycling input rate (including both new and old scrap) is 32% for the total cobalt production.³ This implies that about 1/3 of cobalt is supplied from the recycled source.



Fig. 15.6. Production of high-purity cobalt from cobalt-copper sulfide concentrate,¹⁴ adapted from Grundwell *et al.*

Cobalt from alloy scrap: Old scrap cobalt from super-alloys and other alloys can be recycled both in primary smelters and in secondary smelters.¹⁶ In the primary nickel sulfide smelter (e.g. Xstrata's Falconbridge in Sudbury), various types of cobalt-bearing scrap are added to different stages of matte smelting or converting. Co and Ni from the scrap alloys will be reported to low or high grade Ni matte, and cobalt will be separated and recovered from nickel refineries. In the secondary smelter, various types of cobalt-based alloy and miscellaneous Ni/Co reverts in different shapes (solid scrap, spills, grindings, turnings, swarfs, sludges, oxides in the form of dust and pellets) can be melted and refined into new alloys. Furthermore, cobalt scrap from Ni-Co alloys is also recycled by using hydrometallurgical techniques, typically at smaller operations, mainly for recovering and separating nickel and cobalt, and/or recovering other valuable metals which would otherwise be lost in a smelter (such as Ta, W, Re).

Cobalt from spent batteries: depending on the type of cobalt-containing battery, various options are available to recycle the cobalt within primary sulfide smelters¹⁶ like Xstrata's Falconbridge smelter, or in dedicated secondary smelters such as Umicore's battery recycling plant in Hoboken. During the high temperature melting, all the base metals are produced as an alloy that could be refined and separated into individual constituents. Lithium or REEs are reported to slag and are not recovered at the present due to economic reasons, however, technologies are available for recovering Li and the REEs when economics are favorable in the future. Furthermore, hydrometallurgical technologies are also available to recover Co and Ni from spent Li-ion battery and Ni-M Hydride batteries, through various leaching and precipitation processes.

Cobalt from spent catalysts: Similar to cobalt-containing alloys and spent batteries, this type of secondary cobalt can be recovered either in primary sulfide nickel smelters¹⁶ like Xstrata's Falconbridge, or in dedicated secondary smelters like Umicore's Hoboken plant. Spent cobalt catalysts can also be regenerated in-situ or externally by burning off the carbon and sulfur deposited on the catalyst during operation and gaining 70–80% of its original capacity. Hydrometallurgical processes are also available for recovery of cobalt and other metals in the spent catalysts through leaching and precipitation as high grade sulfide cobalt concentrates for further cobalt extraction in sulfide smelters.

Cobalt from metallurgical wastes and residues: This is another lowgrade source of secondary cobalt, and can be used for cobalt extraction. This type of cobalt bearing waste includes¹⁶:

- (1) flotation tailings from the mineral processing of cobalt-bearing ores
- (2) slags generated during the smelting of Cu-Co and Ni-Co ores

- (3) nickel refinery sludge residues
- (4) zinc smelter waste streams

Both pyrometallurgical smelting and hydrometallurgical leaching-based technologies are used to recover cobalt and other valuable metals from this type of waste. For detailed technology information, the reader can refer to the review paper by Ferron,¹⁶ or the monograph by Rao for a broader coverage of metals recovery from metallurgical wastes and scrap.¹⁷

15.5 Concluding Remarks

Metals are produced both from primary resources after mining and from various secondary resources (urban mining). A large number of technologies are available for the extraction and refining of metals from both types of metal resources (concentrates, scrap and residues): pyrometallurgy, hydrometallurgy, and electrolysis (electrowinning and electro-refining). These metallurgical technologies are quite often used in combination to produce refined metals by using their best merits.

For metals production from recycled sources, a distinction is made between metal scrap (in metallic form) and process residues (metal in different forms of compounds). Metal scrap is better directly re-melted to new metal if it is relatively pure and clean (production or manufacturing scrap), or melted and refined to pure metal or alloys without unnecessary oxidation and reduction. For very complex scrap, hydrometallurgical extraction and separation are also used to produce pure metals. EOL metal scrap can be refined both in primary smelters (such as steel, copper, nickel and cobalt) at different process steps, but can also be refined in standalone secondary smelters (such as copper and aluminum). For process residues, both pyrometallurgical and hydrometallurgical technologies are used, very similar to those used in primary production. Quite often the residues are processed in primary smelters together with concentrates.

Critical metals are normally produced as by-products or co-products of the bulk or big metals. Their use is generally in trace amounts and at low concentrations. Therefore, EOL recycling of critical metals is much more challenging than recycling the big metals. More efficient and cost effective extraction and refining technologies are needed in the future.

The extraction and recycling of cobalt, one of the most critical metals, is discussed as an example to illustrate how different metallurgical technologies are used together to extract a metal from many different types of raw materials.

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