



People's Democratic Republic of Algeria  
Ministry of Higher Education and Scientific Research

Mohamed Khider University – Biskra  
Faculty of Science and Technology  
Department: Mechanical Engineering  
Specialization: Metallurgy

# Extractive metallurgy

2<sup>nd</sup> Year ST Students

Dr. Abdelhakim Begar

## **Preface**

This course on extractive metallurgy is intended for second-year students in the common core of Science and Technology (ST), specializing in metallurgy. It is designed in accordance with the common core curriculum for the 4th semester of ST.

By the end of this course, students will be able to describe the main industrial processes for the production of metals, as well as the unit operations involved in pyrometallurgy and hydrometallurgy. Particular attention is given to the thermodynamic aspects of pyrometallurgical transformations, especially those involving solid particles.

This course material aims to provide an in-depth understanding of the fundamental principles of extractive metallurgy and their application to modern industrial processes. It is based on essential theoretical concepts and illustrates their practical implementation through concrete examples. The objective is to help students develop the necessary skills to analyze and optimize metallurgical processes for industrial applications.

**Contents:**

**Introduction**

**Chapter I: Industrial Processes for the Production of Metals and Alloys**

- 1- Production of steel
- 2- Production of aluminum
- 3- Production of nickel
- 4- Production of copper
- 5- Production of zinc
- 6- Production of titanium and zirconium

**Chapter II: Unit Operations**

- 1- Operations for solid/solid and solid/liquid separation
- 2- Operations for separation of a fluid phase
- 3- Chemical unit operations and reactors in pyrometallurgy
- 4- Chemical unit operations and reactors in hydrometallurgy

**Chapter III: Thermodynamics of Pyrometallurgical Transformations:**

**Transformations of Solid Particles**

- 1- Thermodynamic data on oxide formation reactions
- 2- Reduction of oxides
- 3- Roasting of sulfides
- 4- Chlorination of oxides

## **Introduction**

Metals such as aluminum, copper, iron, silver, gold, chromium, lead, and zinc are essential for manufacturing hundreds of products used by humanity for centuries. Their production involves mining, ore processing, and extraction through hydro- and/or pyrometallurgical processes.

The operations involved in processing metals from their ores, as well as the production and treatment of alloys, are collectively referred to worldwide as "extractive metallurgy". This field encompasses all processes aimed at extracting valuable metals from raw ores or composite materials and producing materials with specific characteristics. Whether in Francophone or Anglophone countries, extractive metallurgy includes all stages from ore extraction to obtaining purified metal ready for various industrial applications.

Extractive metallurgy is divided into two main branches: pyrometallurgy and hydrometallurgy.

Pyrometallurgy encompasses processes for preparing metals and metallic alloys that require high-temperature transformations. Steelmaking, which has been central to industrial development and remains critical with 93% of metals produced today being steels, exemplifies pyrometallurgical industry. Temperatures during the production of molten alloys can reach around 1600°C, necessitating precise procedures for steelmaking enterprises. Beyond iron, metals such as lead, zinc, silicon, nickel, titanium, gold, copper, and aluminum (extracted via high-temperature electrolysis) are also treated through pyrometallurgy. For instance, aluminum is produced by electrolysis in cells operating at approximately 950°C, while copper is often extracted through smelting at temperatures exceeding 1000°C.

Hydrometallurgy involves chemical processes characterized by the dissolution of a metal and its extraction from solution. Key stages include:

Lixiviation: Dissolving metals from ores using acidic or alkaline solutions,

Purification: Removing impurities from the solution,

Production of the desired metal: Recovering and precipitating purified metal.

Purifying the solution may not always be necessary if the concentrate contains minimal soluble impurities. Often, refining of the produced metal is required to achieve the desired purity. For example, gold extraction via hydrometallurgy often involves cyanide leaching followed by electrolytic or chemical precipitation.

In Algeria, the extractive metallurgy sector plays a crucial role in the national economy. The country boasts significant reserves of iron, zinc, lead, and other precious minerals like

gold and phosphate. Developing these resources, alongside investments in modern pyrometallurgical and hydrometallurgical technologies, positions Algeria as a key player in the global metallurgical industry. Major projects, such as the Gara Djebilet iron ore deposit in the southwest, illustrate Algeria's ambitions. Once fully operational, this project is expected to produce several million tons of iron ore annually, supplying local and international steel industries. Economic diversification initiatives aim to further strengthen this strategic sector, fostering sustainable growth and job creation in the country. Developing new mining and metallurgical infrastructure, along with training specialized workforce, are critical to maximizing the economic potential of these resources.

# **Chapter I: Industrial Processes for Metal and Alloy Production**

## **Introduction**

Minerals are natural substances containing various metals, either in native form or as chemical compounds such as sulfides, oxides, or carbonates. In most cases, direct use of minerals is impractical, as valuable metals must be extracted using specialized processes in a treatment plant. This extraction is crucial for diverse industries, ranging from construction to electronics manufacturing.

Extractive metallurgy involves transforming these minerals to extract essential metals. The two primary operations in extractive metallurgy are smelting to separate useful ore components and reducing components to obtain sought-after metals. These processes require advanced technologies and a deep understanding of the chemical and thermodynamic reactions involved, ensuring efficient and sustainable production of metals and alloys.

In 2023, global metal production continued to grow, reaching approximately 190 million tonnes. Here's an overview of detailed production for some key metals:

Steel: Approximately 90 million tonnes

Aluminium: Approximately 70 million tonnes

Copper: Approximately 24 million tonnes

Zinc: Approximately 6 million tonnes

This diverse production meets the varied needs of industrial sectors, including construction, automotive, aerospace, electronics, and more.

## **I-1- Steel Production**

### **I-1-1- Iron Ores**

Iron, an essential element for the global economy, ranks as the fourth most abundant constituent in the Earth's crust, comprising approximately 5% of its total mass. With a hardness ranging from 4 to 5 on the Mohs scale, iron is prized for its malleability and high thermal conductivity, making it indispensable in various industrial applications, including construction, automotive, and steel production.

Iron ores, the primary source for extracting the metal, are diverse but primarily focus on a few key types. Hematite ( $\text{Fe}_2\text{O}_3$ ), found in both red and brown varieties, and magnetite ( $\text{Fe}_3\text{O}_4$ ) are the most extensively mined globally. Hematite, abundant in Australia, Brazil, and Algeria, is known for its high iron content, reaching up to 70%. Magnetite, also found in Sweden, Russia, and Algeria, though less abundant, is valued for its purity, with iron concentrations reaching up to 72%. Other ores such as goethite ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and siderite ( $\text{FeCO}_3$ ) are also utilized, albeit typically with lower iron content.

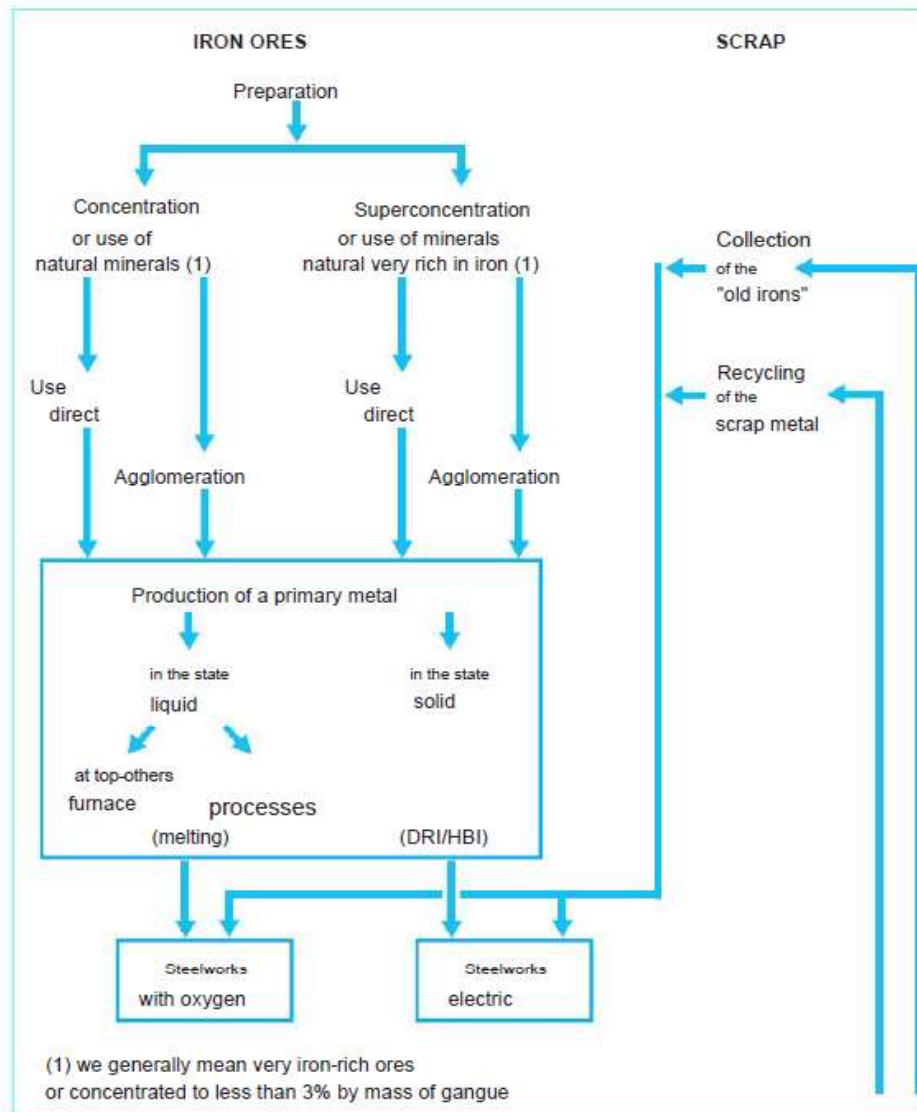
In Algeria, iron production is a significant component of the mining industry. The country possesses substantial iron ore reserves, primarily located in the regions of Tindouf and Tebessa. Exploitation of these deposits contributes to Algeria's domestic iron production, although the local steel industry is still developing compared to major global producers.

The quality of iron ore is crucial in determining its use in the steel industry. High-grade ores, typically containing between 60% and 70% iron, are preferred as they reduce production costs and improve metallurgical process efficiency. Conversely, low-grade ores require more advanced technologies and complex processes to extract pure iron.

The evolution of the steel industry over recent centuries reflects a transition from traditional methods to more advanced technologies. In the 19th century, Martin furnaces allowed for flexible but often inefficient use of iron and scrap metal combinations. The advent of oxygen converters in the 1950s revolutionized steel production, enhancing final product quality and process efficiency. Concurrently, the growing adoption of electric furnaces in "mini-mills" facilitated increased use of recycled scrap metal as a primary raw material.

Figure I-1-1 graphically illustrates significant differences between steelmaking based on iron ores versus those predominantly using scrap metal. While the former depends on ores extracted from natural deposits, requiring complex mining and processing operations, the latter focuses on recyclability of metal waste to produce new materials. This divergence has

reshaped the global steel industry structure and influenced economic and environmental dynamics associated with steel production.



**Figure I-1-1- Detail of the production or collection of primary metals**

Iron ores continue to be essential for the global steel industry, requiring sustainable management of natural resources and adaptation to technological advances. The future of steel production may increasingly involve alternative iron sources like recycled metal waste, aiming to meet economic, environmental, and social needs.

The overall steel production chain consists of four processes (Figure I-1-2):

- Agglomeration
- Coking
- Blast furnace

- Converter

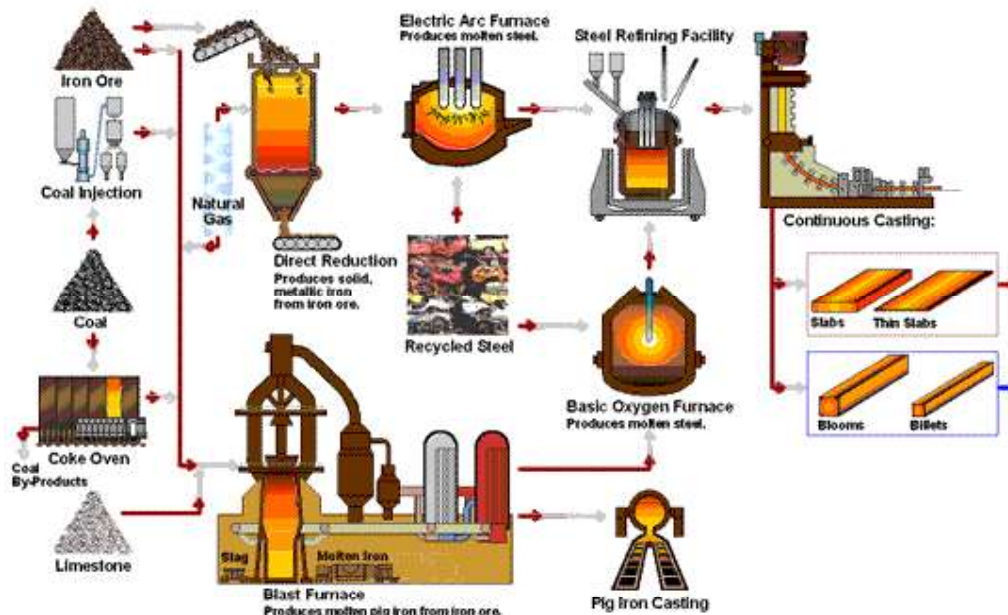


Figure I-1-2- Iron and steel manufacturing scheme l'acier

These processes form the backbone of steel production, each playing a crucial role in transforming raw materials into finished steel products.

### I-1-2 -1- Agglomeration

#### I-1-2 -1 -1- Presentation

Before being directly introduced into the blast furnace, iron ore is first transformed into a more suitable agglomerate of appropriate size. The agglomeration process plays a crucial role in enhancing the handling characteristics of the ore and preparing a more homogeneous charge for the blast furnace. This step not only reduces the energy consumption required for ore reduction but also optimizes the quality and quantity of the molten iron produced.

An agglomeration unit typically includes several stages, such as crushing, screening, the actual agglomeration process (via sintering or pelletization), and sometimes additional treatments like drying or beneficiation. Each stage aims to improve the chemical, mineralogical, and physical nature of the ore, making it more reactive and efficient when it enters the blast furnace.

Figure I-1-3, depicting these installations, details the equipment used in the agglomeration process, such as crushers, mills, pelletizing drums, and material transport



<b>Precipitation in the vitreous slag</b>	1150
<b>Formation of silicates and calcium ferrites</b>	
<b>Reoxidation of magnetite</b>	500
<b>Formation of microcracks in the vitreous phase</b>	

### **I-1-2 -2- The coking**

The coking plant plays a crucial role in the process of converting natural coal into coke, a vital carbonaceous material used in blast furnaces. This complex process offers several significant advantages for the steel industry:

**Reduction of volatile minerals:** Coking reduces the percentage of volatile minerals present in natural coal, improving the purity and quality of the produced coke.

**Agglomeration of coal grains:** During the process, coal grains are fused together to form a solid and cohesive mass of coke. This facilitates handling and use in blast furnaces.

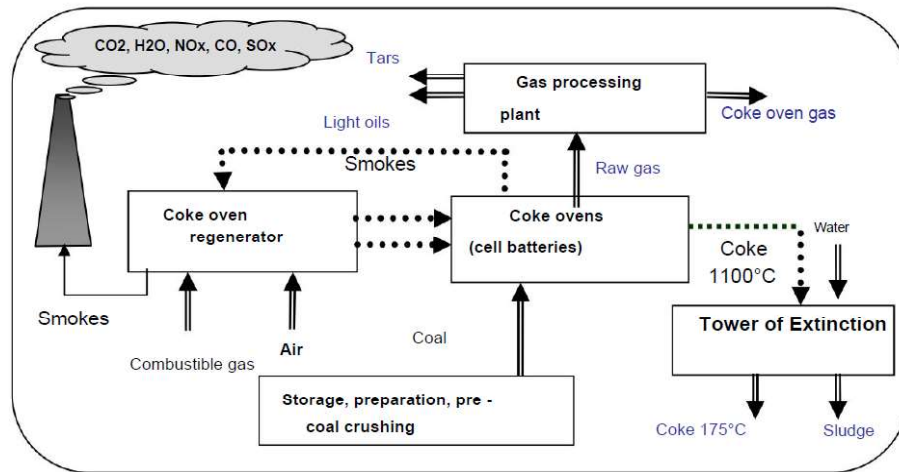
**Adapted particle size:** The coke produced by the coking plant has a specific particle size that makes it ideal for use in blast furnaces. This uniform size ensures efficient combustion and even heat distribution during the smelting of iron ore.

**Recovery of hydrocarbons:** During coking, hydrocarbons contained in coal are released as gases and tars. These by-products can be recovered and used as energy sources or raw materials for other chemical processes.

Coking itself is a controlled process where coal is heated to high temperatures, typically between 900°C and 1200°C, in the absence of oxygen to prevent combustion. This process, known as pyrolysis, transforms coal into coke while releasing volatile components as gases. To stabilize the coke and prevent it from igniting, it is rapidly cooled by immersion in water.

The typical coking plant, schematically represented in Figure I-1-4, consists of several essential sections, including coking ovens, gas and tar recovery systems, and processing facilities to purify and condition the produced coke.

The coking plant is not only crucial for producing high-quality coke needed in the steel industry but also contributes to the recovery of valuable energy and raw materials, making it an essential step in the steelmaking process from iron ore.

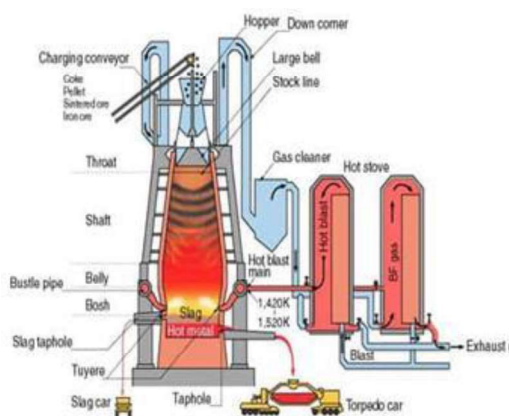


**Figure I-1-4- Diagram of a coking plant**

### **I-1-2 -3- The Blast Furnace**

#### **I-1-2 -3- 1- Introduction**

The blast furnace is an essential industrial installation for the production of pig iron, a crucial material in steel manufacturing. It is a counter-current thermal reactor where solid raw materials (coke, iron ore, and fluxes) are introduced from the top, while hot reducing gases ascend from the base. These reactors can reach impressive heights, sometimes up to 90 meters, and diameters of 1 to 14 meters at the hearth. Daily production can range from a few hundred to 9000 tons of pig iron. Figure I-1-5 provides a detailed view of a blast furnace in operation, highlighting the complexity of its components and the precise interaction between each section to achieve optimal performance.



**Figure I-1-5- overall diagram and a photograph of a blast furnace**

### I-1-2 -3- 2- Description of the Blast Furnace

The blast furnace is designed to optimize thermal and chemical exchanges between the descending solid materials and the ascending hot gases. Its structure is divided into several distinct zones, each playing a crucial role in the reduction and melting of ores.

#### Main zones of the blast furnace:

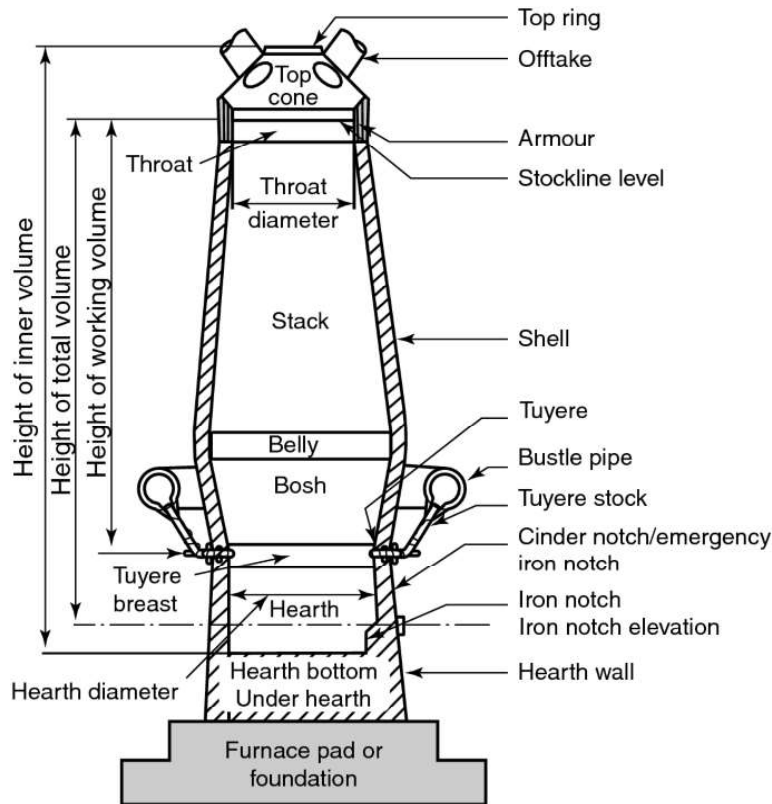


Figure I-1-6 : vertical section of a blast furnace

- **The throat:** Located at the top of the blast furnace, it serves as the entry point for solid materials and the exit for combustion gases. A distribution device evenly spreads the charges, ensuring optimal operation.

- **The stack:** This conical section, widened towards the bottom, promotes the gravitational flow of solid materials and initiates the pre-reduction of iron oxides by the ascending reducing gases. The geometric shape of the stack contributes to better charge distribution and efficient initial reduction.

- **The belly:** The part where the furnace reaches its maximum width. Here, the pre-reduced charge in the stack completes its reduction to metallic iron. The melting zone also begins in this section, where temperatures are high enough for iron to melt.

- **The bosh:** A region shaped like an inverted truncated cone, where incompletely reduced ore enters the melting phase. This shape improves the regulation of the charge descent and facilitates the distribution of gas to the upper part of the furnace.

- **The hearth:** Located at the base, the hearth is a cylindrical container lined with refractories where the liquid products (pig iron and slag) accumulate. The pig iron and slag are extracted from the bottom, with the pig iron then separated by decantation to be refined and enriched with carbon.

The raw materials are introduced in alternating layers of coke, iron ore, and fluxes; this distribution is crucial for ensuring the proper operation of the blast furnace.

### I-1-2 -3- 3- Physico-chemical Description of the Blast Furnace

The operation of the blast furnace relies on complex physico-chemical processes that occur under varying temperature and pressure conditions across different zones of the reactor.

#### Details of chemical reactions:

- **Drying zone:**

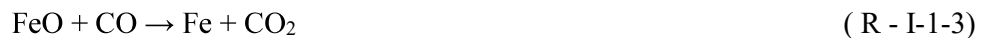
- At temperatures below 320°C, hematite (Fe<sub>2</sub>O<sub>3</sub>) is reduced to magnetite (Fe<sub>3</sub>O<sub>4</sub>) by carbon monoxide (CO):



- Between 320°C and 620°C, magnetite is reduced to ferrous iron (FeO):



- At temperatures between 950°C and 1100°C, FeO is then reduced to metallic iron (Fe):



- **Intermediate zone:**

- The reduction of iron oxides continues, primarily due to reactions with CO and hydrogen (H<sub>2</sub>), which form from the decomposition of coke:



- Increasing temperatures in this zone favor the Boudouard reaction:



- This reaction is crucial as it regenerates carbon monoxide, essential for subsequent reduction reactions.

- **Melting zone:**

Temperatures reach levels where impurities and fluxes form slag by melting. Simultaneously, iron and unreduced FeO also liquefy. Carburization reactions also begin to occur:



- **Active zone:**

- In this zone, the final reduction of FeO occurs, and the molten iron further carburizes. The carburization reaction transforms the molten iron into pig iron:



- The molten pig iron gradually enriches with carbon until the desired saturation.

- **At the tuyeres:**

- Coke burns in the presence of oxygen to produce CO, through the following reactions:



- The CO<sub>2</sub> formed reacts with carbon to generate more CO via the Boudouard reaction, maintaining the necessary reducing atmosphere in the blast furnace:



- **Hearth:**

In the hearth, the pig iron and slag separate by decantation. The pig iron is refined, purifying itself from impurities and enriching with carbon. Decantation allows for high-quality pig iron, ready for subsequent processing or casting.

## **Conclusion**

The blast furnace is a crucial device in the steel industry, enabling the efficient transformation of raw materials into essential metallurgical products like pig iron and steel. Continuous technological advancements aim to improve its energy efficiency, reduce emissions, and address environmental challenges. Despite these challenges, the blast furnace remains a cornerstone of global metal production, significantly contributing to various industries.

#### I-1-2-4 - The Converter

This process transforms molten iron into steel. The converter is an industrial reactor composed of a steel shell lined internally with refractory bricks. It operates discontinuously with stages of loading, refining, and pouring of slag and metal.

##### Conversion Process

The molten iron from the blast furnace undergoes a "conversion" operation achieved by oxidizing the dissolved elements (C, Si, Mn, Ti, P, and S) in the liquid or solid iron to reduce their content. In modern converters, pure oxygen is blown from the top through a lance placed above the metal bath. For efficient mixing of the metal bath, an inert gas (nitrogen or argon) is injected from the base of the converter. Figure I-1-7 illustrates a converter with oxygen blowing from the top.

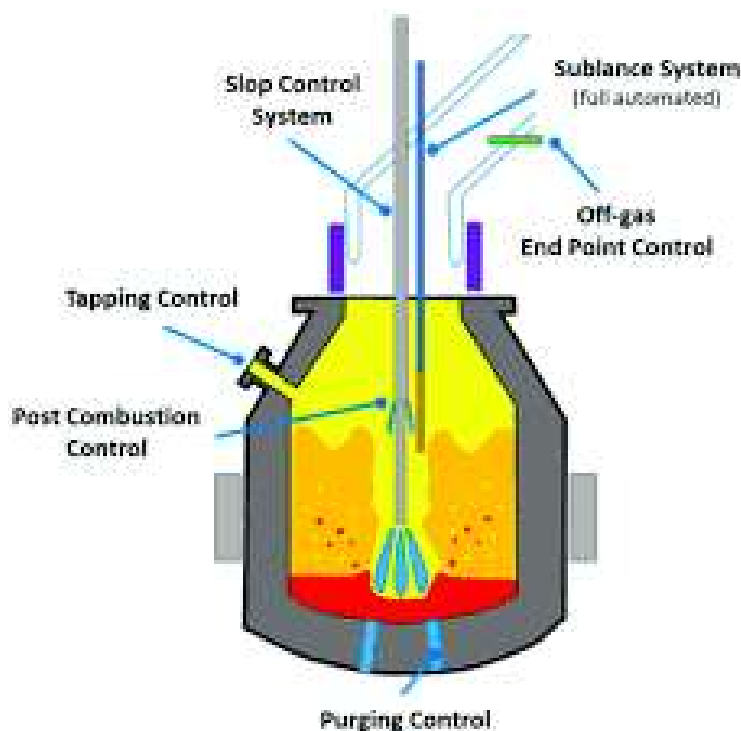


Figure I-1-7 : diagram of an oxygen converter

The heat generated by the refining reactions compensates for thermal losses, heats, and melts all necessary additions for metallurgical operations, and raises the metal's temperature above its initial temperature. The raw materials introduced into the converter are noted by Béranger (1994):

- **Molten Iron:** It arrives at the converter at an approximate temperature of 1370°C.

Additions containing iron (ores and scrap, solid iron...): Generally introduced at ambient temperature to adjust the thermal balance and achieve the desired steel temperature.

- **Additions to form slag and adjust its composition:** Consisting of lime and calcined dolomite (CaO - MgO). Lime facilitates the transfer of silicon and phosphorus from the steel to the slag and controls the basicity of the mixture by reacting with silica. Dolomite saturates the slag with magnesia to limit refractory wear. The slag mainly comprises lime, silica, and iron oxides.

- **Oxygen:** Injected through a multi-hole lance. The dissolution of oxygen in the liquid steel during blowing requires precise calculation of the amount to inject, based on the composition of the liquid steel and the oxidation priorities of the present elements.

- **Nitrogen Injection:** Promotes the mixing of the metal bath. Part of this inert gas dissolves in the liquid bath, and the rest is found in the converter gas.

### **Critical Phases of the Conversion Process**

**1. Preparation and Loading:** Molten iron is poured into the converter. The exact quantities of molten iron, scrap, and additives are carefully measured to optimize the process. Precision in dosing the raw materials is essential to achieve the correct chemical composition of the final steel.

**2. Oxygen Blowing:** Oxygen is blown through a multi-hole lance to oxidize undesirable elements. This step generates a large amount of heat, necessary to maintain the metal bath temperature and melt additional materials. The duration and intensity of the blowing are controlled by automated systems to maximize oxidation efficiency.

**3. Slag Formation:** Additives like lime and dolomite react with the impurities in the steel to form slag. The slag, which floats on the metal bath surface, can be easily removed. It plays a crucial role in purifying the steel, capturing elements like sulfur and phosphorus, and ensuring high-quality steel.

**4. Metal Bath Mixing:** Injection of nitrogen or argon from the base of the converter ensures homogeneous mixing of the bath, promoting uniform distribution of temperature

and chemical elements. This also helps remove dissolved undesirable gases. This step is crucial to avoid gas pockets and ensure the homogeneous quality of the steel.

**5. Control and Adjustment:** Metal samples are regularly taken for chemical analysis. Based on the results, adjustments can be made by adding more materials or modifying the blowing conditions. Precision in this step is essential to ensure the final steel meets the required specifications for its applications.

**6. Metal Pouring:** Once the steel reaches the desired chemical composition and temperature, it is poured into molds to form ingots or sent directly to a continuous casting machine to produce raw forms like slabs, billets, or blooms. Continuous casting is often preferred for its efficiency and ability to produce long forms without interruption.

**7. By-Product Management:** Slag and converter gases are important by-products. Slag can be processed to recover residual metals or used in construction. Converter gases, mainly containing carbon monoxide and nitrogen, can be captured and used as fuel in other parts of the plant. Efficient by-product management is essential to minimize environmental impact and maximize the economic efficiency of the plant.

### **Safety and Environment**

Safety and environmental management are crucial aspects of converter operations. Modern converters are equipped with advanced systems to control gas and dust emissions. Filters and scrubbers capture fine particles and harmful gases before they are released into the atmosphere. Additionally, continuous monitoring systems allow for the detection and quick correction of any pollution issues. Ongoing personnel training and adherence to safety protocols are essential to prevent accidents and ensure a safe working environment.

### **Maintenance and Durability**

Regular maintenance of converters is essential to ensure their proper functioning and prolong their lifespan. Refractory bricks need to be inspected and replaced periodically to prevent leaks and accidents. Additionally, the energy efficiency of the converter is optimized through continuous innovations in oxygen lance design and blowing methods. Preventive maintenance programs reduce downtime and improve overall productivity.

## **Technological Innovations**

The steel industry is constantly evolving, with innovations aimed at improving the efficiency, quality, and environmental impact of conversion processes. Research is ongoing to develop conversion techniques using renewable energy sources and more durable refractory materials. Advanced automated control systems are also being deployed to monitor and adjust the metal bath conditions in real-time, allowing for more precise production and less waste. Advances in artificial intelligence and machine learning optimize production parameters, reducing costs and increasing the final product's quality.

## **Challenges and Perspectives**

One of the main challenges of the steel industry is reducing CO<sub>2</sub> emissions and complying with increasingly strict environmental regulations. Initiatives such as using hydrogen as a reducing agent and developing low-carbon steel production processes are underway to address these challenges. The industry's future relies on continuous innovation, energy efficiency, and environmental sustainability, with a growing focus on circularity and material recycling.

### **I-1-3 Direct Reduction of Iron Ore**

The steel industry is a major emitter of CO<sub>2</sub>. Steel production primarily involves reducing iron ore, separating iron from oxygen using a carbon-containing reducing agent. This process requires significant energy expenditure, mainly from fossil fuels, leading to substantial CO<sub>2</sub> emissions. To address this issue, the steel industry has adopted various direct reduction methods to reduce its carbon footprint. These recent technologies, such as the MIDREX, HyL, and FIOR processes, aim to decrease emissions and waste.

Iron in ores exists as hematite (Fe<sub>2</sub>O<sub>3</sub>) or magnetite (Fe<sub>3</sub>O<sub>4</sub>). During the reduction of Fe<sub>2</sub>O<sub>3</sub>, two intermediate oxides, Fe<sub>3</sub>O<sub>4</sub> and (Fe<sub>1-x</sub>O), are formed, especially at temperatures above 570°C, according to the Fe-O stability diagram. The progress of iron oxide reduction reactions is characterized by the degree of reduction (R) and the metallization degree (M).

#### **I-1-3-1 Direct Reduction Technologies**

##### **I-1-3-1-1 MIDREX Process**

The MIDREX process (Figure I-1-8) typically uses natural gas as an energy and reducing gas source, though the MXCOL variant utilizes gasified coal. A MIDREX plant consists of

two main parts: the shaft furnace where iron ore is reduced, and the reformer which generates the reducing gas, along with a heat production and recovery system.

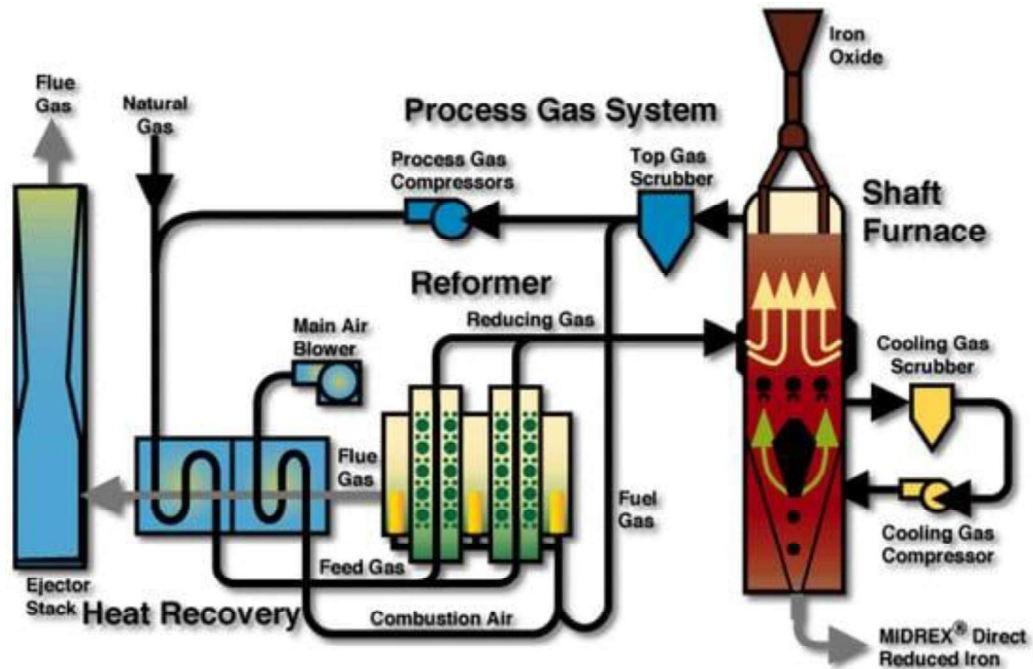


Figure I-1-8 : MIDREX process

Iron ore, in the form of pellets or lumps, is introduced into the top part of the shaft furnace. As it descends gravitationally through the furnace, the charge heats up and oxygen is removed from the ore by countercurrent reducing gases ( $H_2$  and  $CO$ ). These gases reduce iron oxides ( $Fe_2O_3$ ,  $Fe_3O_4$ , and  $FeO$ ) into metallic iron, simultaneously producing water vapor and carbon dioxide. Direct Reduced Iron (DRI) is cooled and cemented by methane in the lower zone of the shaft furnace. Cold DRI is typically stored for use in an electric arc furnace, while hot DRI can be discharged to feed a briquetting machine or electric furnace.

The off-gas, after  $CO_2$  washing and removal, is divided into two streams: one used as a fuel gas and the other mixed with methane to feed the reformer. The gas is heated and reformed as it passes through the tubes, following the reactions:



The reformed gas (syngas) is introduced into the shaft furnace as the reducing gas. Heat is generated at multiple points by natural gas combustion, and the shaft furnace is heated by reducing gases. A heat recovery system upstream of the reformer recovers some sensible heat from the combustion gas to preheat the feed gas mixture, burner combustion air, and natural gas. This process significantly reduces CO<sub>2</sub> emissions by recycling and reusing a large portion of thermal energy.

**The MIDREX process involves several key steps:**

**1. Iron Ore Charging:** Iron ore, in the form of pellets or lumps, is charged into the shaft furnace through an airlock mechanism.

**2. Iron Ore Reduction:** The ore descends gravitationally through the shaft furnace, where it is heated by hot countercurrent reducing gases from the gas heater. The reducing gases remove oxygen from the ore, transforming iron oxides into metallic iron.

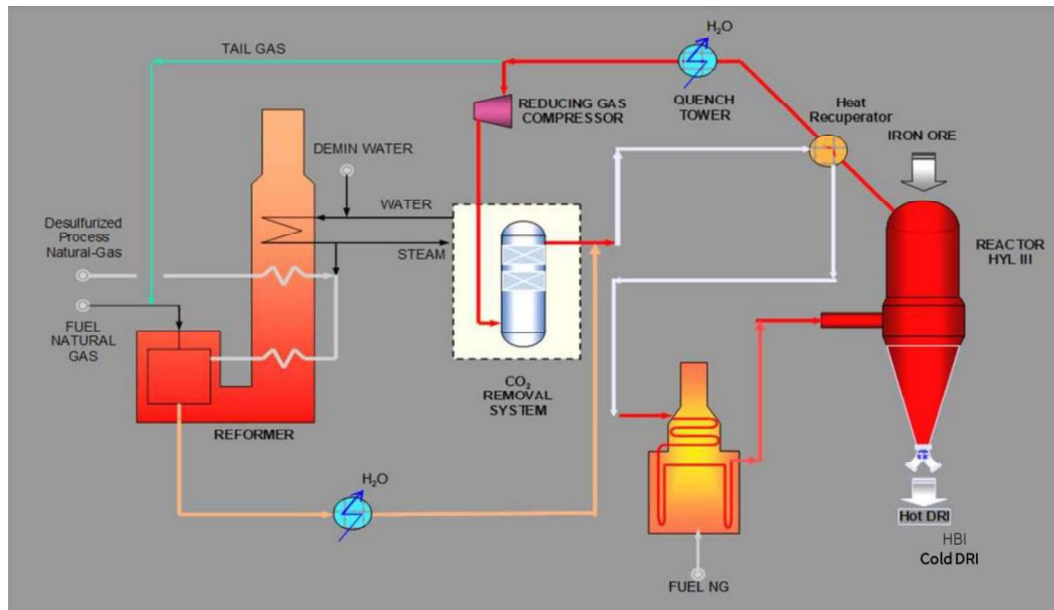
**3. Cooling and Cementation:** The solid cooling zone in the lower part of the shaft furnace is fed with recycled cooling gas through a gas compressor. After cooling, DRI is evacuated through a similar sealing mechanism as the entrance of the reactor.

**4. Gas Reforming:** The reducing gas entering the reactor contains controlled concentrations of water and carbon dioxide, allowing in situ reforming (self-reforming). This process begins by injecting methane with recycled gas into a humidifier. The amount of water is controlled to prevent carbon deposition on the DRI. The syngas is then preheated in the heat exchanger and heated in the gas heater to 900°C. An amount of oxygen is injected for combustion of the reducing gas, raising its temperature to approximately 1020°C.

**I-1-3-1-2. HyL III Process**

HyL III reactors (Figure I-1-9) are characterized by a pressure shaft furnace (6-8 atm). The iron oxide charge (pellets or lumps) is introduced through a sealing mechanism, and an automated valve system regulates pressurization and depressurization of the inlet bins. The descent rate is controlled by a rotary valve at the reactor outlet. The upper zone of the furnace is fed with hot reducing gases from a gas heater, receiving cooled and purified reducing gas from the top of the reactor as well as fresh reduction gas from the natural gas reformer. The solid cooling zone in the lower part of the shaft furnace is fed with cooling

gas, which is recycled via a gas compressor. After cooling, the DRI is evacuated through a sealing mechanism similar to the reactor inlet.



**Figure I-1-9 : HYL III process**

CH<sub>4</sub>-based direct reduction processes use a reformer to produce a CO-H<sub>2</sub> reducing syngas, requiring a catalyst to enhance reaction kinetics. The metallic iron in the DRI serves as a catalyst. The reducing gas entering the reactor contains controlled concentrations of water and carbon dioxide, enabling in situ reforming (self-reforming). This process begins by injecting methane with recycled gas into a humidifier, with the amount of water controlled to avoid carbon deposition on the DRI. The syngas is then preheated in the heat exchanger and heated in the gas heater to 900°C. An amount of oxygen is injected to combust the reducing gas, raising its temperature to approximately 1020°C.

**The HyL III process involves several key steps:**

**1. Iron Ore Charging:** Iron ore, in the form of pellets or lumps, is introduced into the pressure shaft furnace through a sealing mechanism.

**2. Reduction under Pressure:** The iron ore descends gravitationally through the pressure shaft furnace, where it is heated by hot reducing gases from the gas heater. The reducing gases remove oxygen from the ore, transforming iron oxides into metallic iron.

**3. Cooling:** The solid cooling zone in the lower part of the shaft furnace is fed with cooling gas recycled via a gas compressor. After cooling, the DRI is evacuated through a sealing mechanism similar to the reactor inlet.

**4. Gas Reforming:** The reducing gas entering the reactor contains controlled concentrations of water and carbon dioxide, enabling in situ reforming (self-reforming). This process begins by injecting methane with recycled gas into a humidifier. The amount of water is controlled to prevent carbon deposition on the DRI. The syngas is then preheated in the heat exchanger and heated in the gas heater to 900°C. Oxygen is injected for combustion of the reducing gas, raising its temperature to approximately 1020°C.

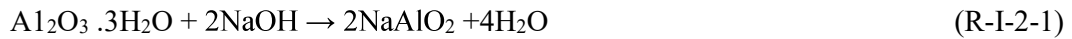
The MIDREX and HyL III processes offer efficient alternatives to traditional steel production methods, significantly reducing CO<sub>2</sub> emissions and improving energy efficiency. These direct reduction technologies play a crucial role in transitioning to a more environmentally friendly steel industry.

## I-2- Aluminum Production

### I-2-2- The Bayer Process

The Bayer process (Figure I-2-1) facilitates the extraction of alumina from bauxite. The basic principle of the Bayer process involves dissolving  $\text{Al}_2\text{O}_3$  in a caustic medium ( $\text{NaOH}$ ), according to the equations below:

#### Alumina trihydrate:



#### Alumina monohydrate:



The products of these reactions are subsequently precipitated, according to reaction R-I-2-3, and then proceed to the final stage, calcination, according to reaction R-I-2-4:

#### Precipitation:



#### Calcination:

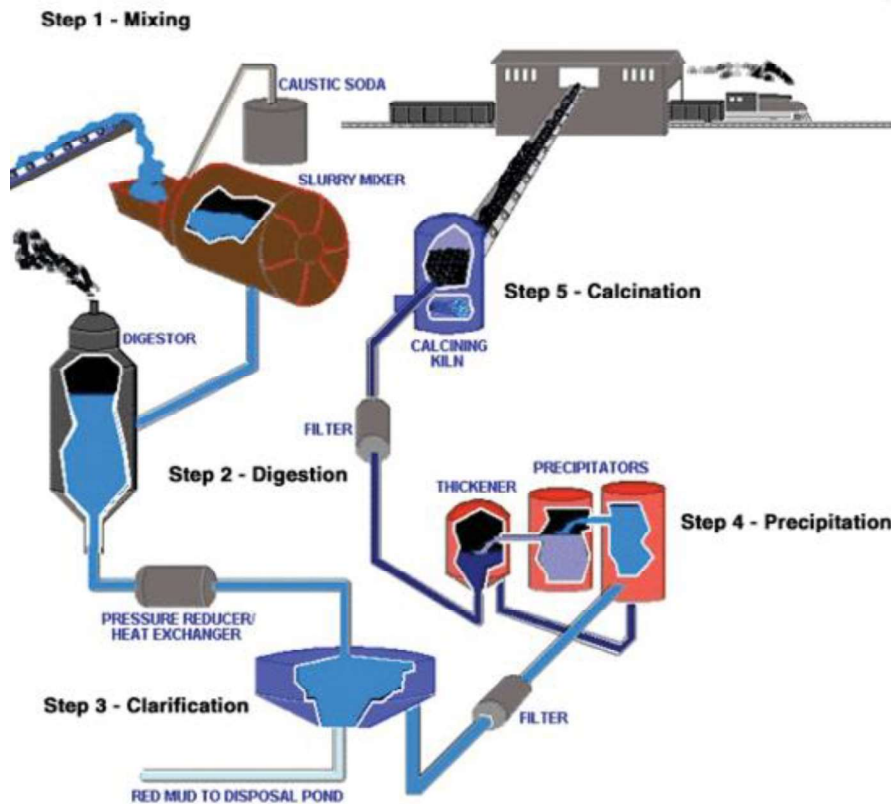
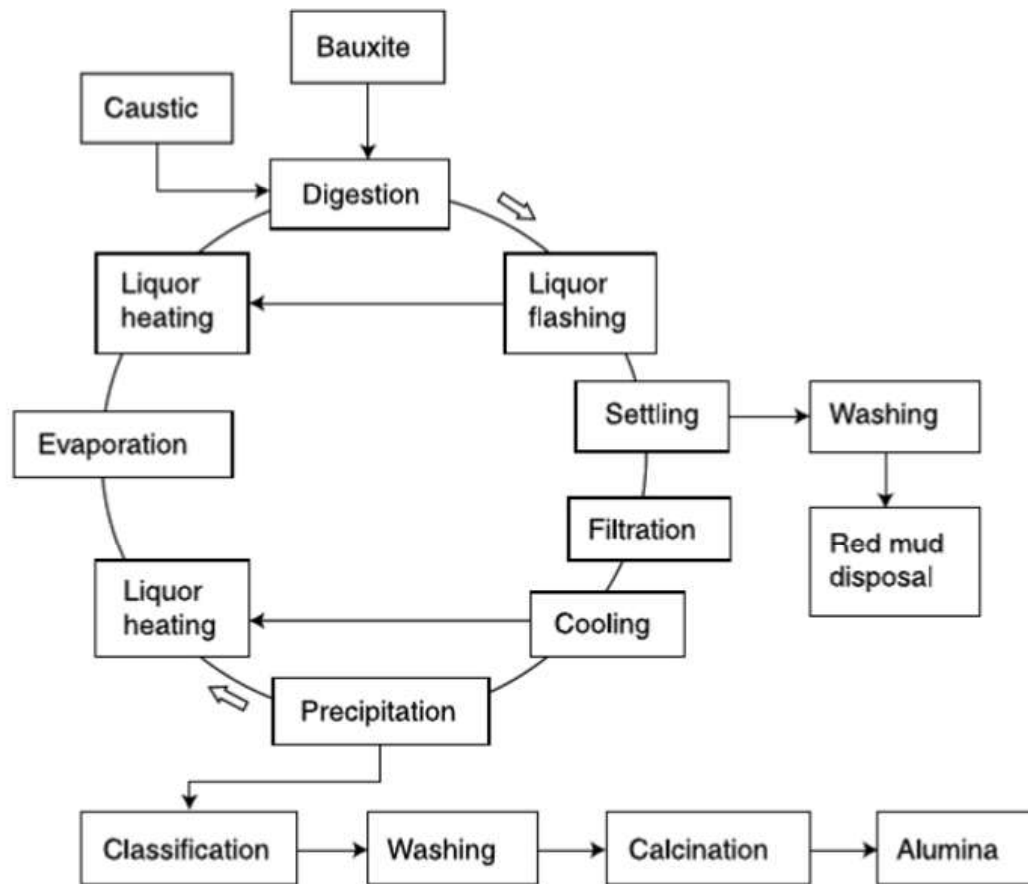


Figure I-2-1- Extraction of alumina using the Bayer process



**Figure I-2-2- Bayer process diagram**

The Bayer process occurs in 7 distinct stages (Figure I-2-2):

- 1. Bauxite Grinding:** The bauxite is ground to facilitate its dissolution.
- 2. Mixing:** The ground bauxite is mixed with lime (CaO) and 90% of the spent liquor recovered from the precipitation stage, at a temperature of 85°C.
- 3. Autoclaving:** The mixture is introduced into autoclaves at a temperature of 154°C. Before introducing the extraction pulp into the thickeners, it undergoes several decompression stages to reduce pressure.
- 4. Decantation:** Impurities are extracted in a gravity thickener. The solid obtained during separation (red mud) will be treated later.
- 5. Filtration:** The liquid is filtered to recover impurities, which are sent to red mud treatment. The liquid produced by filtration is called mother liquor.
- 6. Precipitation:** The mother liquor is slowly cooled to initiate precipitation in a tank where hydrate is added. The precipitation reaction is represented by equation R-I-2-3. The

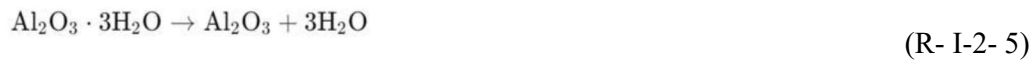
spent liquor is heated using the heat removed from the cooling stage and returned to the autoclaves.

**7. Calcination:** Before calcination, the product is washed and dried to reduce its caustic concentration. Then it is heated in a rotary kiln to accelerate the chemical reaction R-I-2-4. Finally, the material is cooled in a fluidized bed.

### Dissolution of Alumina

There are two types of alumina: sandy alumina and pasty alumina. The solubility of alumina mainly depends on the chemical composition and the temperature of the bath. The dissolution of alumina occurs in several distinct stages:

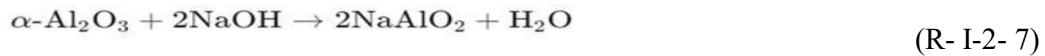
- **Heating of Alumina:** Heating alumina to the bath temperature.



- **Transformation of Gamma to Alpha:** Transformation of gamma alumina to alpha alumina.



- **Dissolution of Alpha Alumina:** Dissolution of alpha alumina in the bath.



- **Chemical Reactions:** Chemical reactions of dissolved alumina with bath ions to form complex ions.



- **Dispersion:** Dispersion of complex ions in the bath.

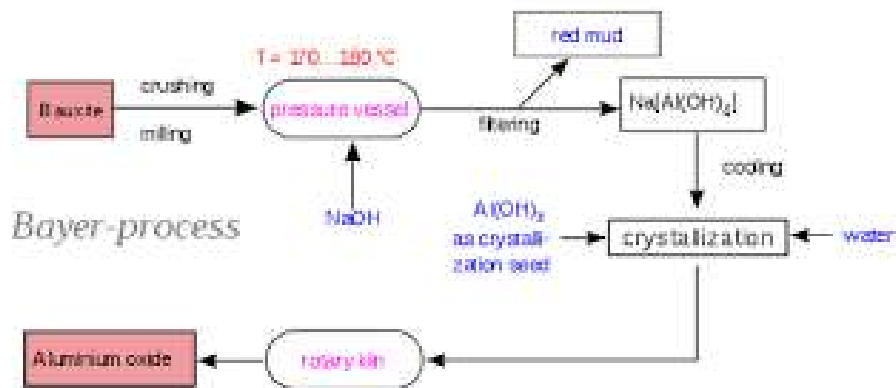
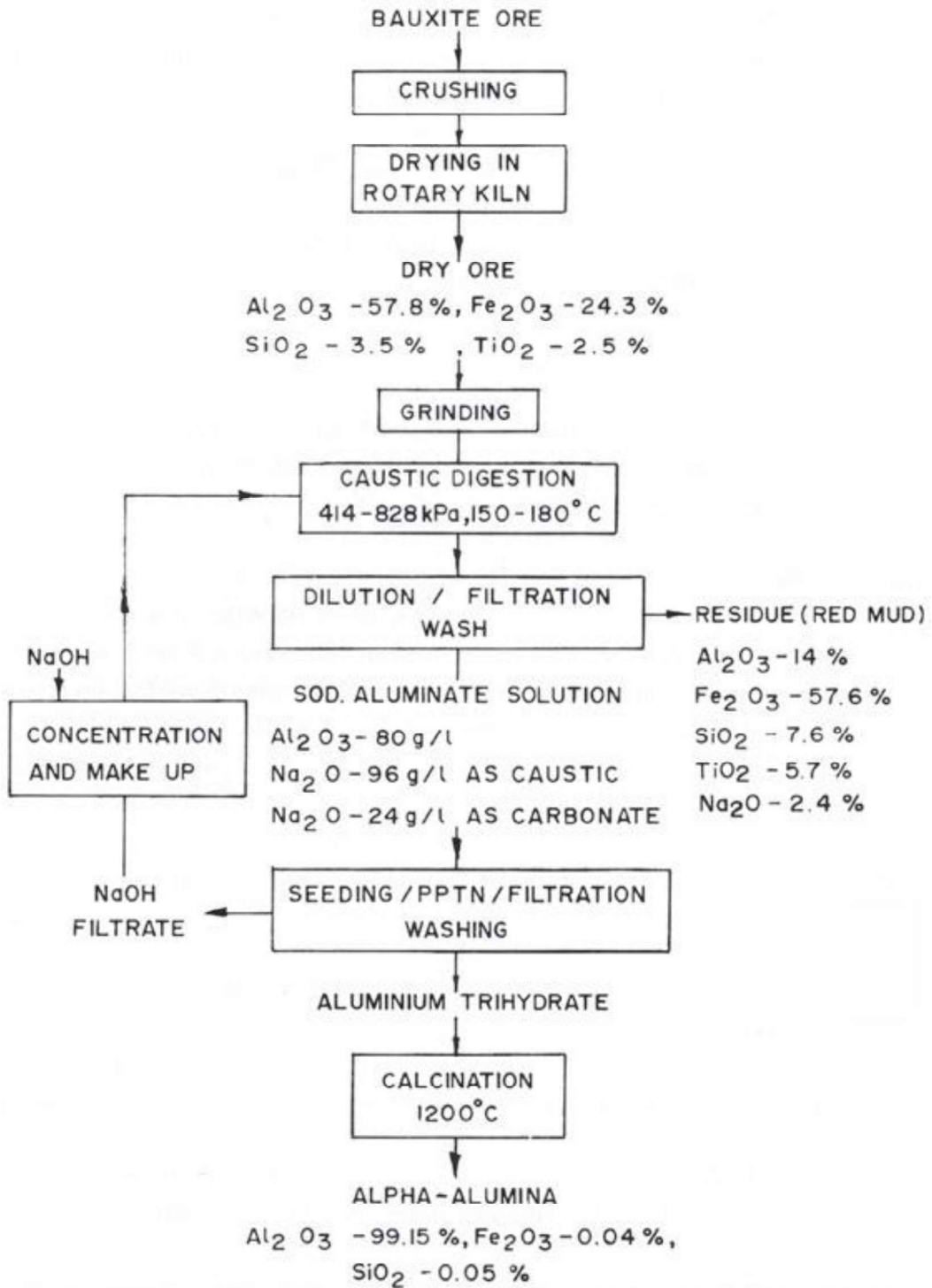


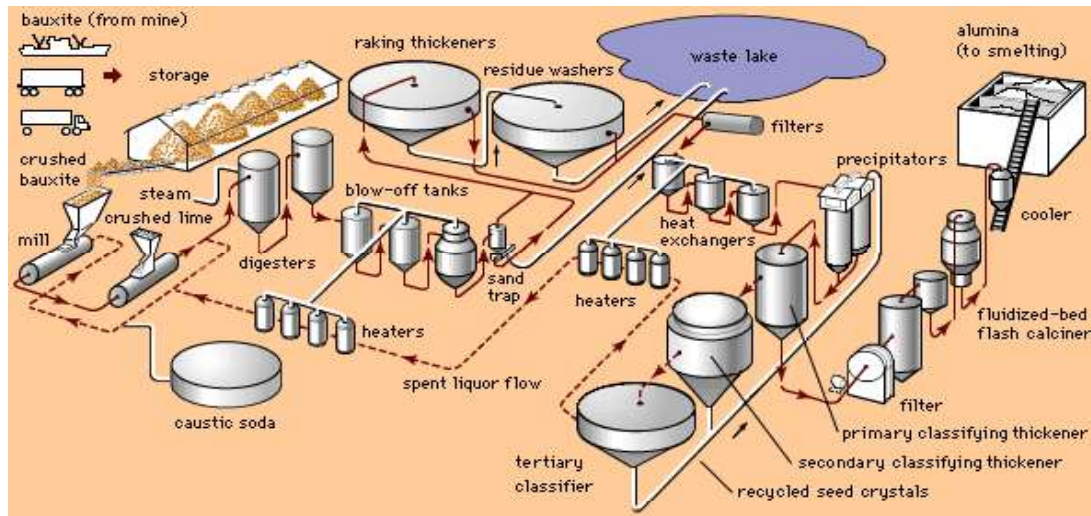
Figure I-2-3-. Simplified diagram of the Bayer process



**Figure I-2-4. Detailed diagram of the Bayer process**

Figure I-2-3 illustrates these simple stages that constitute the Bayer process, while Figure I-2-5 elucidates the unit operations. Figure I-2-4 provides more details on the operations of

the Bayer process unit, with the alumina process flows (white side) and red mud process flows (red side).



**Figure I-2-5. Bayer processing unit operations with alumina (white side) and red mud (red side) process streams shown**

### I-2-3-Hall-Hérault Process

The Hall-Hérault process (Figure I-2-6) involves dissolving alumina extracted from various ores in a bath of molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) contained in an electrolytic cell maintained at a temperature between 950 and 980 °C. The alumina is electrolyzed by passing a direct current between the anode and the cathode. The main reaction is:

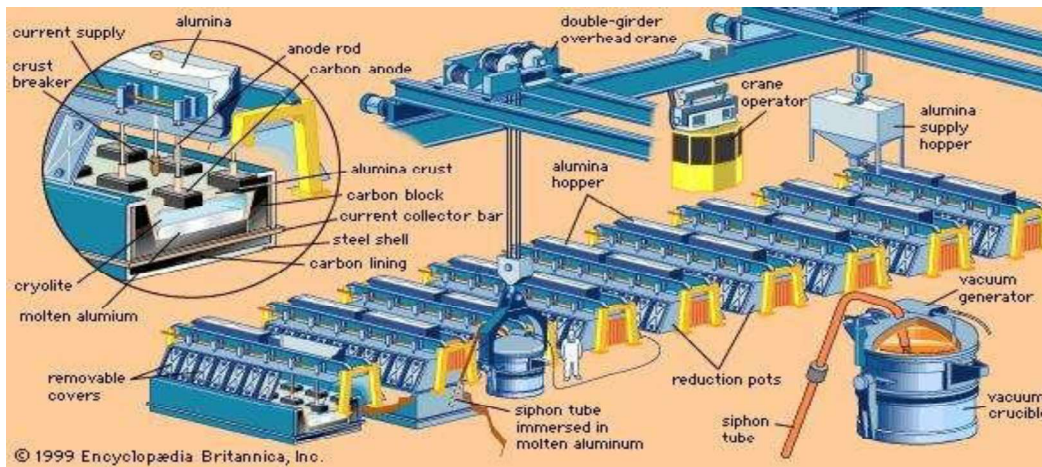


The cell generally consists of pre-baked anodes, an electrolyte bath, multi-layer insulating walls, a metal layer, an alumina feeding system, and the cathode block, which includes the carbon block, collector bars, and an insulation block (see Figure I-2.7).

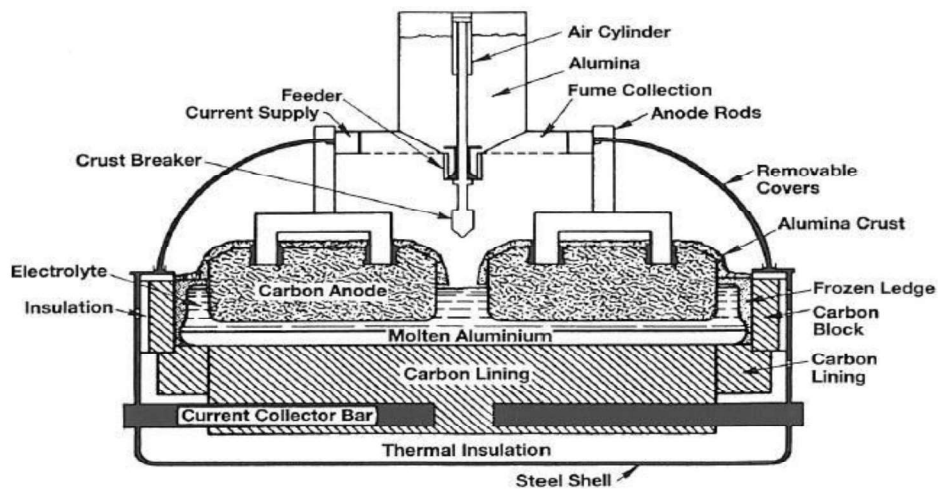
The modern Hall-Hérault process uses carbon anodes made from a mixture of crushed petroleum coke and coal tar pitch. These anodes are produced using two techniques: baking or self-baking.

Theoretically, the liquid aluminum layer is considered the cathode of the electrolytic cell, although technically the cathode is actually the entire assembly of the carbon block, collector bars, and insulating layer. The carbon block consists of numerous pre-baked carbon blocks made of semi-graphite or anthracite. The collector bars, located under the

carbon block, serve to carry the current. The insulating layer, composed of bricks and refractory materials (high thermal inertia), aims to minimize heat loss from the bottom of the cell.



**Figure I-2-6 Part of a modern vessel line based on the Hall-Héroult electrolytic fusion process.**



**Figure I-2-7- Diagram of a Hall-Héroult tank with pre-baked anodes**

### I-2-3-1 Electrolytic Bath

The electrolytic bath aims to reduce the liquidus temperature of the bath, which is generally composed of cryolite and additives. Adding these additives lowers the liquidus temperature to about 940°C, compared to 1020°C for a bath composed solely of cryolite. The main additives are fluorides:

**Aluminum fluoride (AlF<sub>3</sub>):** Improves electrical conductivity and lowers the melting point.

**Calcium fluoride (CaF<sub>2</sub>):** Stabilizes the bath and reduces oxide solubility.

**Magnesium fluoride (MgF<sub>2</sub>):** Used to control the viscosity of the bath.

**Lithium fluoride (LiF):** Increases the solubility of alumina in the bath and improves electrical conductivity.

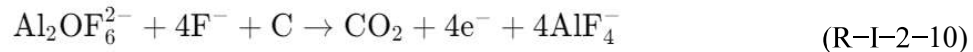
**Potassium fluoride (KF):** Used to further lower the melting point and improve alumina solubility.

Alumina represents between 2% and 4% by mass of the bath. It is regularly added through a point-feeding process, introducing alumina at various locations in the cell, typically between two and five positions. This point-feeding process maintains a uniform concentration of alumina in the electrolytic bath, promoting efficient electrolysis.

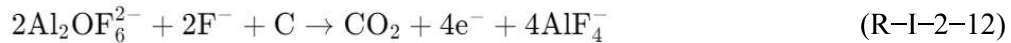
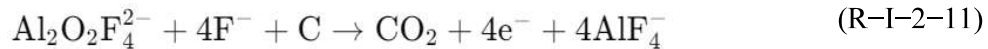
### I-2-3-2 Anodic and Cathodic Reactions

The dissolved alumina reacts with carbon to release electrons and produce carbon dioxide gas. Anodic reactions are classified into two categories, depending on the concentration of alumina.

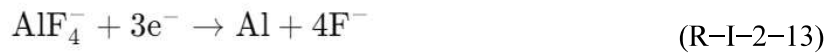
#### Low alumina concentration:



#### High alumina concentration:



Cathodic reactions allow the transfer of electrons from the liquid aluminum layer to the electrolytic bath:



These reactions are crucial for depositing aluminum onto the cathode, where it separates from the electrolytic bath to form liquid metal.

### **I-2-3 Recycling**

Recycling aluminum is highly advantageous in terms of energy. Remelting aluminum scrap consumes only 5% of the energy required to produce primary aluminum from bauxite. "In-process" scrap from the manufacture of sheets, forged parts, and extrusions has been returned to the melting furnace since production began.

Before World War I, "new" scrap produced during the manufacture of commercial and domestic aluminum products was collected by entrepreneurs, initiating the secondary aluminum industry. The chemical composition of new scrap is generally well-defined; therefore, it is often resold to primary aluminum producers to be reconstituted into the same alloy.

"New" scrap is now largely supplemented by "old" scrap generated by recycling end-of-life consumer products, such as cars or garden chairs. Since old scrap is often contaminated and forms a mix of many alloys, it is usually found in foundry alloys, which contain higher levels of alloying elements.

Used aluminum beverage containers represent a unique type of old scrap. Although the bodies and lids of these cans are made from different aluminum alloys, they both contain magnesium and manganese. Therefore, recycled beverage containers can be used to replenish the stock of either product. The energy required to produce a beverage can from scrap is about 30% of the energy needed to produce the can from primary metal. For this reason, recycling used beverage containers represents a growing source of metal for primary metal producers.

In conclusion, the Hall-Héroult process, coupled with effective recycling practices, enables the production of aluminum in an economically and ecologically viable manner. Continuous improvement in electrolysis and recycling techniques contributes to the sustainability of the aluminum industry by reducing energy and natural resource needs.

### **I-3-Élaboration du nickel**

Metals play a fundamental role in the industrial and technological development of our society. Among them, nickel holds a strategic position due to its exceptional properties, such as corrosion resistance, hardness, and its ability to form high-performance alloys. It is widely used in various sectors, including steelmaking, aerospace, electronics, and renewable energy.

The production of nickel relies on complex metallurgical processes involving the extraction and processing of ores, which can be either sulfide or oxide-based. These processes are mainly classified into two major categories: pyrometallurgy, which involves high-temperature thermal treatments, and hydrometallurgy, which uses chemical solutions to extract and purify the metal. However, these methods present significant technical and environmental challenges, requiring continuous optimization to enhance efficiency and reduce ecological impact.

In the context of energy transition and increasing industrialization, the demand for nickel continues to rise, particularly for the production of stainless steel and batteries used in electric vehicles. Thus, mastering nickel production processes, along with the development of more sustainable technologies, is crucial for the future of this industry.

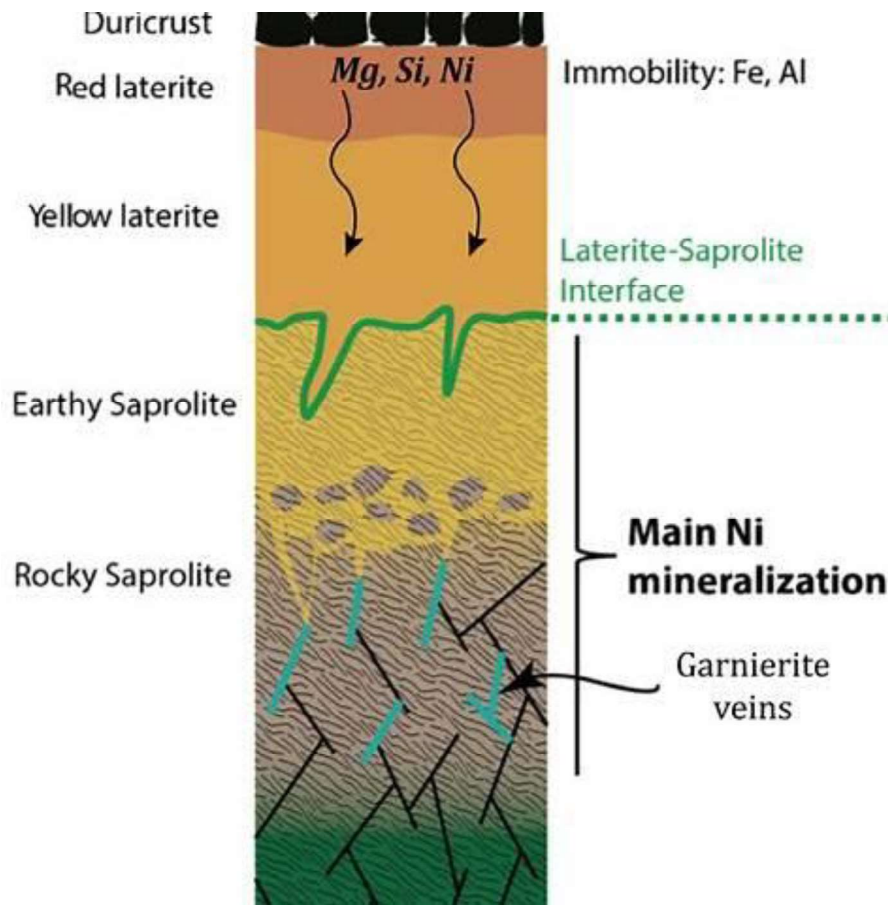
#### **1. Extraction of Nickel Ores**

Nickel is a strategic metal widely used in alloys, battery manufacturing, and the steel industry. Its extraction is based on two main types of deposits: laterites and sulfides. These ores differ in their chemical composition, geographical location, and extraction processes.

##### **1.1. Types of Nickel Ores**

###### **1.1.1. Laterites**

Laterites are ores rich in nickel oxide, formed by prolonged chemical weathering of ultramafic rocks in a humid tropical climate. This weathering process results in the concentration of nickel in the form of oxides and hydroxides. Laterites account for approximately 60-70% of the world's nickel resources.



**Figure 3-1: Formation of laterite deposits.**

### **Formation of Laterites**

The formation of laterites involves erosion and leaching of nickel-bearing minerals due to heavy rainfall. Water infiltrates the parent rocks, dissolving silicates and concentrating iron and nickel oxides. This process can take several million years.

### **Major Laterite Deposits**

Laterites are mainly found in tropical and subtropical regions, including Indonesia, the Philippines, New Caledonia, Australia, Brazil, and Cuba.

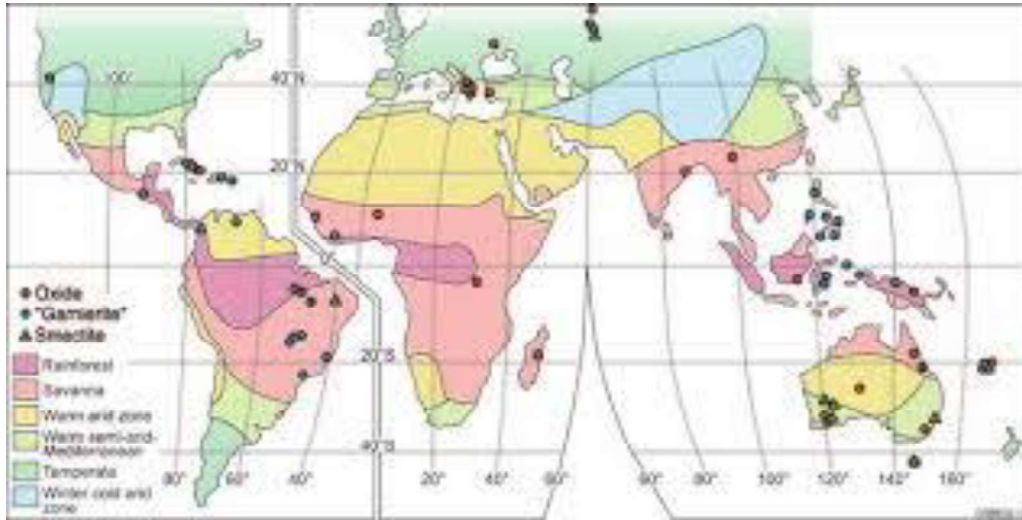


Figure 3-2: Location of major laterite deposits worldwide.

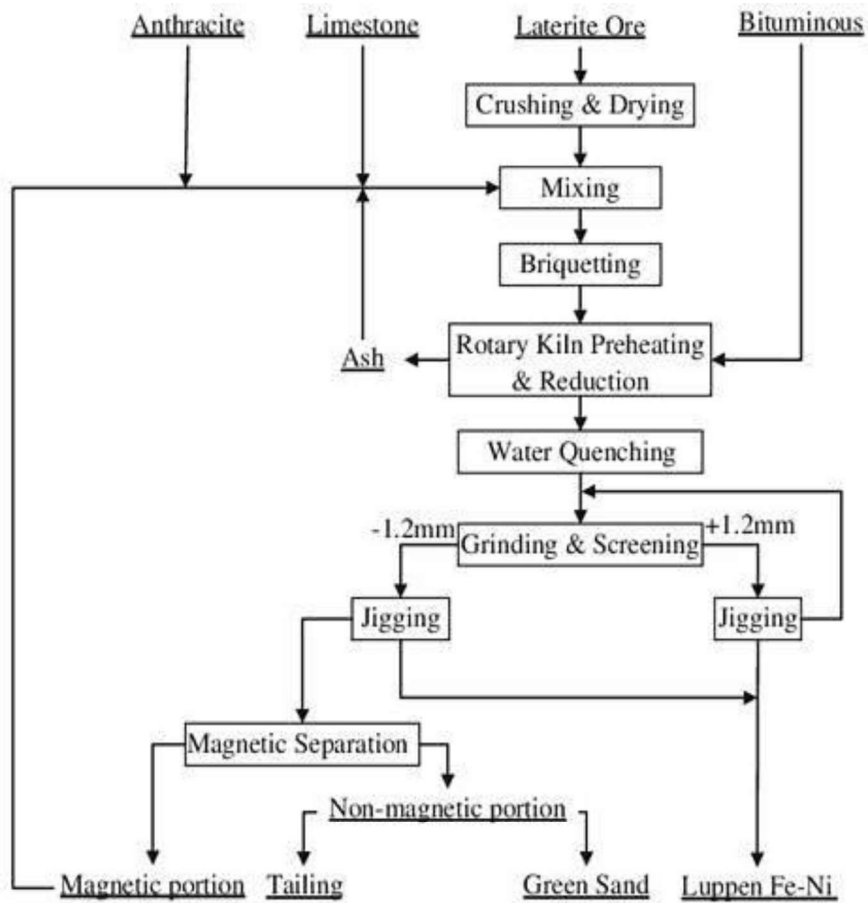


Figure 3-3: Diagram of lateritic ore processing methods.

## Processing of Lateritic Ores

Nickel extraction from laterites relies on two main processes:

- **Pyrometallurgical process:** The ore is calcined and smelted in an electric furnace to produce ferronickel or nickel matte.
- **Hydrometallurgical process:** The ore is leached at high pressure in sulfuric acid (HPAL - High-Pressure Acid Leaching) to extract nickel.

### 1.1.2. Sulfide Ores

Sulfide ores contain nickel in the form of sulfide, often associated with copper and iron. These deposits account for approximately 30-40% of the world's nickel resources and are generally mined underground using deep mining techniques.

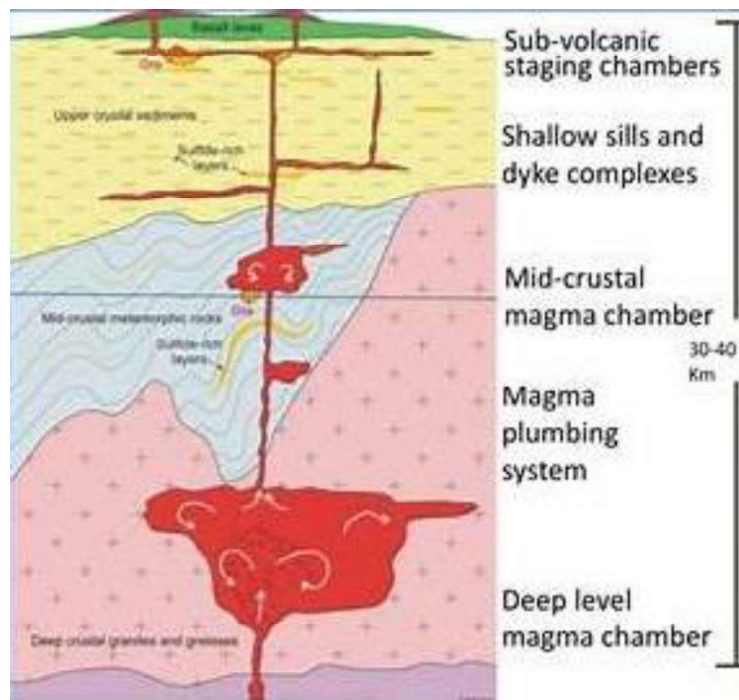


Figure 3-4: Formation of sulfide ore deposits.

### Major Sulfide Deposits

The leading producers of sulfide ores are Canada (Sudbury, Voisey's Bay), Russia (Norilsk), Australia (Kambalda), and Finland.

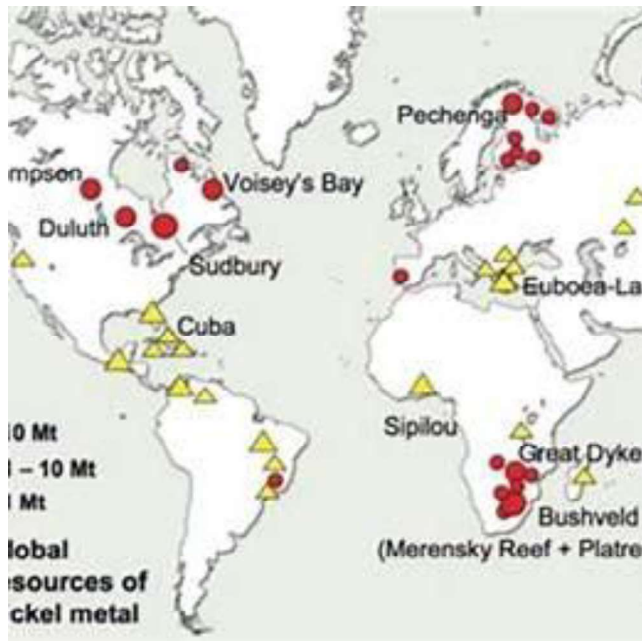


Figure 3-5: Location of major sulfide deposits worldwide.

### Processing of Sulfide Ores

Nickel extraction from sulfide ores follows several steps:

- **Crushing and grinding:** The ore is reduced to fine particles.
- **Flotation:** Nickel is separated from other minerals through a flotation process.
- **Smelting and refining:** The concentrate is smelted to produce nickel matte, then refined using pyrometallurgical or hydrometallurgical methods.

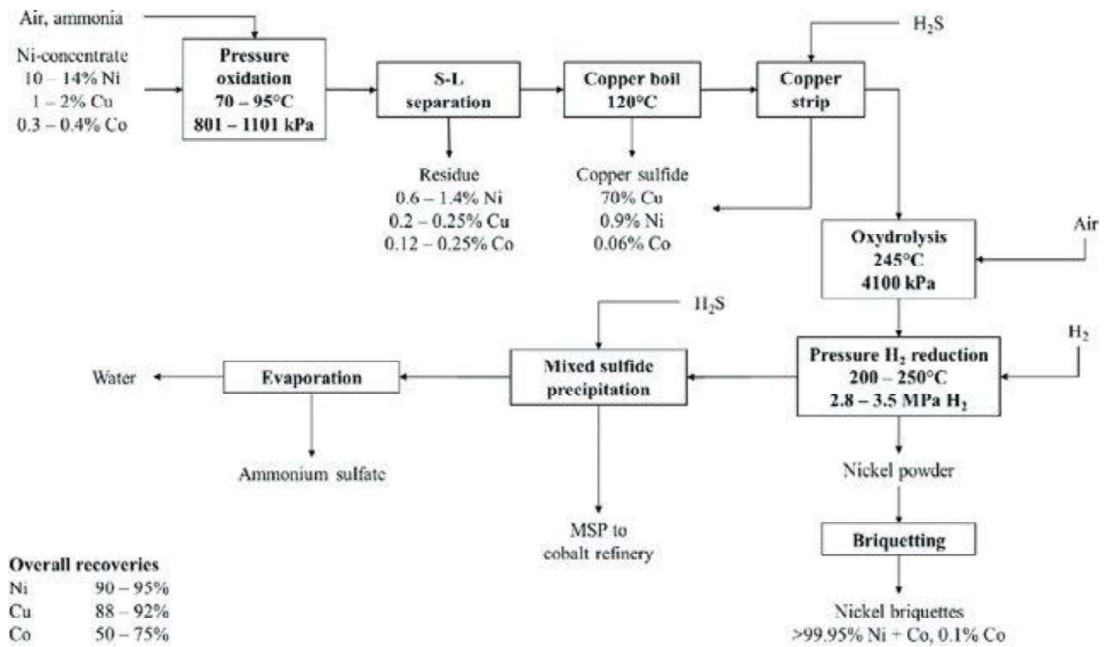


Figure3- 6: Diagram of sulfide ore processing methods.

## 1.2. Comparison Between Laterites and Sulfides

Table 3-1: Comparison of laterite and sulfide deposit characteristics.

Characteristics	Laterites	Sulfides
<b>Formation</b>	Chemical weathering in tropical climates	Crystallization of ultramafic magma
<b>Composition</b>	Nickel oxides and hydroxides	Nickel, copper, and iron sulfides
<b>Location</b>	Tropical regions (Indonesia, Philippines, Brazil)	Cold and temperate regions (Canada, Russia, Australia)
<b>Nickel content</b>	1-3%	1.5-4%
<b>Extraction method</b>	Open-pit mining (shallow laterites)	Underground mining
<b>Processing</b>	Pyrometallurgy, hydrometallurgy	Flotation, smelting, and refining

Nickel extraction is therefore a complex process that varies depending on the type of ore being mined. Laterites are more abundant but harder to process, whereas sulfide ores have higher nickel content and are easier to refine. Optimizing extraction methods and developing more sustainable technologies remain essential to ensuring an efficient and environmentally friendly nickel supply.

## 2. Pyrometallurgical Processes

Pyrometallurgical methods are primarily used for processing sulfide ores. These processes involve high-temperature steps aimed at concentrating and purifying nickel through smelting, conversion, and refining.

### 2.1 Smelting and Conversion

**Smelting:** The nickel sulfide ore is first dried and preheated before being introduced into a smelting furnace (electric or reverberatory furnace). The furnace temperature is maintained between 1350 and 1600°C to enable the separation of nickel matte from slag. The matte contains nickel, iron, and sulfur, while the slag, primarily composed of silicates, is removed. This process is essential for concentrating nickel and facilitating its subsequent processing.

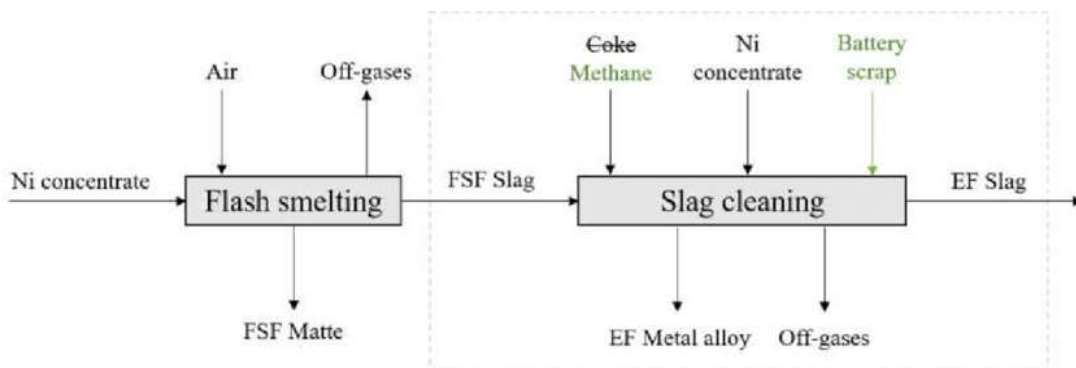
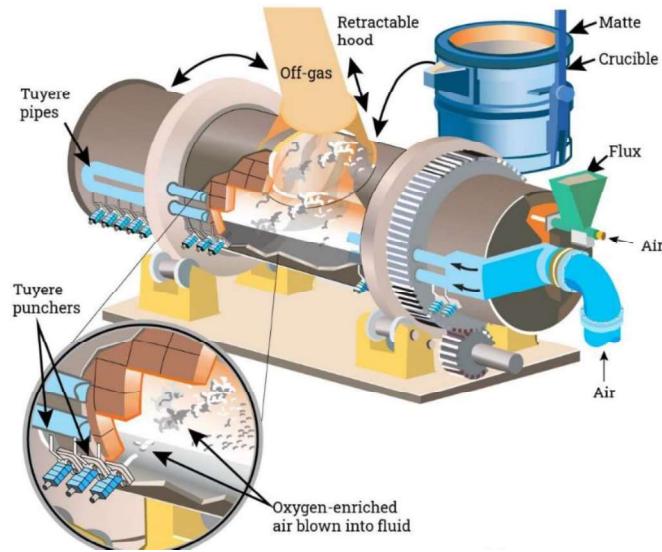


Figure 3- 7: Diagram of nickel ore smelting

**Conversion:** The matte is then introduced into a converter where it undergoes oxidation through the blowing of air or pure oxygen. This chemical reaction transforms the iron into iron slag (FeO) and oxidizes the nickel sulfide into nickel oxide (NiO). The nickel oxide is then reduced to metallic nickel using a reducing agent such as carbon or natural gas.



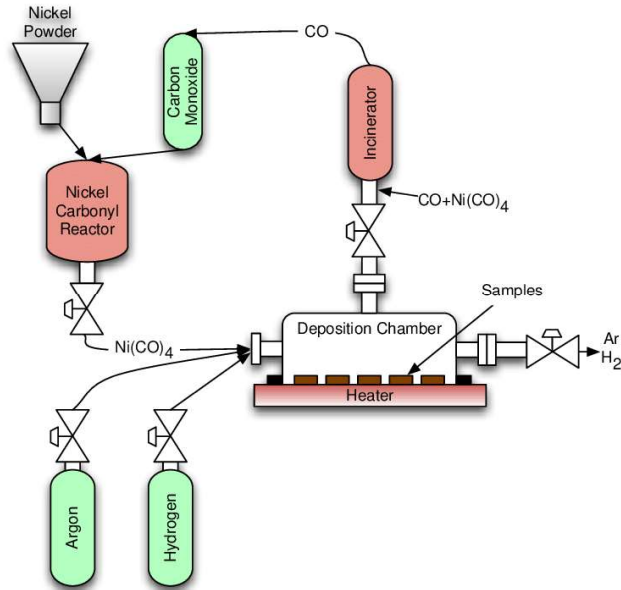
**Figure 3-8: Matte conversion process**

## 2.2 Carbonylation Process (Mond Process)

The Mond process relies on the reaction of nickel with carbon monoxide (CO) to form nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ), which is subsequently decomposed into pure nickel by heating.

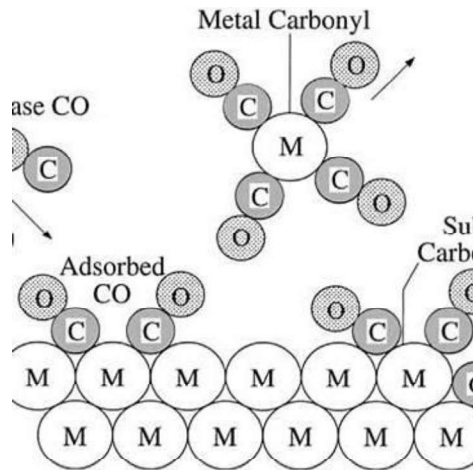
The process steps are as follows:

1. The nickel matte is first reduced to obtain metallic nickel in fine powder form, increasing its reactivity with carbon monoxide.
2. This powder is exposed to carbon monoxide (CO) at a temperature of around 50-60°C, forming gaseous nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ), a highly volatile compound. This step allows for precise nickel extraction while eliminating metallic impurities.



**Figure 3-9: Formation of nickel carbonyl**

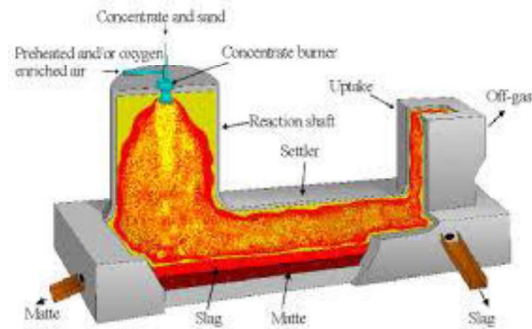
3. The obtained gas is then directed into a decomposition chamber heated between 200 and 250°C, where the nickel carbonyl decomposes into pure nickel deposited as powder or pellets. This process yields highly pure nickel, used in high-precision industrial applications.



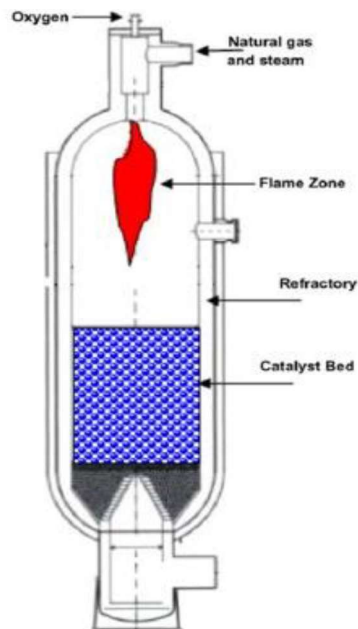
**Figure 3-10: Decomposition of nickel carbonyl**

### 2.3 Modern Processes and Optimization

With technological advancements, processes such as flash smelting and the use of Teniente converters enable greater energy efficiency and reduced pollutant emissions. These techniques involve more controlled reaction conditions and a more efficient recovery of nickel. In flash smelting, fine ore particles are injected into a reaction furnace with an oxygen-enriched air stream, resulting in rapid and efficient smelting.



**Figure 3-11: Flash smelting and Teniente converter**



**Figure 3-12: Diagram of an autothermal reactor and by-product recovery**

Innovations also include the use of autothermal reactors, allowing better utilization of the energy produced during oxidation reactions. By recovering the generated heat, these

reactors help reduce overall energy consumption and optimize process efficiency. Additionally, the recovery of by-products such as sulfur (converted into sulfuric acid) and slag is integrated into the processes to improve profitability and minimize industrial waste.

Pyrometallurgical nickel processes have evolved to maximize efficiency, minimize environmental impact, and optimize metal recovery. The integration of advanced technologies and improvements in energy and by-product recovery systems now allow for more sustainable and economically viable nickel exploitation.

### **3. Hydrometallurgical Processes**

Lateritic ores are often processed through hydrometallurgical methods to extract nickel and other valuable metals such as cobalt. This approach involves selective dissolution of metal components, followed by purification and recovery of nickel in metallic form.

#### **3.1 Acid Leaching**

Acid leaching is a key step in the hydrometallurgical processing of lateritic ores. This process dissolves nickel contained in the ore using an acid, typically sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Two main leaching techniques are employed:

##### **3.1.1 High-Pressure Acid Leaching (HPAL)**

High-pressure acid leaching is an intensive process that operates under severe conditions to accelerate nickel dissolution.

##### **Operating conditions:**

- Temperature: 240-270°C
- Pressure: 4-5 MPa
- Acid:  $\text{H}_2\text{SO}_4$  (concentration ~30-50 g/L)
- Reaction time: 1 to 2 hours

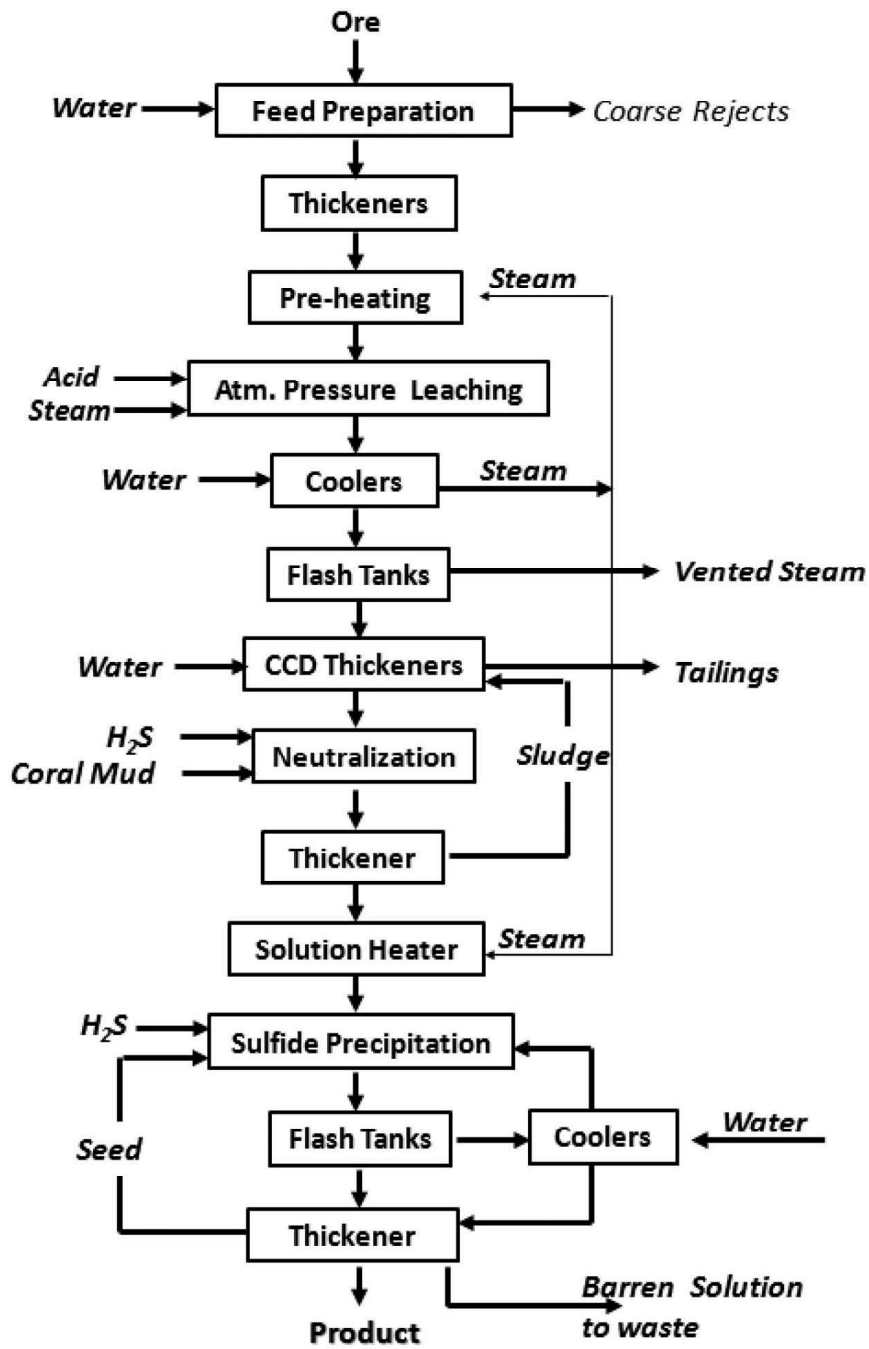
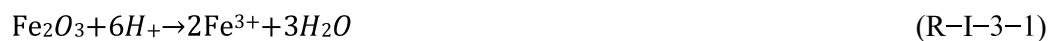


Figure 3.13: HPAL Process Diagram

Main chemical reactions:



A significant feature of HPAL is that it also dissolves iron, necessitating further purification steps.

**Advantages:**

- High nickel extraction rate (>90%)
- Fast processing time

**Disadvantages:**

- High cost of corrosion-resistant autoclaves
- Complex management of acidic effluents

### **3.1.2 Atmospheric Leaching (AL)**

This process operates at ambient pressure, reducing capital costs, but it is less efficient.

**Operating conditions:**

- Temperature: 70-100°C
- Pressure: 1 atm
- Acid: H<sub>2</sub>SO<sub>4</sub> (~10-20 g/L)
- Reaction time: Several hours to several days

**Advantages:**

- Lower cost than HPAL
- Easier implementation

**Disadvantages:**

- Slower kinetics
- Lower nickel extraction rate (~50-80%)

**Table 3.2: Comparison Between High-Pressure and Atmospheric Leaching**

<b>Aspect</b>	<b>High-Pressure Acid Leaching (HPAL)</b>	<b>Atmospheric Leaching (AL)</b>
<b>Operating Conditions</b>	High temperature (220-250°C) and pressure (up to 5,400 kPa)	Lower temperature (up to 95°C) and atmospheric pressure
<b>Equipment Requirements</b>	Specialized autoclaves capable of withstanding aggressive conditions, leading to higher capital and maintenance costs	Standard equipment without the need for high-pressure vessels, resulting in lower capital costs
<b>Metal Recovery Rates</b>	High recoveries; for example, nickel recoveries around 90% have been reported	Comparable recoveries; nickel recoveries of around 90% have been achieved under optimized conditions
<b>Acid Consumption</b>	Lower net acid consumption; some iron precipitates as hematite during the process	Generally higher acid consumption; iron remains in solution and requires additional neutralization steps
<b>Process Duration</b>	Shorter leaching times due to aggressive conditions	Longer leaching times required to achieve similar metal recoveries
<b>Environmental Considerations</b>	Potential for more complex waste management due to the formation of hematite and other precipitates	Simpler waste management but may require additional steps to handle dissolved iron and other impurities

## 3.2 Solvent Extraction and Electrowinning

Once leaching is complete, the resulting solution contains nickel in ionic form along with other impurities such as iron, cobalt, and aluminum. Nickel is purified in two main steps:

### 3.2.1 Solvent Extraction (SX)

Solvent extraction relies on selective organic solvents to transfer nickel from an aqueous phase to an organic phase.

#### Commonly used solvents:

- Cyanex 272
- D2EHPA (Di-(2-ethylhexyl) phosphoric acid)
- Versatic Acid

#### Typical chemical reaction:



where

R-OH represents the organic solvent.

#### Advantages:

- High selectivity
- Removal of metallic impurities before electrowinning

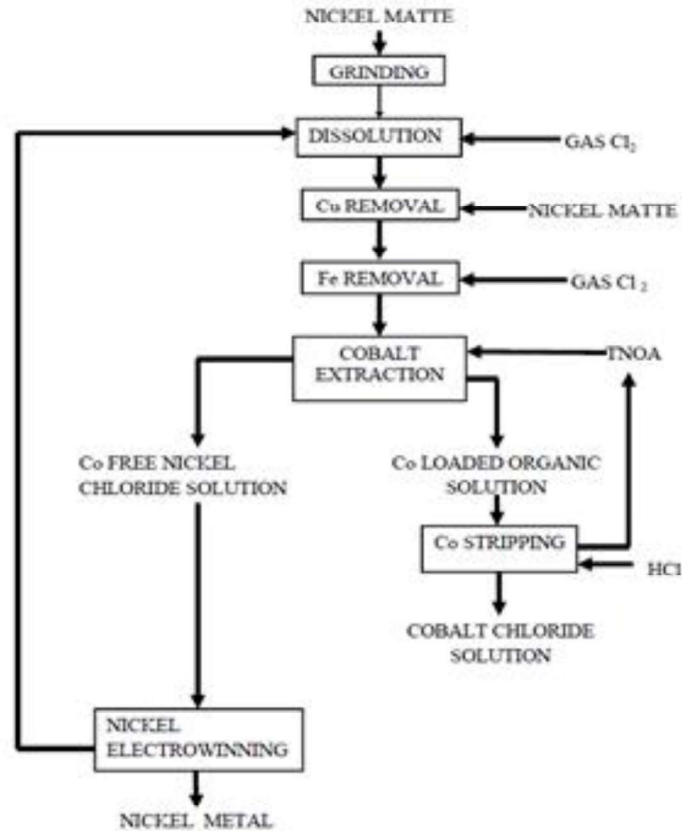


Figure 3.14: Solvent Extraction Process Diagram

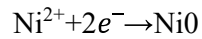
### 3.2.2 Electrowinning (EW)

After purification, the concentrated nickel solution undergoes electrolysis to recover nickel in solid form.

#### Operating conditions:

- Anode: Lead (*Pb*) or platinum (*Pt*)
- Cathode: Stainless steel
- Electrolyte: Nickel sulfate solution (*NiSO<sub>4</sub>*)
- Applied voltage: 2-3 V

**Electrochemical reaction at the cathode:**



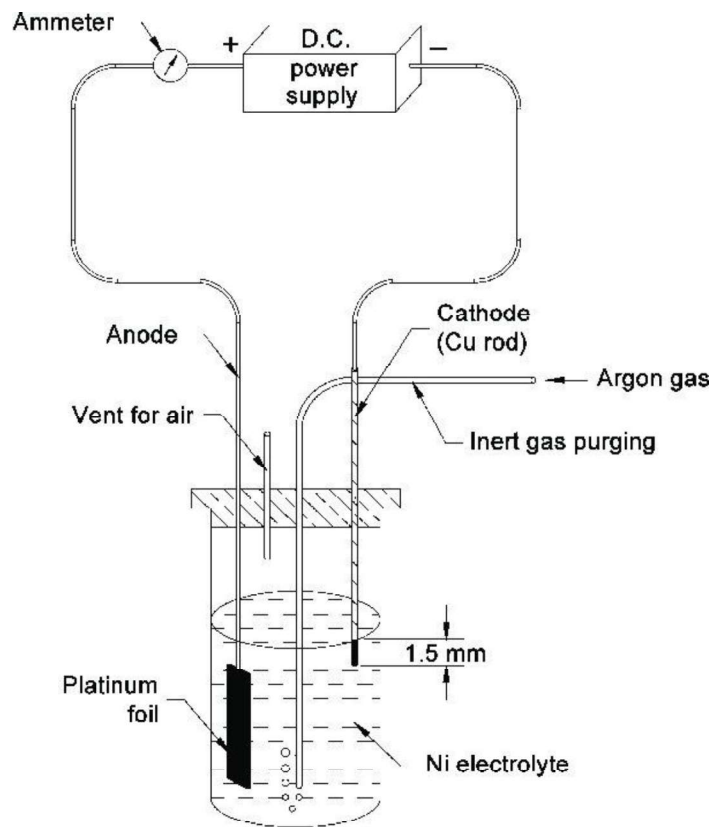
(R-I-3-4)

**Advantages:**

- Production of high-purity nickel (>99%)
- Efficient metal recovery method

**Disadvantages:**

- High energy consumption
- Irregular deposition if conditions are not well controlled



**Figure 3.15: Nickel Electrowinning Process Diagram**

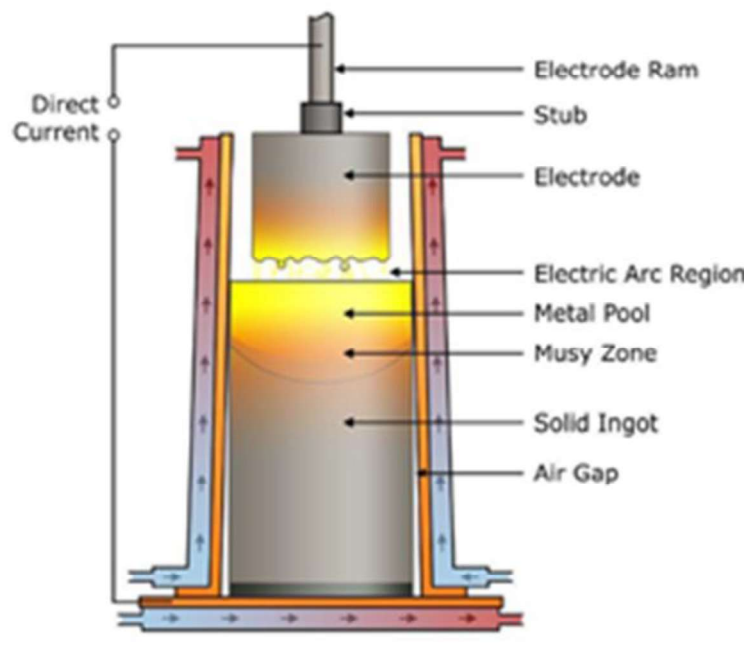
## 4. Refining and Production of Pure Nickel

The nickel obtained through previous metallurgical processes is not pure enough for certain demanding industrial applications, such as the manufacturing of high-performance alloys, electronic components, and batteries. Therefore, several refining methods are implemented to obtain high-purity nickel.

### 4.1. Vacuum Melting

Vacuum melting is a process used to remove volatile impurities and unwanted residual elements from crude nickel. This process involves heating the metal to a high temperature under reduced pressure, thus promoting the evaporation of low-boiling-point impurities.

In this process, crude nickel is placed in a refractory crucible and heated by induction or resistance under high vacuum ( $<10^{-5}$  atm). Unwanted elements such as sulfur, carbon, and certain metallic oxides are removed through evaporation or controlled chemical reactions. Once refining is complete, the molten nickel is cooled and solidified into ingots or high-purity cathodes.

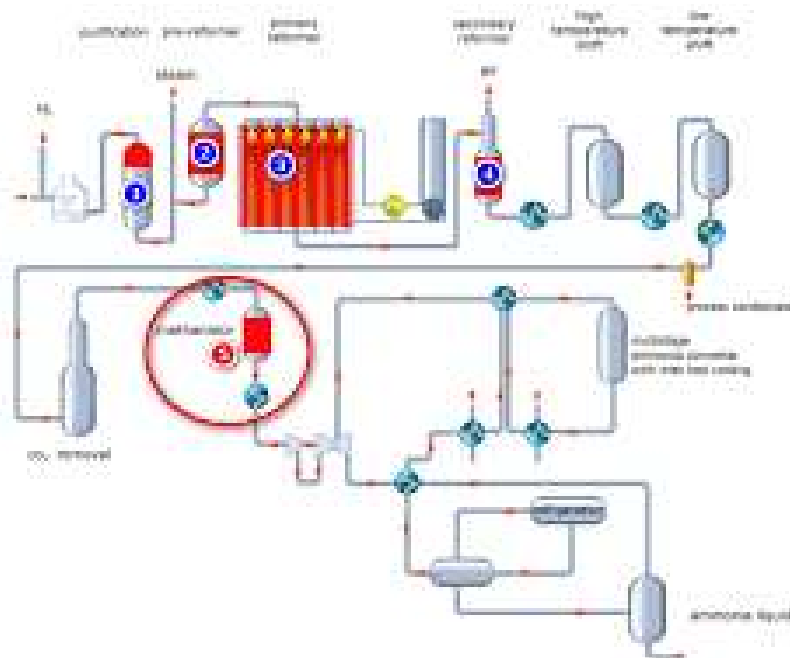


**Figure 3.16: Schematic diagram of the vacuum melting process for nickel purification.**

## 4.2. Chemical Reduction

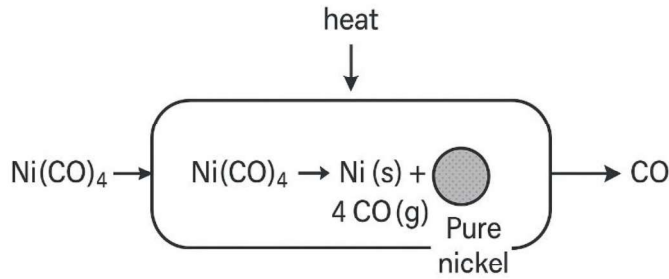
Another commonly used method is the chemical reduction of nickel in solution. This technique is mainly implemented in the Mond process, which relies on the formation of nickel carbonyl ( $\text{Ni}(\text{CO})_4$ ) at low temperatures ( $50\text{-}80^\circ\text{C}$ ). The process follows these steps:

1. Impure nickel is exposed to carbon monoxide (CO) under pressure. The nickel reacts with CO to form  $\text{Ni}(\text{CO})_4$ , a volatile compound .



**Figure 3.17: Reaction of impure nickel with carbon monoxide to form nickel carbonyl.**

2. The carbonyl gas is then heated to a higher temperature ( $\sim 200^\circ\text{C}$ ), where it decomposes into pure metallic nickel and recycled carbon monoxide .



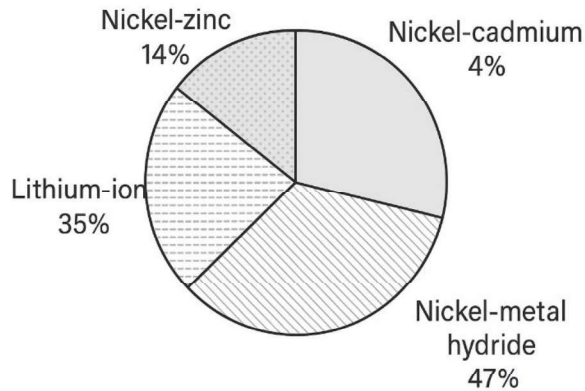
**Figure 3.18: Thermal decomposition of nickel carbonyl into pure nickel and recycled carbon monoxide.**

This process yields nickel with a purity greater than 99.9%, which is particularly suitable for applications requiring high-quality materials, such as the electronics and aerospace industries.

### 4.3. Applications of Pure Nickel

Refined nickel is used in various industries due to its remarkable mechanical and chemical properties. Its main applications include:

- **Alloys:** Nickel is a key element in the production of stainless steels and special alloys, such as superalloys used in aircraft turbines and nuclear reactors.
- **Electroplating:** Nickel is widely used to coat other metals to improve their corrosion resistance and aesthetic appearance.
- **Batteries:** Nickel is an essential component in rechargeable batteries, including Ni-Cd and Ni-MH batteries, as well as modern lithium-ion batteries containing nickel in their cathodes (Figure 4.4).



**Figure 4.4: Use of nickel in modern battery compositions.**

#### **4.4. Advanced Nickel Refining Techniques**

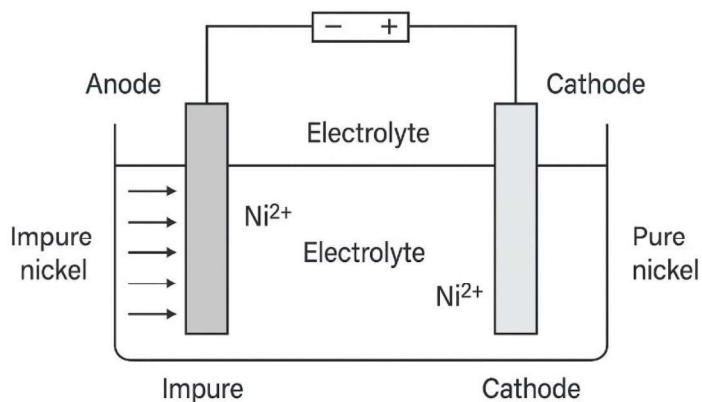
Traditional refining methods are often combined with other advanced techniques to improve efficiency and final product purity. Among these methods are:

##### **4.4.1. Electrolytic Nickel Refining**

Electrolysis is an efficient method for refining nickel on an industrial scale. Impure nickel is used as the anode and immersed in an electrolytic solution containing nickel sulfate ( $\text{NiSO}_4$ ). Under the effect of an electric current:

- $\text{Ni}^{2+}$  ions migrate to the cathode, where they are reduced to pure metallic nickel.
- Impurities remain in solution or form an anodic sludge (anode residues), which is recovered to extract other valuable metals such as copper or cobalt.

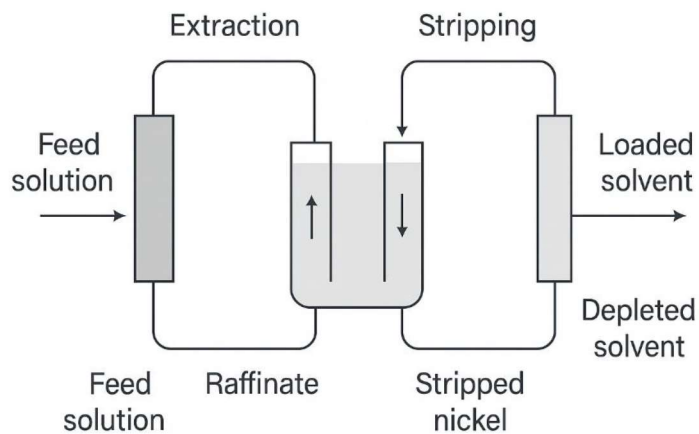
This process yields nickel with extremely high purity (>99.95%), suitable for industries requiring ultra-pure materials (Figure 4.5).



**Figure 4.5: Principle of electrolysis for nickel refining.**

#### 4.4.2. Solvent Extraction and Selective Precipitation

Solvent extraction is a method used to separate nickel from other metals present in ore or leach concentrates. It is based on the selective solubility of nickel in specific organic solvents.



**Figure 4.6: Schematic diagram of the nickel solvent extraction process.**

**The process steps include:**

1. Contacting a nickel-containing solution with a selective organic solvent.
2. Transferring  $\text{Ni}^{2+}$  ions to the organic phase.

3. Recovering nickel through chemical washing and precipitation as purified nickel hydroxide or sulfate.

This process is commonly used for the treatment of lateritic and sulfide ores.

#### 4.5. Environmental Impact and Sustainability of Nickel Refining

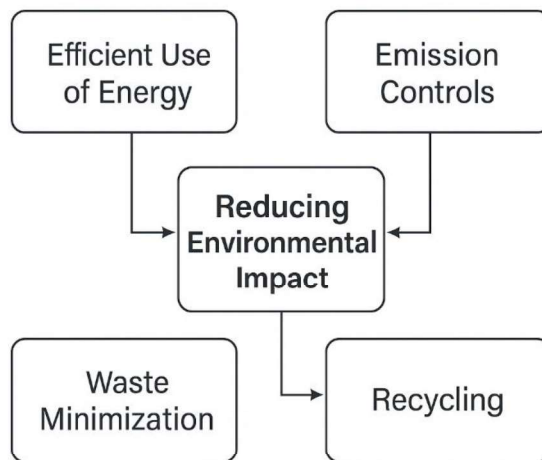
Nickel refining, while crucial to industry, presents significant environmental challenges. The main concerns include:

- **CO<sub>2</sub> and toxic gas emissions:** Thermal processes such as vacuum melting generate carbon dioxide and sulfur emissions.

- **Management of residues and anode sludge:** Electrolysis produces sludge containing heavy metals that must be treated to prevent soil and water contamination.

- **Energy consumption:** Nickel refining is an energy-intensive process requiring optimization to reduce its carbon footprint.

Efforts are underway to improve energy efficiency and recycle metallurgical waste to minimize the environmental impact of nickel refining (Figure 4.7).



**Figure 4.7: Strategies for reducing environmental impact in nickel refining.**

Nickel refining is a crucial step in ensuring a high-purity metal suitable for modern industrial requirements. Vacuum melting, chemical reduction, electrolysis, and solvent

extraction processes enable the production of exceptionally pure nickel, used in the aerospace, electronics, and energy sectors. However, the sustainability and environmental impact of these processes must be considered to develop more eco-friendly production methods.

## **I-4. Copper Production**

Copper (Cu) is a non-ferrous metal of paramount importance in various industrial sectors, including electronics, construction, energy, and transportation. Its excellent electrical and thermal conductivity, corrosion resistance, and malleability make it a preferred material for manufacturing electrical wires, heat exchangers, electronic components, and metal alloys such as brass and bronze.

Copper extraction primarily relies on the processing of sulfide ores, with chalcopyrite ( $\text{CuFeS}_2$ ) being the most abundant source. These ores require complex concentration and metallurgical extraction processes, including flotation, smelting, and electrolytic refining. Additionally, although less common, oxide ores are processed using hydrometallurgical methods such as acid leaching, solvent extraction, and electrowinning.

Given the increasing demand for copper and the environmental challenges associated with its extraction and refining, researchers strive to optimize metallurgical processes to improve efficiency, reduce ecological impact, and promote copper recycling. Innovation in these areas is essential to ensuring a sustainable supply of this strategic metal.

### **I-4. 1. The Main Copper Ores**

#### ***1.1. Chalcopyrite ( $\text{CuFeS}_2$ ) – The Primary Source of Copper***

Chalcopyrite is the most abundant and widely exploited copper ore in the metallurgical industry. It consists of copper (Cu), iron (Fe), and sulfur (S). Its copper content is approximately 34.5% by mass, making it an essential resource for global copper extraction.

It is generally associated with other metallic ores in sulfide deposits, including pyrite ( $\text{FeS}_2$ ) and sphalerite ( $\text{ZnS}$ ). Chalcopyrite is found in igneous and metamorphic rocks as well as in hydrothermal veins.

#### ***1.2. Bornite ( $\text{Cu}_5\text{FeS}_4$ ) – A Secondary but Copper-Rich Ore***

Bornite, also known as "peacock ore" due to its iridescent sheen, is a mixed copper and iron sulfide. It contains about 63% copper and is often found in the same deposits as chalcopyrite.

Although less abundant than chalcopyrite, bornite is a valuable copper source when present in exploitable quantities. It often transforms into chalcocite ( $\text{Cu}_2\text{S}$ ) due to natural alteration in enrichment zones of ore deposits.

### ***1.3. Chalcocite ( $\text{Cu}_2\text{S}$ ) – A High-Copper Ore***

Chalcocite is a sulfide ore with a very high copper content, reaching up to 79% by mass. It primarily forms in sulfide deposits through supergene enrichment processes (chemical alteration and copper migration to lower zones of the deposit).

Due to its high copper content and ease of metallurgical processing, chalcocite is highly sought after when available in sufficient quantities.

### ***1.4. Cuprite ( $\text{Cu}_2\text{O}$ ) – A Copper Oxide in Oxidized Zones***

Cuprite is a copper ore in oxide form, primarily developing in oxidized zones of sulfide deposits, where primary sulfide ores such as chalcopyrite and bornite are transformed by the action of oxygen and water.

It contains approximately 88.8% copper by mass, making it an extremely rich copper source. However, cuprite deposits are often limited in volume and less exploited than sulfides.

### ***1.5. Malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) – An Iconic Copper Carbonate***

Malachite is a hydrated copper carbonate that also forms in oxidized zones of sulfide deposits. It is easily recognizable by its characteristic green color and has historically been used as a pigment.

It contains about 57% copper by mass, and although it is an exploitable copper source, its industrial significance is lower due to the complexity of processing compared to sulfide ores.

### ***1.6. Azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ) – A Blue Ore Often Associated with Malachite***

Azurite is another copper carbonate closely related to malachite. It is identifiable by its intense blue color and is often found associated with malachite in oxidized zones of sulfide deposits.

It contains 55% copper, and while less exploited than other ores, it can serve as a secondary copper source in certain operations.

#### **I-4. 2. Global Distribution of Copper Deposits**

Copper deposits are mainly found in regions with geological formations favorable to the accumulation of sulfide and oxide ores. The largest copper reserves are located in:

Chile (Escondida Mine – the world's largest copper mine)

Peru

United States (Arizona)

Democratic Republic of the Congo

Zambia

China

Russia

Australia

#### **I-4. 3. Main Copper Ores in Algeria**

Algerian deposits primarily contain sulfide and oxide copper ores, including:

***Chalcopyrite ( $CuFeS_2$ )***: The primary copper ore, found in deposits such as those in the Hoggar region.

***Bornite ( $Cu_5FeS_4$ )***: Present in some regions of the Algerian Sahara.

***Chalcocite ( $Cu_2S$ )***: Observed in specific zones of Saharan deposits.

***Cuprite ( $Cu_2O$ )***: Found in oxidized zones of certain deposits.

***Malachite ( $Cu_2(OH)_2CO_3$ ) and Azurite ( $Cu_3(OH)_2(CO_3)_2$ )***: Copper carbonates present in oxidized zones of deposits.

#### **I-4. 4. Major Copper Deposits in Algeria and Their Estimated Reserves**

***Tan Chaffao Deposit (Hoggar)***: Contains approximately 6.6 million tons of ore with copper grades ranging from 0.56% to 1.2%, along with zinc (1.65%) and lead (0.43%).

***Bou Kaïs Deposit (Sahara)***: Estimated reserves of 50 million tons of copper ore.

**Kherzet Youcef Deposit (Sétif)**: Primarily known for its lead and zinc ores, with remaining reserves estimated at 1.6 million tons containing 18% zinc and 3.6% lead.

#### **I-4. 5. Copper Production Processes**

The production of copper from ores generally follows two main routes, depending on the type of ore being processed:

- The pyrometallurgical route, primarily used for sulfide ores (such as chalcopyrite and bornite). This process involves concentration, smelting, and refining stages to obtain high-purity copper. It is particularly suitable for high-grade ores and enables large-scale production.
- The hydrometallurgical route, employed for oxide ores or low-sulfur ores (such as malachite and azurite). It relies on chemical reactions in solution, including leaching, solvent extraction, and electrowinning, to recover copper in its pure form. This method is more environmentally friendly and suitable for low-grade ores.

The choice of process mainly depends on ore composition, economic factors, and environmental considerations.

#### **I-4. 6. Pyrometallurgical Route**

The pyrometallurgical route is mainly used to process copper sulfide ores. This high-temperature process includes several essential steps to obtain high-purity copper.

##### **I-4. 6.1. Ore Concentration**

Copper extraction begins with ore enrichment to increase the copper content and separate gangue minerals.

- Process used: Froth flotation, which separates copper sulfide minerals (chalcopyrite  $\text{CuFeS}_2$ , bornite  $\text{Cu}_5\text{FeS}_4$ , chalcocite  $\text{Cu}_2\text{S}$ , covellite  $\text{CuS}$ ) from gangue minerals (silicates, carbonates, iron oxides, etc.).
  - **Chemical reagents used:**
    - **Collectors:** Xanthates selectively adsorb copper.
    - **Frothers:** Create foam bubbles to carry copper.
    - **Depressants:** Prevent flotation of impurities.
  - **Enrichment:**

- The initial copper content (usually 0.5 - 2% Cu) is increased to 20-30% Cu in the concentrate.
- The concentrate is then filtered, dried, and sent for smelting.

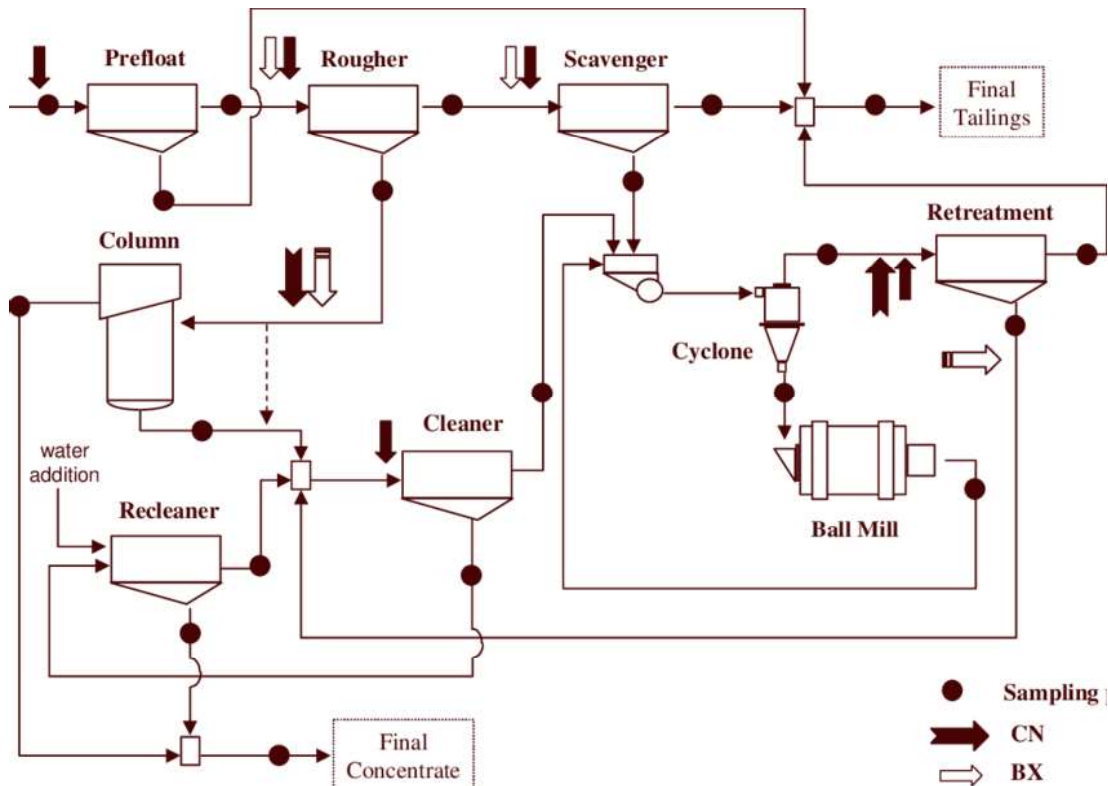


Figure I-4. 1: Diagram of the copper ore flotation process.

#### I-4. 6.2. Matte Smelting

This step involves melting the copper concentrate to separate iron and impurities as slag while obtaining a copper matte rich in  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .

- **Furnaces used:** Reverberatory furnace, flash furnace, or electric furnace.
- **Main chemical reactions:**

##### 1. *Partial oxidation of chalcopyrite:*



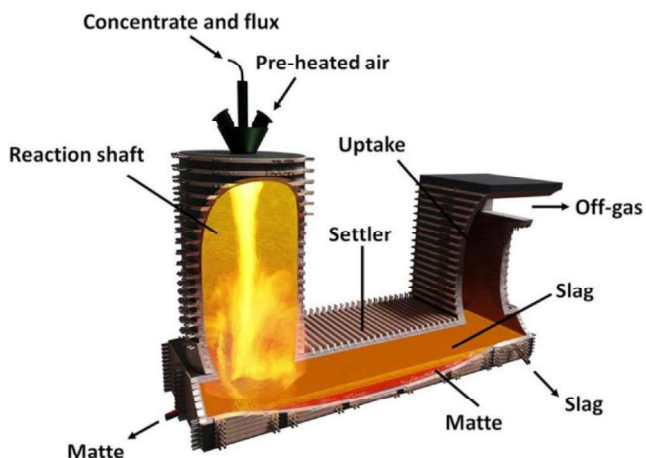
##### 2. *Iron oxidation:*



### 3. Slag formation by reaction with silica:



- **Copper content in matte:** Between 40 and 65% Cu.
- The liquid matte is then cast into molds or directed to the conversion stage.



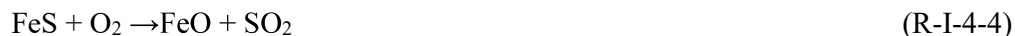
**Figure I-4. 2: Diagram of the matte smelting furnace and slag formation.**

#### I-4. 6.3. Matte Conversion into Blister Copper

The obtained matte is treated in a converter furnace (Peirce-Smith type) to remove remaining sulfur and iron.

- **Main reactions:**

1. Oxidation of remaining iron:



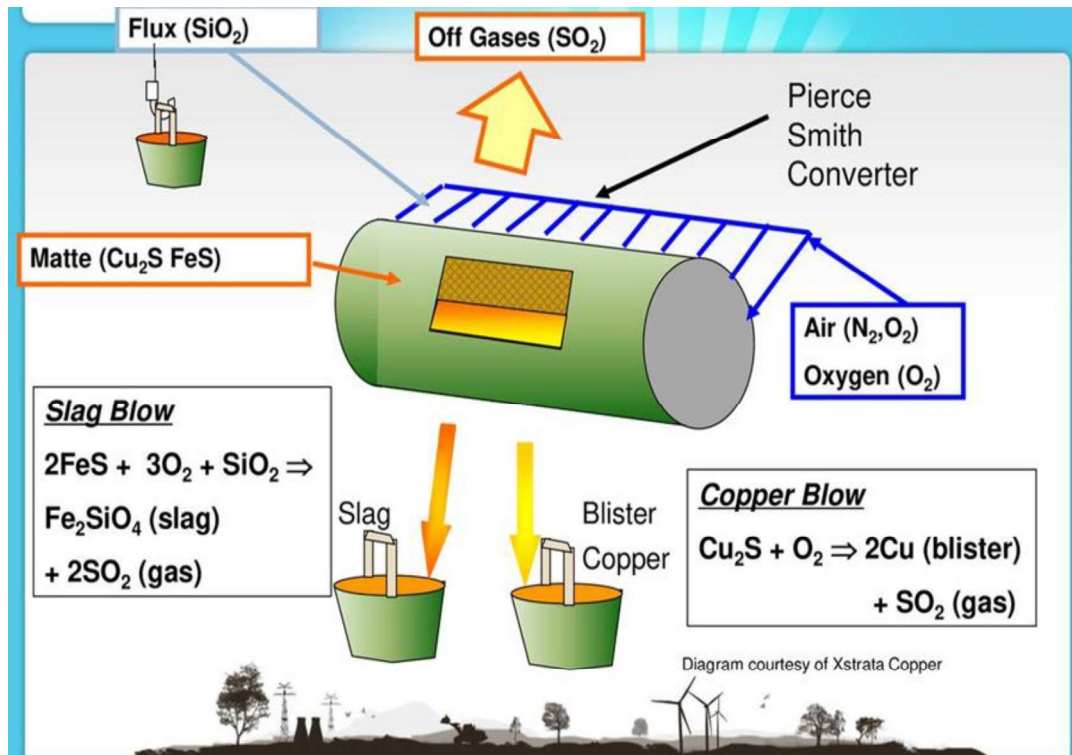
2. Oxidation of copper sulfide:



3. Reduction of  $\text{Cu}_2\text{O}$  to metallic copper:



- **Obtained copper:** "Blister" copper containing 98-99% Cu.
- The released sulfur as  $\text{SO}_2$  is captured for sulfuric acid production.



**Figure I-4. 3: Peirce-Smith converter and stages of matte conversion into blister copper**

#### **I-4. 6.4. Copper Refining**

##### **I-4. 6.4.1. Thermal Refining (Oxidation and Reduction of Impurities)**

- **Oxygenation:** Injection of oxygen to remove the last traces of iron and sulfur as oxides.
- **Reduction:** Addition of reductants such as carbon or natural gas to eliminate dissolved oxygen in the copper.
- The obtained copper is cast into anodes for the electrolytic phase.

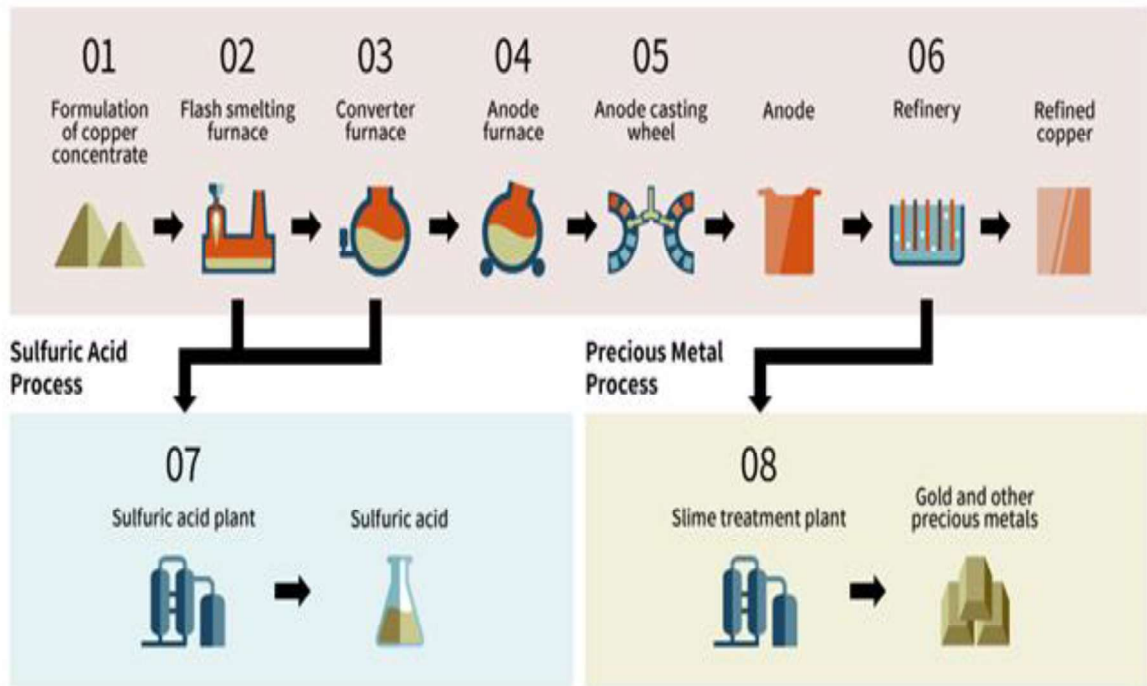
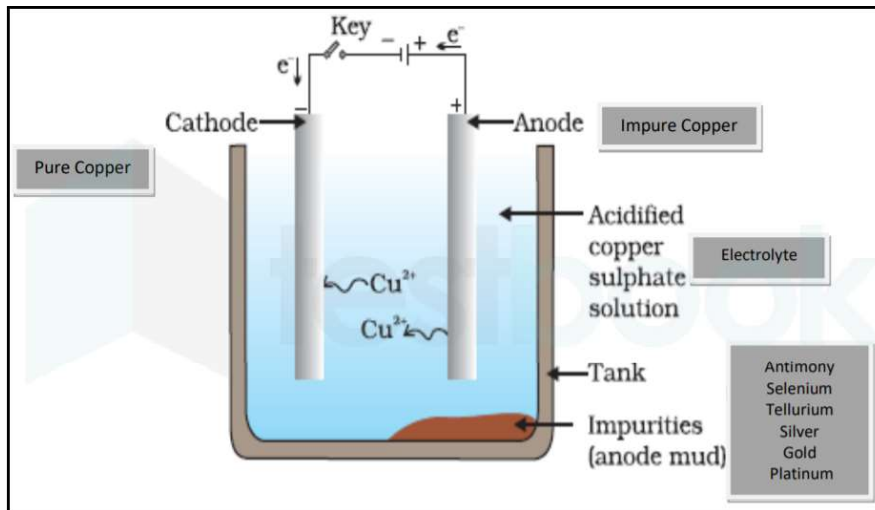


Figure I-4. 4: Illustration of copper thermal refining.

#### I-4. 6.4.2. Electrolytic Refining

- **Principle:** The obtained copper is used as an anode in a bath of copper sulfate ( $\text{CuSO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ).
- **Mechanism:**
  - The anode dissolves into the solution.
  - Pure copper is deposited at the cathode.
  - Noble impurities (Ag, Au, Pt) settle as anode sludge.
- **Refined copper obtained:** 99.99% Cu.



**Figure I-4. 5: Diagram of the copper electrolytic refining process.**

#### **I-4. 6.5. Environmental Impact and By-Product Valorization (Figure I-4. 6)**

- Sulfur dioxide (SO<sub>2</sub>) capture: Used for sulfuric acid production.
- Slag recycling: Reused in construction and cement manufacturing.
- Anode sludge valorization: Extraction of precious metals.
- Energy optimization: Improvement of smelting technologies to reduce carbon footprint.

#### **I-4. 7. Hydrometallurgical Route**

The hydrometallurgical route is widely used for the extraction of copper from oxidized ores, secondary resources, and low-sulfur residues. This method is preferred due to:

- Lower energy consumption compared to pyrometallurgy.
- Minimal environmental impact, as it reduces sulfur dioxide (SO<sub>2</sub>) emissions.
- Efficient processing of low-grade ores, making it viable for many mining operations.

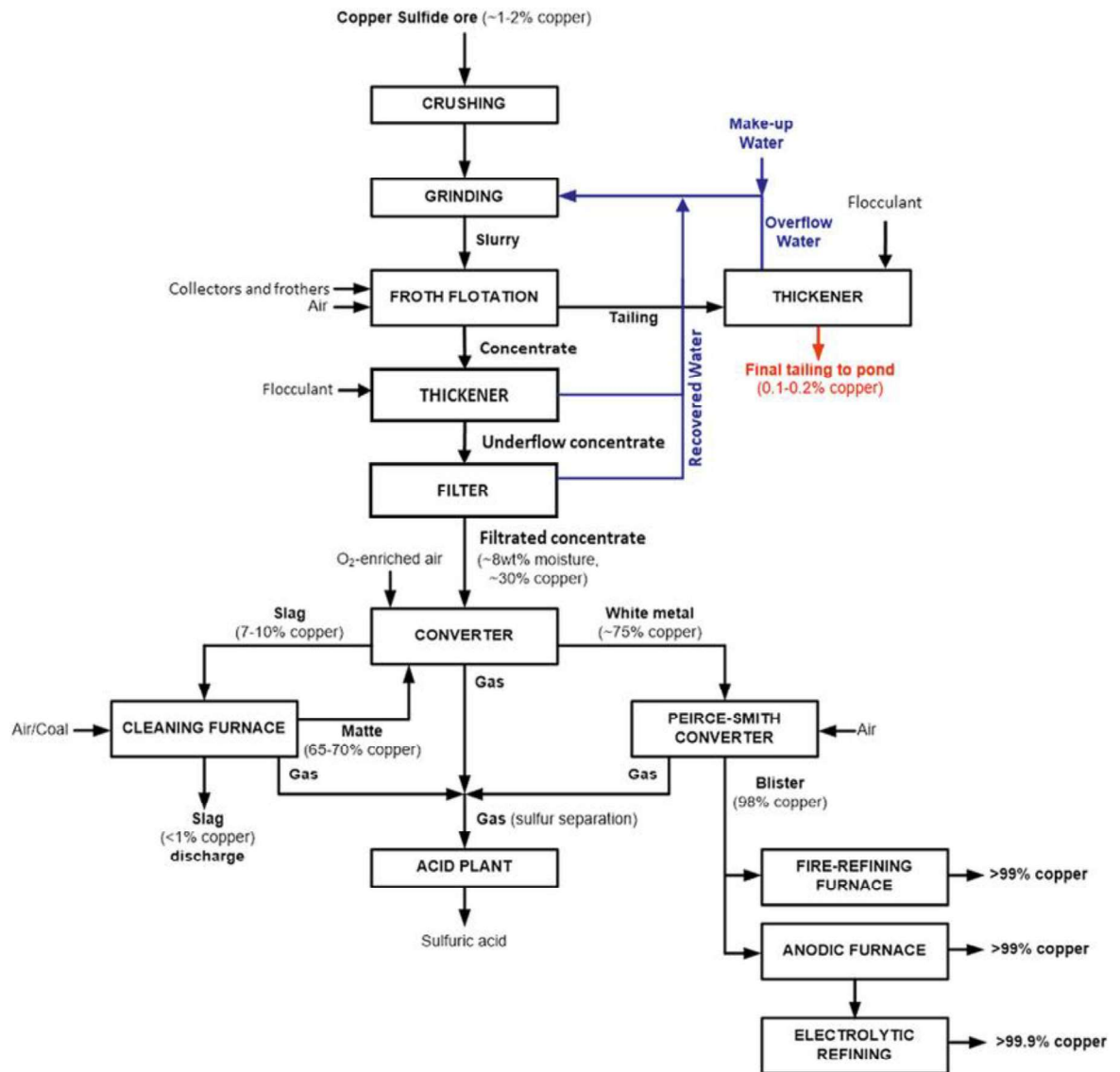


Figure I-4. 6: Management of by-products in copper pyrometallurgy.

Hydrometallurgy consists of three main stages:

1. **Leaching:** Dissolving copper from the ore into a solution.
2. **Solvent Extraction (SX):** Separating and purifying copper ions.
3. **Electrowinning (EW):** Electrochemical recovery of pure copper.

Each stage involves specific chemical reactions, operational parameters, and challenges, which will be discussed in detail below.

## **I-4. 7.1. Leaching**

Leaching is the first step of hydrometallurgy, where copper is extracted from ore using a chemical solvent. The efficiency of leaching depends on factors such as temperature, acidity, ore mineralogy, and oxidizing agents.

### **I-4. 7.1.1. Acid Leaching**

#### **Application:**

- Used for oxidized ores, including:
- Malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ )
- Chrysocolla ( $\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$ )
- Azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ )

#### **Reagent:**

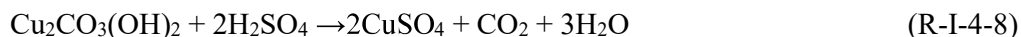
- Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is commonly used due to its ability to dissolve copper oxides efficiently.

#### **Chemical Reactions:**

##### **1. For Copper Oxide:**

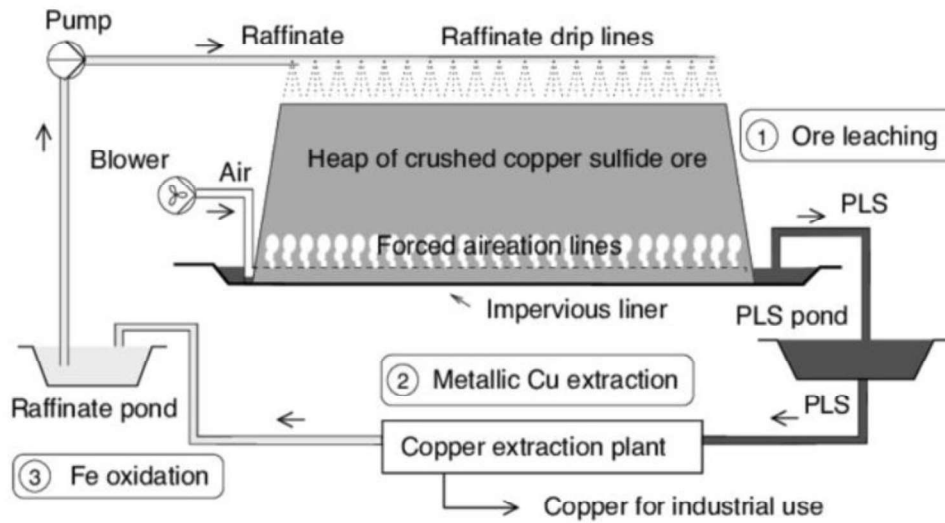


##### **2. For Malachite:**



#### **Process Optimization:**

- Higher temperature (50–90°C) accelerates dissolution.
- Fine grinding (75–150  $\mu\text{m}$ ) increases surface area for leaching.
- Controlled acid concentration (0.5–2.0 M) prevents excessive reagent consumption.



**Figure I-4. 7: Acid Leaching Process for Oxidized Copper Ores**

#### **I-4. 7.1.2. Bioleaching (Bacterial Leaching)**

Bioleaching is a microbial process that uses bacteria to oxidize sulfide ores, facilitating the release of copper ions into solution.

#### **Application:**

- Used for low-grade sulfide ores, such as:
- Chalcopyrite ( $\text{CuFeS}_2$ )
- Covellite ( $\text{CuS}$ )

#### **Key Bacteria:**

- *Acidithiobacillus ferrooxidans*
- *Leptospirillum ferrooxidans*

#### **Chemical Reactions:**

1. Oxidation of Ferrous Ions ( $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ):



2. Copper Sulfide Oxidation by Ferric Ions:



### Process Optimization:

- Aeration enhances bacterial activity.
- pH maintained at 1.5–2.5 for bacterial survival.
- Temperature controlled between 30–50°C for optimal microbial growth.

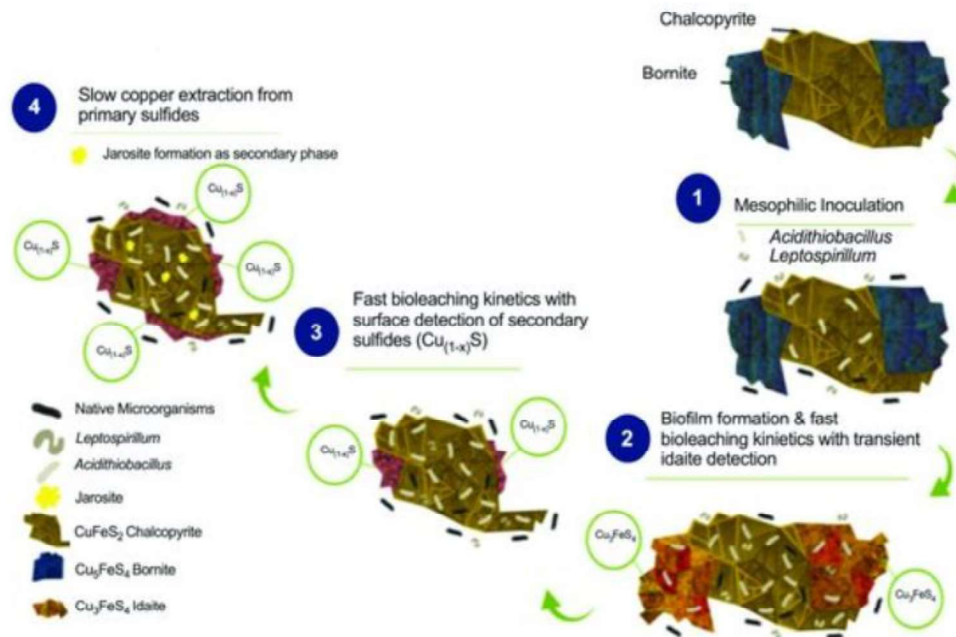


Figure I-4. 8: Bacterial Leaching of Sulfide Copper Ores

### I-4. 7.2. Solvent Extraction (SX - Solvent Extraction)

After leaching, the solution contains dissolved copper ions ( $\text{Cu}^{2+}$ ) along with impurities. Solvent extraction (SX) is used to selectively remove copper from the solution.

#### I-4. 7.2.1. Process Steps

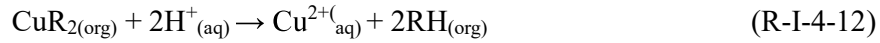
##### 1. Extraction:

- Copper ions move from the aqueous phase into an organic solvent.
- Common extractants: LIX, Acorga, Cyanex.
- Reaction:



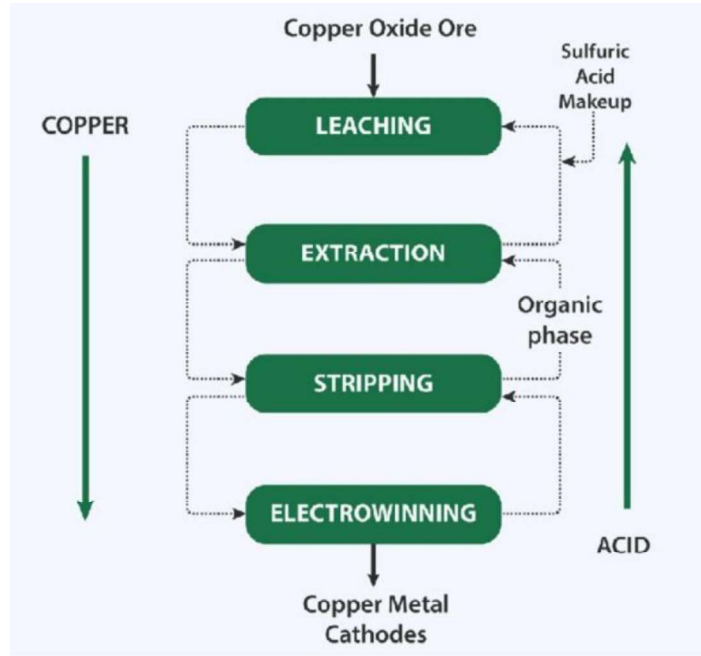
##### 2. Stripping:

- Copper is re-extracted into an acidic aqueous phase for electrowinning.
- Reaction:



### 3. Purification:

- Impurities (iron, manganese) are removed, producing a high-purity  $\text{Cu}^{2+}$  solution.



**Figure I-4. 9: Solvent Extraction Process for Copper**

#### I-4. 7.3. Electrowinning (EW - Electroextraction)

Electrowinning is an electrochemical process used to recover pure metallic copper (99.99%) from the SX solution.

##### I-4. 7.3.1. Electrochemical Reactions

###### 1. Cathodic Reaction (Copper Deposition):



###### 2. Anodic Reaction (Oxygen Formation):





**Figure I-4. 10: Electrowinning Process for Copper Recovery**

#### **I-4. 7.4. Environmental and Economic Considerations**

##### **I-4. 7.4.1. Environmental Impact**

- **Lower emissions:** No SO<sub>2</sub> pollution compared to smelting.
- **Efficient resource utilization:** Enables low-grade ore processing.
- **Wastewater treatment:** Recycles leach solutions for sustainability.

##### **I-4. 7.4.2. Economic Considerations**

- Hydrometallurgy is cost-effective for low-grade ores.
- Lower CAPEX and OPEX than smelting plants.
- **Challenges:**
  - Slow processing time in bioleaching.
  - High reagent costs in solvent extraction.

**Table I-4.1: Comparison Between Pyrometallurgical and Hydrometallurgical Copper Production**

<b>Aspect</b>	<b>Pyrometallurgical Copper Production</b>	<b>Hydrometallurgical Copper Production</b>
<b>Process</b>	Type High-temperature smelting & refining	Aqueous-based leaching & electrowinning
<b>Ore Type</b>	Sulfide ores (chalcopyrite, bornite)	Oxide ores (malachite, azurite) & some low-grade sulfides
<b>Main Steps</b>	Crushing → Concentration → Smelting → Converting → Refining	Leaching → Solvent Extraction (SX) → Electrowinning (EW)
<b>Energy Consumption</b>	High (due to smelting & refining)	Lower (ambient or moderate temperatures)
<b>Copper Recovery Rate</b>	High (80-90%)	Moderate (60-70%)
<b>Environmental Impact</b>	High emissions (SO <sub>2</sub> , CO <sub>2</sub> )	Lower emissions, but risks of leachate contamination
<b>Capital Cost</b>	High (large-scale smelters required)	Lower (simpler plant setup)
<b>Operating Cost</b>	Lower per ton for high-grade ores	Can be higher for complex ores
<b>Suitability</b>	Best for high-grade sulfide ores	Best for low-grade ores & heap leaching

## **I-5. Elaboration of Zinc**

### **1. Introduction**

Zinc (Zn) is one of the most important non-ferrous metals in modern industry. It is used in galvanization, die-casting alloys, the manufacture of brass and bronze, batteries, and various chemical reagents. The metal's unique ability to provide cathodic protection makes it indispensable in the fight against corrosion. Beyond its protective role, zinc contributes to the global economy as a strategic resource for energy transition technologies, including electric-vehicle batteries and renewable-energy storage.

Zinc production relies primarily on mineral concentrates derived from sulfide and carbonate ores. Globally, major producers include China, Australia, Peru, and the United States. In Algeria, significant occurrences exist in Bou Kaïs (Sahara), Kherzet Youcef (Sétif) and Tan Chaffao (Hoggar), where zinc minerals are often associated with lead, copper, and cadmium. Developing these deposits could support national industrial diversification and create a domestic metallurgical chain.

### **2. Zinc Ores and Mineralogical Species**

In nature, zinc occurs mainly in sulfide, oxide, and carbonate forms. The most common minerals are:

- *Sphalerite (ZnS)* – the principal source of zinc worldwide, containing 67 % Zn by mass.
- *Willemite (Zn<sub>2</sub>SiO<sub>4</sub>)* – a zinc silicate typical of oxidized deposits.
- *Zincite (ZnO)* – a natural oxide found in metamorphic environments.
- *Smithsonite (ZnCO<sub>3</sub>)* – a secondary carbonate formed during weathering.
- *Franklinite (ZnFe<sub>2</sub>O<sub>4</sub>)* – a spinel-type zinc-iron oxide.
- Hemimorphite (Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>·H<sub>2</sub>O) – a hydrated zinc silicate.
- *Marmatite ((Zn,Fe)S)* – an iron-rich variety of sphalerite.

Among these, sphalerite is the most economically important, representing nearly 90 % of global zinc reserves. In Algeria, sphalerite frequently coexists with galena (PbS) and

chalcopyrite ( $\text{CuFeS}_2$ ). These polymetallic ores provide not only zinc but also valuable by-products such as silver and germanium.

### 3. Ore Concentration

Once mined, zinc ores undergo concentration to separate valuable minerals from gangue. The main method is froth flotation, preceded by crushing and grinding to liberate particles.

#### 3.1 Principle of Flotation

In a flotation cell, the finely ground ore is mixed with water and reagents: collectors (xanthates) make zinc surfaces hydrophobic, frothers stabilize bubbles, and modifiers adjust pH. Air injection produces bubbles that selectively carry zinc particles to the surface as froth. The froth is skimmed, dried, and filtered to yield a concentrate containing 40–60 % Zn.

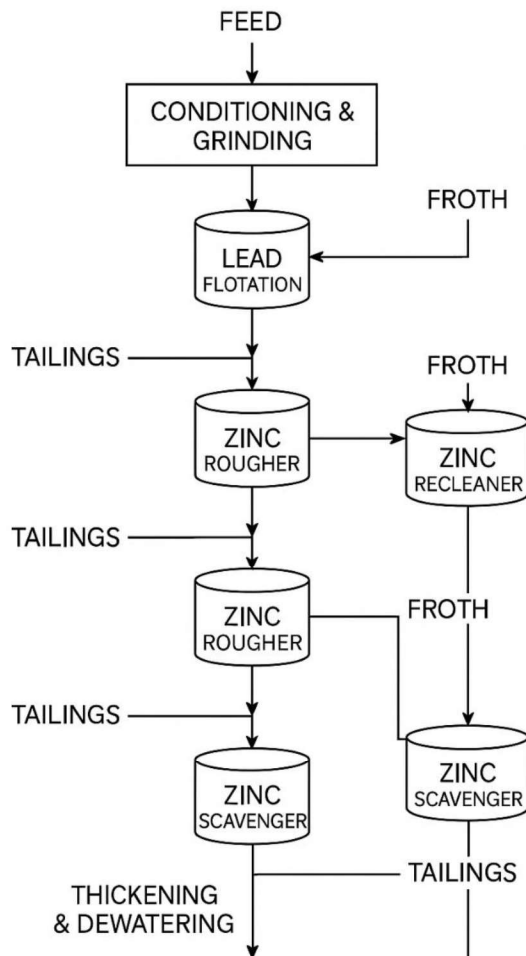


Figure I-5-1 – Flotation Circuit for Lead–Zinc Ores.

### 3.2 Selective Separation

Depressants such as sodium cyanide can suppress galena flotation, allowing selective recovery of sphalerite. Conversely, activators like  $\text{CuSO}_4$  promote sphalerite flotation by forming a thin copper-sulfide film on the mineral surface. This selectivity enables efficient processing of polymetallic ores typical of Algerian deposits.

## 4. Pyrometallurgical Process

The pyrometallurgical route converts zinc concentrates into metallic zinc through high-temperature reactions: roasting, reduction, and refining. It remains suitable for high-grade sulfide concentrates despite being energy-intensive.

### 4.1 Roasting of Zinc Sulfides

Roasting converts  $\text{ZnS}$  to  $\text{ZnO}$  by controlled oxidation in multiple-hearth or fluidized-bed furnaces operating at 910–980 °C:



The solid product, calcine, contains mainly  $\text{ZnO}$ . Evolved  $\text{SO}_2$  gas is captured for sulfuric-acid production, reducing atmospheric pollution.

### 4.2 Reduction of Zinc Oxide

The reduction step uses carbon monoxide as a reducing agent:



At approximately 1300 °C in vertical retorts or blast furnaces, zinc vapor forms and is condensed to liquid zinc. Fluxes such as silica and limestone are added to melt the gangue, forming a slag easily separated from the metal.

### 4.3 Refining of Crude Zinc

Crude zinc from reduction contains impurities (Fe, Pb, Cd). Refining involves liquation and distillation. Liquation separates metals based on solubility in molten lead, while fractional distillation isolates metals according to their boiling points.

This yields zinc of  $\geq 99.95\%$  purity. The process may follow the ISP (Imperial Smelting Process), where lead and zinc are simultaneously recovered from mixed concentrates.

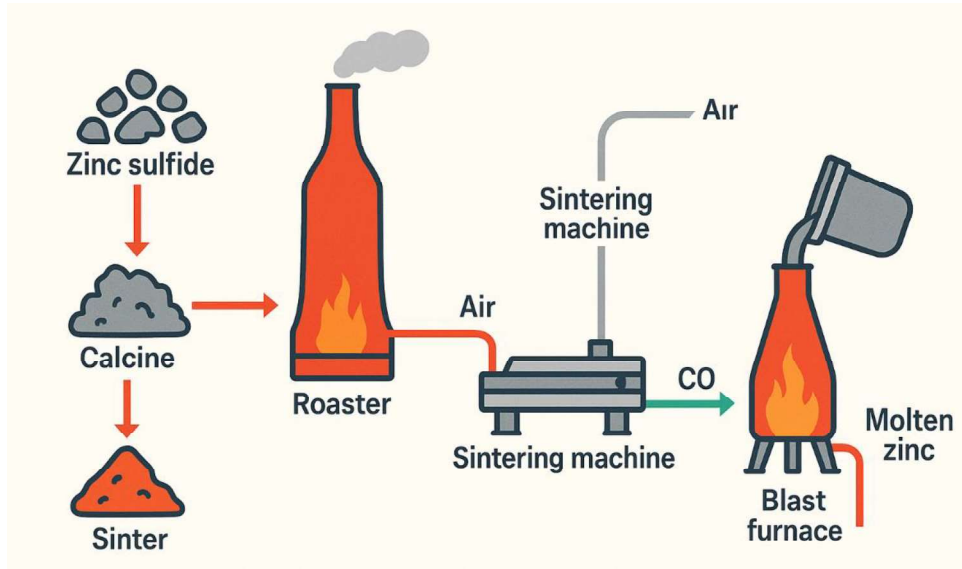


Figure I-5-2 – Flow Diagram of Zinc Pyrometallurgical Process.

### 5. Energy and Process Control

Modern zinc smelters employ heat-recovery systems and oxygen-enriched air to optimize combustion. Temperature control is critical: below 950 °C, oxidation is incomplete; above 1000 °C, sintering of ZnO particles reduces surface area. Energy integration between roasting and acid-plant units minimizes fuel consumption.

### 6. Summary of Pyrometallurgical Route

Table I-5-1: Summary of the Main Stages of the Zinc Pyrometallurgical Process

Stage	Purpose	Temperature (°C)	Main Reaction
<b>Roasting</b>	Convert ZnS to ZnO	910–980	$ZnS + 3/2 O_2 \rightarrow ZnO + SO_2$
<b>Reduction</b>	Produce Zn vapor	1200–1350	$ZnO + CO \rightarrow Zn + CO_2$
<b>Condensation</b>	Recover liquid Zn	420–500	$Zn(g) \rightarrow Zn(l)$
<b>Refining</b>	Purify metal	>600	Phase separation

## **7. Industrial Example – Bou Kaïs Deposit (Algeria)**

At Bou Kaïs, zinc and lead sulfide ores of approximately 50 million tons contain 1.5–2 % Zn and 1–3 % Pb. A pilot study conducted by Algerian geological services suggested a flotation-smelting sequence similar to that used in the ISP process. Local limestone could serve as flux, and SO<sub>2</sub> from roasting could feed a regional acid plant for fertilizer production.

Pyrometallurgy transforms zinc sulfides into pure metal through well-defined high-temperature reactions. Although gradually supplanted by hydrometallurgy, it remains essential for complex concentrates and integrated lead–zinc operations. The Algerian context offers favorable conditions for adopting modern pyrometallurgical technologies linked to local acid and energy networks.

### **Hydrometallurgy**

Hydrometallurgy is the most widespread method for industrial zinc production today. This process is based on the dissolution of zinc oxide (calcine) in aqueous solutions, followed by purification and electrolysis. Hydrometallurgy offers several advantages: lower energy consumption, higher metal purity, and reduced atmospheric pollution compared to pyrometallurgy.

#### **1. Principle of Hydrometallurgical Processing**

The hydrometallurgical process involves three major stages: leaching, purification, and electrolysis. Leaching dissolves zinc oxide into a sulfate solution, purification removes metallic impurities, and electrolysis recovers pure zinc by electrodeposition.

This method is especially adapted for oxidized ores and roasted concentrates. The general reactions are carried out in aqueous media, where zinc oxide reacts with sulfuric acid to form zinc sulfate (ZnSO<sub>4</sub>), which is then subjected to electrolysis.

#### **2. Leaching**

Leaching is the process of dissolving zinc oxide (calcine) into a sulfuric acid solution. It can be carried out in two modes: neutral and acid leaching.

## 2.1 Neutral Leaching

Neutral leaching is conducted at moderate acidity and temperature (60–80 °C). It dissolves the bulk of the zinc oxide according to the following reaction:



This reaction is exothermic and rapid under well-agitated conditions. The resulting solution is rich in ZnSO<sub>4</sub> and contains impurities such as Fe<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> that must be removed during purification.

## 2.2 Acid Leaching

Acid leaching treats residues from neutral leaching to recover additional zinc. This step increases the overall metal yield. It is carried out at lower pH (around 1.5) and higher temperature (80–90 °C):



Iron impurities are oxidized to Fe<sup>3+</sup> and precipitated as Fe(OH)<sub>3</sub>. Additives such as MnO<sub>2</sub> or KMnO<sub>4</sub> are introduced to oxidize any remaining ZnS. Figure I-5-3 illustrates the hydrometallurgical flow of zinc leaching and solid–liquid separation.

## 3. Purification

After leaching, the zinc sulfate solution contains unwanted impurities (Cu, Cd, Co, Ni). These must be removed to prevent contamination of cathodic zinc. Purification is achieved by cementation using zinc dust and by filtration.

### 3.1 Cementation

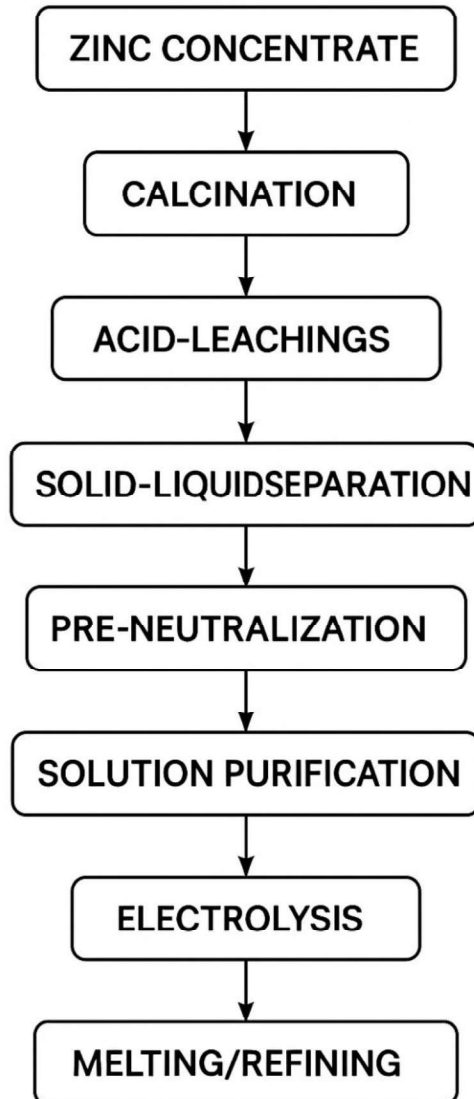
Cementation is a redox process where more noble metals are displaced from solution by metallic zinc according to reactions such as:



This operation removes copper, cadmium, cobalt, and nickel impurities. The solid products (cement residues) are filtered and washed. The purified electrolyte is then ready for electrolysis.

### 3.2 Filtration and Repulping

Filtration eliminates suspended particles and cementation residues. Repulping may follow to treat solid decants in order to recover residual zinc and other metals. The resulting zinc sulfate solution should have purity exceeding 99.9 % to ensure smooth electrolysis.



**Figure I-5-3 – Hydrometallurgical Leaching and Separation of Zinc Solutions.**

### 4. Electrolysis

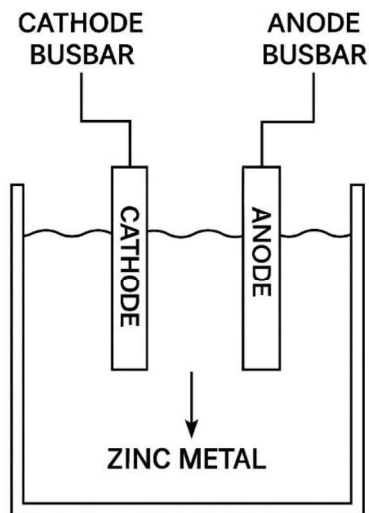
Electrolysis transforms the purified  $ZnSO_4$  solution into metallic zinc by applying direct current. This stage produces high-purity zinc (99.99 %) and oxygen gas as a by-product.

#### 4.1 Principle and Reactions



The electrolyte contains 150–200 g/L  $\text{ZnSO}_4$  and 50–100 g/L  $\text{H}_2\text{SO}_4$ . The process operates at about 35 °C. Oxygen released at the anode is vented, and metallic zinc is deposited on aluminum cathodes.

After deposition, cathodes are stripped, melted, and cast into ingots. The overall current efficiency reaches 90–95 %. Energy consumption typically ranges from 3200 to 3600 kWh per ton of zinc.



**Figure I-5-4 – Electrolytic Cell for Zinc Refining.**

#### 4.2 Cell Design

A typical electrolytic cell is rectangular, equipped with alternating aluminum cathodes and lead-silver alloy anodes. The spacing between electrodes (30–40 mm) ensures efficient current distribution. The cells are connected in series and powered by low-voltage DC.

## 5. Comparison of Pyrometallurgical and Hydrometallurgical Routes

**Table I-5-2: Comparison between Pyrometallurgical and Hydrometallurgical Routes for Zinc Production**

Aspect	Pyrometallurgy	Hydrometallurgy
<b>Ore Type</b>	Sulfide ores	Oxide and roasted ores
<b>Energy Requirement</b>	High (smelting)	Low (electrolysis)
<b>Metal Purity</b>	99.95%	99.99%
<b>Pollution</b>	SO <sub>2</sub> emissions	Low gaseous emissions
<b>Main Product</b>	Molten zinc	Electrolytic zinc
<b>Best Use</b>	High-grade ores	Low-grade or oxidized ores

## 6. Industrial Example – Kherzet Youcef (Algeria)

The Kherzet Youcef deposit in Sétif province hosts lead–zinc ores with high carbonate content. Preliminary studies suggest that hydrometallurgical processing, particularly leaching and electrolysis, is economically viable due to the proximity of sulfuric-acid supply and low energy cost. This makes hydrometallurgy an appropriate method for future Algerian zinc production plants.

Hydrometallurgy provides an efficient and environmentally friendly method for zinc production. It allows processing of low-grade and complex ores while producing high-purity zinc metal. For Algeria, adopting hydrometallurgical technology represents a sustainable strategy for developing local mineral resources.

### Environmental Aspects, Algerian Context & Conclusion

#### 1. Environmental Management in Zinc Refining

Modern zinc metallurgy places a strong emphasis on environmental protection and sustainable resource management. Both pyrometallurgical and hydrometallurgical processes have potential environmental impacts, but through proper engineering controls, these effects can be minimized or even converted into valuable by-products.

The main environmental issues in zinc production arise from sulfur dioxide emissions during roasting, solid waste generation, and wastewater contamination. New technologies focus on the recovery, recycling, and safe disposal of process residues.

### **1.1 Control of Sulfur Dioxide (SO<sub>2</sub>) Emissions**

Sulfur dioxide (SO<sub>2</sub>) gas, generated during roasting of zinc sulfide concentrates, is one of the most critical pollutants. In modern plants, SO<sub>2</sub> is not vented directly into the atmosphere; instead, it is captured and converted into sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) in contact acid plants. The reaction chain is as follows:



This integration between roasting and acid plants not only eliminates toxic emissions but also produces sulfuric acid as a valuable by-product for fertilizer and chemical industries. In this way, a closed-loop environmental and economic system is established.

### **1.2 Slag and Solid Waste Management**

Slags produced during reduction and refining contain oxides of Fe, Si, Ca, and Al. These materials are non-toxic when stabilized and can be repurposed in the construction industry as aggregates or cement additives. Metallic residues from purification and electrolysis are recycled internally to recover zinc, copper, and cadmium.

In hydrometallurgy, jarosite and goethite residues (iron hydroxides) are filtered, neutralized with lime, and stored safely in tailing facilities with impermeable barriers to prevent leaching into groundwater.

### **1.3 Wastewater Treatment and Recycling**

Effluents from leaching, purification, and electrolysis contain sulfates, metals, and acid traces. Treatment is performed in several stages: neutralization with lime, precipitation of heavy metals, and filtration. The treated water is often recycled back into the process, reducing overall water consumption by up to 90 %.

Advanced treatment methods such as ion exchange, membrane filtration, and reverse osmosis are increasingly adopted in modern zinc refineries. This allows near-zero liquid discharge (ZLD) operation, a major step toward sustainable metallurgy.

## **2. Energy Recovery and Circular Economy**

Energy recovery plays a vital role in reducing operational costs and minimizing greenhouse gas emissions. Heat generated during roasting and acid production is recovered

through waste-heat boilers to generate steam and electricity. This cogeneration reduces fossil fuel dependency.

Circular economy principles are applied to reintroduce process by-products into the production cycle. For instance, sulfuric acid from SO<sub>2</sub> recovery is reused in leaching, while zinc dust from purification can serve in cementation reactions. Such integration creates a nearly closed metallurgical circuit.

### **3. Zinc Metallurgy in Algeria**

Algeria holds significant potential for zinc production due to its polymetallic deposits. The most studied sites include Bou Kaïs (in the southwest), Kherzet Youcef (in the east), and Tan Chaffao (in the Hoggar region). Each site exhibits distinct geological characteristics influencing the choice of metallurgical process.

#### **3.1 Bou Kaïs Deposit**

The Bou Kaïs deposit consists of stratiform lead–zinc ores with an average grade of 2 % Zn and 1.5 % Pb. Pilot-scale flotation tests demonstrated the feasibility of producing high-quality zinc and lead concentrates. A combined roasting–acid plant is proposed to recover sulfuric acid and supply fertilizer industries in southwestern Algeria.

#### **3.2 Kherzet Youcef Deposit**

Located in Sétif province, Kherzet Youcef hosts carbonate-type ores with sphalerite and smithsonite as dominant minerals. The proximity to industrial infrastructures and the availability of limestone fluxes make it ideal for hydrometallurgical processing. An integrated leaching–electrolysis unit could produce zinc metal of 99.99 % purity for domestic consumption and export.

#### **3.3 Tan Chaffao Deposit**

In the Hoggar region, Tan Chaffao exhibits complex sulfide mineralization associated with copper and silver. Due to its remote location, modular processing units powered by renewable energy sources (solar PV) are being considered. This represents a promising model for decentralized, low-carbon zinc production in desert regions.

#### **4. Green and Digital Metallurgy**

The zinc industry is evolving toward greener and smarter production systems. Future metallurgical plants will integrate artificial intelligence (AI) for process control, predictive maintenance, and energy optimization. Automation will ensure real-time monitoring of emissions and resource efficiency.

Research is increasingly focusing on bioleaching and microbial-assisted extraction, which replace chemical reagents with naturally occurring bacteria. Electrowinning cells are also being redesigned to improve current efficiency and reduce energy demand.

In Algeria, collaboration between universities, geological institutes, and industrial partners will be key to developing a sustainable zinc sector based on innovation, training, and circular economy principles.

Zinc production through pyrometallurgical and hydrometallurgical routes forms a cornerstone of modern metallurgy. While pyrometallurgy offers robustness for sulfide ores, hydrometallurgy provides higher efficiency and environmental performance. Integrating both technologies with effective environmental management ensures sustainable and profitable zinc production.

For Algeria, the valorization of zinc deposits represents a strategic opportunity to diversify its mining sector, reduce imports, and promote industrial development. With its significant mineral potential and access to renewable energy, Algeria is well positioned to establish a new generation of eco-efficient metallurgical plants.

#### **6. Review Questions for Students**

1. What are the main environmental impacts of zinc production and how are they mitigated?
2. Explain the role of sulfuric acid recovery in sustainable zinc metallurgy.
3. Compare the environmental footprint of pyrometallurgical and hydrometallurgical processes.
4. Describe how energy recovery contributes to circular economy principles.
5. Discuss the potential for zinc production in Algeria and the advantages of each deposit type.

## **I-6. Elaboration of Titanium and Zirconium**

### **1. Introduction**

Titanium (Ti) and Zirconium (Zr) are two strategic transition metals widely used in advanced technologies due to their remarkable combination of low density, high mechanical strength, and exceptional corrosion resistance. Both metals play key roles in aerospace engineering, nuclear reactors, biomedical devices, and chemical processing industries.

Titanium, the ninth most abundant element in the Earth's crust, occurs primarily as oxides in heavy mineral sands. Zirconium, though less abundant, is valued for its excellent resistance to heat and chemical attack, especially in nuclear fuel cladding. Together, they represent the foundation of modern high-performance metallurgy.

The elaboration of titanium and zirconium involves complex metallurgical processes. These metals cannot be reduced directly from their oxides using carbon, as this would form carbides. Instead, chlorination and reduction by reactive metals or hydrogen are used to obtain pure titanium and zirconium.

### **2. Mineralogical Sources of Titanium and Zirconium**

Titanium is mainly extracted from two minerals: ilmenite ( $\text{FeTiO}_3$ ) and rutile ( $\text{TiO}_2$ ). Zirconium is derived from zircon ( $\text{ZrSiO}_4$ ) and, to a lesser extent, baddeleyite ( $\text{ZrO}_2$ ). These minerals are concentrated in placer deposits formed by weathering and erosion of igneous rocks.

#### **2.1 Titanium Minerals**

- ***Ilmenite ( $\text{FeTiO}_3$ ):*** The most abundant titanium-bearing mineral, found in beach sands and layered igneous complexes. It contains 40–60 %  $\text{TiO}_2$  and is the main raw material for titanium dioxide pigments and metal production.

- ***Rutile ( $\text{TiO}_2$ ):*** The most valuable titanium mineral, containing up to 95 %  $\text{TiO}_2$ . It is used directly in the Kroll process after chlorination.

- ***Anatase and Leucoxene:*** Secondary alteration products of ilmenite found in tropical deposits.

## 2.2 Zirconium Minerals

- **Zircon ( $ZrSiO_4$ ):** The principal ore of zirconium, often associated with ilmenite and rutile in heavy mineral sands. It typically contains 66–67 %  $ZrO_2$  equivalent.

- **Baddeleyite ( $ZrO_2$ ):** A rare natural form of zirconium dioxide found in carbonatite and alkaline rock complexes, mainly mined in Brazil and Russia.

Zirconium ores frequently contain small amounts of hafnium (Hf), which must be separated for nuclear applications due to hafnium's high neutron absorption cross-section.

## 3. Concentration of Titanium and Zirconium Minerals

The beneficiation of titanium and zirconium ores aims to separate heavy valuable minerals from lighter gangue materials such as quartz and feldspar. This process employs gravity, magnetic, and electrostatic separation methods, depending on the physical properties of the minerals.

### 3.1 Gravity Separation

In placer deposits, heavy mineral sands are first concentrated using gravity separation techniques such as spirals, shaking tables, and sluices. Due to their higher density (4–5  $g/cm^3$ ), ilmenite, rutile, and zircon are easily recovered from quartz sand (2.65  $g/cm^3$ ).

### 3.2 Magnetic and Electrostatic Separation

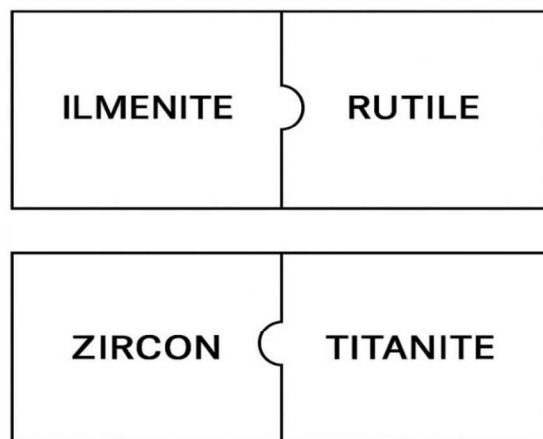
Magnetic separation is used to remove strongly magnetic minerals like magnetite and to separate ilmenite (weakly magnetic) from non-magnetic rutile and zircon. Subsequent electrostatic separation distinguishes conductive minerals (ilmenite, rutile) from non-conductive ones (zircon, quartz). This yields three principal concentrates: ilmenite, rutile, and zircon.

## 4. Mineral Sands in Algeria

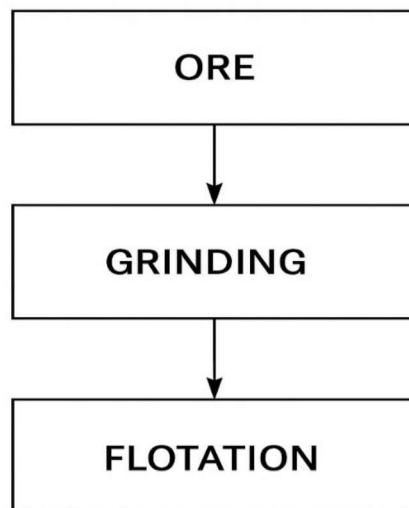
In Algeria, titanium- and zirconium-bearing sands are found mainly in the Hoggar region and in the Oued Saoura basin. Preliminary geological surveys conducted by the National Agency of Mining Activities (ANAM) have identified placer deposits containing ilmenite, rutile, and zircon. These resources represent a potential for developing a local industry for titanium dioxide pigments and refractory materials.

The exploitation of these deposits could support Algeria’s economic diversification and provide raw materials for aerospace, nuclear, and energy applications. Pilot studies have proposed gravity and magnetic separation plants near Bechar and Tamanrasset.

Titanium and zirconium occur naturally in oxide and silicate forms, often within placer deposits rich in heavy minerals. Their extraction begins with physical concentration processes—gravity, magnetic, and electrostatic separation—before chemical treatment. Algeria holds promising mineral sands that could supply future metallurgical industries for titanium dioxide and zirconium compounds.



**Figure I-6-1 – Mineral Forms of Titanium and Zirconium.**



**Figure I-6-2 – Flowchart of Mineral Concentration for Titanium and Zirconium Ores.**

## Pyrometallurgical and Chlorination Processes

### 1. Introduction

The extraction of titanium and zirconium metals from their oxides is not straightforward. Unlike most base metals, titanium and zirconium cannot be reduced directly with carbon, since both elements form stable carbides (TiC and ZrC). Therefore, special metallurgical routes based on chlorination and reduction by active metals or hydrogen are employed. Two major industrial processes dominate: the Kroll process for titanium and the Van Arkel–de Boer process for zirconium purification.

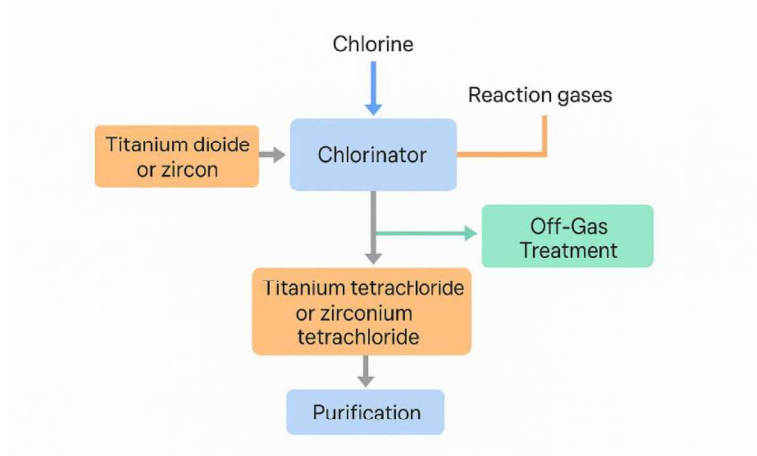
### 2. Chlorination of Titanium and Zirconium Oxides

Before reduction, titanium dioxide (TiO<sub>2</sub>) and zirconium dioxide (ZrO<sub>2</sub>) are converted into volatile tetrachlorides (TiCl<sub>4</sub> and ZrCl<sub>4</sub>). This transformation facilitates purification and later reduction into pure metal. The chlorination step is carried out in a fluidized-bed reactor at 900–1000 °C, using chlorine gas and a reducing agent such as coke.

**The main reactions are as follows:**



The resulting chlorides are gaseous at these temperatures (boiling points: TiCl<sub>4</sub> = 136°C, ZrCl<sub>4</sub> = 331 °C) and are subsequently condensed and purified by fractional distillation to remove impurities such as FeCl<sub>3</sub> and SiCl<sub>4</sub>.



**Figure I-6-3 – Flowchart of the Chlorination Process for Titanium and Zirconium.**

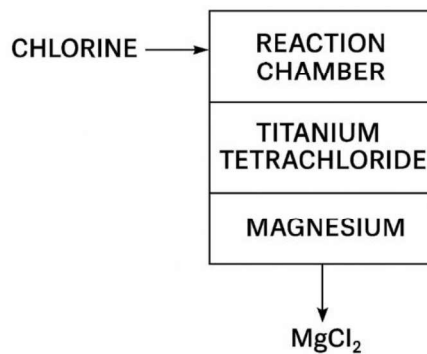
### 3. The Kroll Process for Titanium Production

Developed by William Kroll in 1940, this process remains the main industrial route for titanium production. It involves the reduction of titanium tetrachloride ( $\text{TiCl}_4$ ) by magnesium in an inert atmosphere (argon) at 900–950 °C.



The reaction takes place in a stainless steel retort. Liquid magnesium reacts with gaseous  $\text{TiCl}_4$  to produce solid titanium (in sponge form) and magnesium chloride (a by-product). The sponge titanium is then leached in hydrochloric acid to remove  $\text{MgCl}_2$  residues and vacuum-dried.

The titanium sponge is later melted under vacuum or argon atmosphere in an electric arc furnace to form ingots of high-purity titanium. The final product has a purity exceeding 99.5 %.



**Figure I-6-4 – Schematic Diagram of the Kroll Process for Titanium.**

### 4. Alternative and Emerging Titanium Processes

Before the Kroll process, the Hunter process (using sodium as a reductant) was used:



While efficient, the Hunter process is costlier due to sodium handling difficulties. A more recent method, the FFC Cambridge process, uses electrochemical reduction of solid  $\text{TiO}_2$  directly in molten calcium chloride ( $\text{CaCl}_2$ ) at 900 °C:

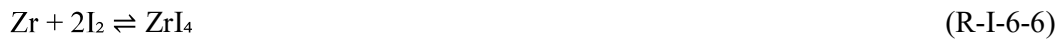


This process is being developed as a potential low-cost and environmentally friendly alternative to the Kroll process, since it avoids chlorine gas and uses electricity instead of chemical reducing agents.

### 5. The Van Arkel–de Boer Process for Zirconium Purification

Zirconium metal is initially produced from zirconium tetrachloride ( $ZrCl_4$ ) by reduction with magnesium or sodium, similar to titanium. However, to obtain ultra-pure zirconium (especially for nuclear applications), the Van Arkel–de Boer process is used.

This process, developed in 1925, is based on the reversible formation and decomposition of zirconium tetraiodide ( $ZrI_4$ ):



At about 200 °C, impure zirconium reacts with iodine vapor to form  $ZrI_4$  gas. The gaseous compound then decomposes on a heated tungsten filament at 1300 °C, depositing pure metallic zirconium while releasing iodine back into the system:



The Van Arkel–de Boer process yields zirconium of extremely high purity (> 99.99 %) suitable for nuclear reactor cladding materials. A similar method is used for titanium and hafnium purification.

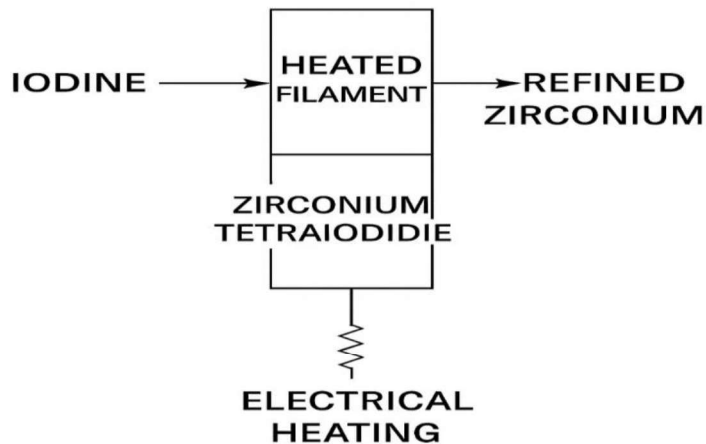


Figure I-6-5 – Van Arkel–de Boer Process for Zirconium Refining.

## **6. Thermodynamic and Kinetic Considerations**

The success of these reduction processes depends on the thermodynamic stability of intermediate compounds. The chlorides of titanium and zirconium have high vapor pressures, allowing easy separation from impurities during distillation. Both reduction reactions (with magnesium or sodium) are strongly exothermic, ensuring rapid kinetics.

Careful control of temperature and gas flow prevents premature condensation or side reactions forming TiN or TiC. For zirconium, hafnium contamination must be minimized by prior separation of HfCl<sub>4</sub> and ZrCl<sub>4</sub> through fractional distillation, as hafnium's high neutron absorption renders it unsuitable for nuclear use.

## **7. Industrial Implementation and Production Capacities**

Titanium and zirconium production plants are highly specialized facilities that require inert atmospheres and corrosion-resistant equipment. China, Japan, and the United States dominate global production of titanium sponge, while zirconium refining is concentrated in Russia and France. Both metals are produced in relatively small quantities compared to base metals, but their high unit value justifies complex extraction routes.

In Algeria, the potential development of a titanium–zirconium processing industry could rely on the chlorination of locally concentrated ilmenite and zircon sands. Such integration would enable production of titanium dioxide pigments and, eventually, metallic titanium or zirconium for strategic applications.

The elaboration of titanium and zirconium metals relies on chemical routes involving chlorination and reduction. Titanium is mainly produced through the Kroll process, while zirconium is refined using the Van Arkel–de Boer process. These technologies demonstrate how advanced metallurgical control allows the transformation of stable oxides into high-purity strategic metals. Future developments aim at cleaner and more economical alternatives such as the FFC Cambridge process.

## **Environmental, Industrial, and Algerian Context**

### **1. Environmental Aspects of Titanium and Zirconium Production**

The metallurgical production of titanium and zirconium involves high temperatures and reactive chemicals such as chlorine and magnesium. Environmental management is therefore essential to prevent air and water pollution, as well as to ensure worker safety. Both metals can be produced sustainably through recovery, recycling, and pollution-control systems.

#### **1.1 Gas Emissions and Control**

The chlorination stage generates chlorine-based gases and hydrogen chloride (HCl), which must be captured and neutralized. Modern plants employ closed systems equipped with scrubbers, where HCl is absorbed in water to form hydrochloric acid that can be reused in leaching or purification steps. Filtration systems prevent the release of fine titanium dioxide or zircon dust into the atmosphere.

Magnesium chloride ( $\text{MgCl}_2$ ), produced as a by-product in the Kroll process, is recovered and electrolyzed to regenerate magnesium and chlorine, creating a closed chemical cycle with minimal emissions.

#### **1.2 Solid Waste Management**

Solid residues such as unreacted chlorides, slag, and magnesium oxide are stabilized through neutralization and stored safely. Slags from zirconium refining, rich in silica and zirconia, are reused in refractory manufacturing. The recycling of titanium machining scraps and zirconium alloys from the nuclear industry is increasingly practiced to reduce raw material demand.

#### **1.3 Water and Energy Management**

Water used in cooling, leaching, and washing operations is treated by precipitation and ion exchange. The recovered water is then recycled, reducing consumption by up to 90 %. Heat recovery systems from chlorination furnaces and vacuum-melting units are used to preheat process gases and reduce energy consumption. The overall objective is to achieve low-carbon, circular metallurgy.

## 2. Industrial Applications of Titanium and Zirconium

Titanium and zirconium possess outstanding properties that make them indispensable in several high-technology sectors.

### 2.1 Titanium Applications

Titanium's high strength-to-weight ratio and resistance to corrosion make it ideal for aerospace, automotive, and marine industries. Titanium alloys such as Ti-6Al-4V are widely used for aircraft components, jet engines, and spacecraft structures. In chemical industries, titanium is used in heat exchangers and reaction vessels resistant to acids and chlorides.

In the biomedical field, titanium's biocompatibility allows its use in surgical implants, dental prostheses, and bone fixation systems.

### 2.2 Zirconium Applications

Zirconium's main application is in the nuclear industry, where it serves as a cladding material for fuel rods due to its low neutron absorption cross-section. Zirconium alloys (Zircaloy) can operate safely at high temperatures in reactor environments. In the chemical industry, zirconium equipment is employed for handling strong acids and alkalis.

Zirconium compounds, particularly zirconia ( $ZrO_2$ ), are used in advanced ceramics, oxygen sensors, dental implants, and thermal barrier coatings.



Figure I-6-6 – Applications of Titanium and Zirconium in Advanced Industries.

### **3. The Algerian Context for Titanium and Zirconium Development**

Algeria possesses mineral resources containing titanium and zirconium, primarily in the form of ilmenite, rutile, and zircon sands located in the Hoggar, Oued Saoura, and Bechar regions. These placer deposits were identified through geochemical and geophysical surveys conducted by the National Agency of Mining Activities (ANAM).

Developing a titanium and zirconium industry in Algeria would enable the country to produce raw materials for pigment manufacturing, aerospace alloys, and refractory products. The abundance of natural gas and renewable energy provides favorable conditions for establishing chlorination and metallurgical facilities powered by clean energy.

#### **3.1 Bou Kaïs and Oued Saoura Prospects**

The Bou Kaïs and Oued Saoura regions contain significant ilmenite–rutile–zircon sands, where initial beneficiation tests have yielded concentrates with over 50 % TiO<sub>2</sub> and 65 % ZrO<sub>2</sub> equivalent. Pilot studies suggest the feasibility of establishing mineral separation plants followed by titanium dioxide pigment production.

#### **3.2 Industrial Opportunities**

An integrated metallurgical chain could be developed in Algeria, from mineral concentration to TiO<sub>2</sub> pigment production and, later, metallic titanium or zirconium refining. This would contribute to national industrial diversification, job creation, and technological advancement.

### **4. Future Perspectives in Titanium and Zirconium Metallurgy**

The future of titanium and zirconium metallurgy lies in cleaner, more energy-efficient technologies. Electrochemical routes such as the FFC Cambridge process and hydrogen-based reduction are being explored to replace conventional chlorination and magnesium reduction.

Research is also directed toward additive manufacturing (3D printing) of titanium alloys, recycling of Ti–Zr scraps, and the development of nanostructured materials. In Algeria, partnerships between universities and industrial sectors could foster applied research in mineral beneficiation and metallurgical process innovation.

Titanium and zirconium are essential materials for advanced industries thanks to their superior mechanical, thermal, and chemical properties. Their extraction and refining require sophisticated technologies, balancing efficiency with environmental responsibility. Algeria's mineral potential and energy resources offer a strong foundation for developing a sustainable titanium–zirconium metallurgical sector.

### **Review Questions for Students**

1. What are the main environmental challenges of titanium and zirconium production?
2. Explain how magnesium chloride is recycled in the Kroll process.
3. Describe the main industrial applications of titanium and zirconium.
4. Discuss Algeria's potential for developing a titanium and zirconium industry.
5. What are the advantages of future electrochemical extraction technologies?

## **Chapter II: Unit Operations**

### **1- Operations for solid/solid and solid/liquid separation**

#### **1.1 Solid–Liquid Separation after Leaching**

##### **1.1.1 Introduction**

Solid–liquid separation is one of the most fundamental unit operations in extractive metallurgy, chemical engineering, and mineral processing. After leaching, the valuable metals are dissolved in an aqueous solution while the remaining solids form an inert residue. The purpose of this operation is to achieve the most efficient separation possible, yielding a clear pregnant leach solution and a solid residue with minimal liquid content. The efficiency of solid–liquid separation directly impacts metal recovery, reagent consumption, and environmental performance of the process.

In hydrometallurgical processing, solid–liquid separation steps occur after leaching, neutralization, and precipitation. The choice of method depends on particle size, pulp viscosity, solid concentration, and desired purity of the solution. Common methods include flotation, sedimentation, filtration, and centrifugation, each based on distinct physical principles.

##### **1.1.2 Principles of Solid–Liquid Separation**

The separation process is governed by physical forces acting between solid particles and the surrounding fluid. These forces include gravitational, centrifugal, capillary, and surface tension effects. The key objectives are:

- To recover the liquid phase (leachate) free from solid impurities.
- To recover the solid residue with minimal entrained liquid.

The theoretical framework for sedimentation and filtration can be derived from Stokes' Law, which expresses the terminal settling velocity of a spherical particle under gravity:

$$v = \frac{2 r^2 (\rho_s - \rho_l) g}{9 \mu}$$

**Table II-1 : Meaning of Each Term**

Symbol	Quantity	Unit	Description
<b>v</b>	<b>Settling velocity</b>	m/s	The steady velocity at which a particle falls through a fluid when gravity and drag are balanced.
<b>r</b>	<b>Particle radius</b>	m	Half the particle's diameter. The law applies to small, spherical particles.
<b><math>\rho_s</math></b>	<b>Density of solid</b>	kg/m <sup>3</sup>	The density of the particle.
<b><math>\rho_l</math></b>	<b>Density of liquid</b>	kg/m <sup>3</sup>	The density of the surrounding fluid.
<b><math>\mu</math></b>	<b>Dynamic viscosity</b>	Pa·s	The resistance of the fluid to flow.
<b>g</b>	<b>Gravitational acceleration</b>	m/s <sup>2</sup>	Typically 9.81 m/s <sup>2</sup> on Earth.

### 1.1-3 Flotation

Flotation (Figure II-1-1) is a physico-chemical separation technique widely employed in mineral processing and hydrometallurgy. It involves introducing gas bubbles into a liquid containing suspended particles. Hydrophobic particles attach to the gas bubbles and rise to the surface, forming a froth layer that can be removed mechanically. Hydrophilic particles remain in the bulk liquid phase.

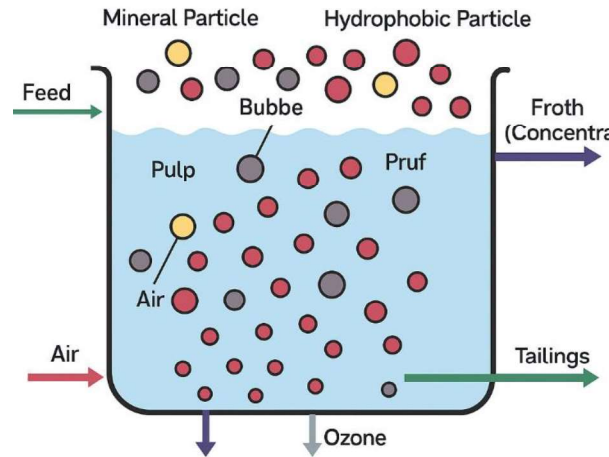
The effectiveness of flotation depends on particle hydrophobicity, bubble size, reagent type, pH, and agitation. Collectors, frothers, and modifiers are added to control the surface properties of minerals. In hydrometallurgical operations, flotation can be used to recover unreacted sulfides or to treat leach residues containing valuable elements.

Mathematically, the probability of particle–bubble collision ( $P_c$ ) can be expressed as:

$$P_c = f(d_p, d_b, v_r, \epsilon)$$

where  $d_p$  and  $d_b$  are particle and bubble diameters,  $v_r$  is relative velocity, and  $\epsilon$  represents the turbulence intensity.

Industrial flotation cells are equipped with mechanical agitators or air injectors to generate fine bubbles. Column flotation offers improved selectivity for fine particles. Applications include recovery of copper, nickel, and zinc sulfides, as well as the removal of organic impurities from process water.



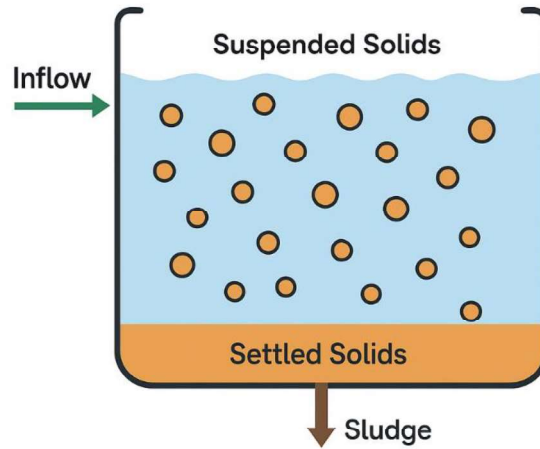
**Figure II-1-1: Conceptual Diagram of Air and Ozone Flotation Process**

#### **1.1.4 Sedimentation and Thickening**

Sedimentation (Figure II-1-2) is the gravitational settling of solid particles in a liquid. It is one of the oldest and simplest methods for solid–liquid separation. The process occurs when the downward gravitational force exceeds the upward drag force acting on a particle. The rate of sedimentation depends on particle size, density difference, and fluid viscosity.

In metallurgical plants, large thickeners are used for continuous separation of solids from leach liquors. The underflow contains concentrated slurry, while the overflow is a clear solution. To accelerate settling, flocculants (typically polyacrylamides) are added to promote aggregation of fine particles.

Modern thickeners are equipped with rakes, feedwell systems, and overflow launders. High-rate and high-density thickeners are used to reduce the footprint of operations.



**Figure II-1-2: Sedimentation Basin**

### 1.1.5 Filtration

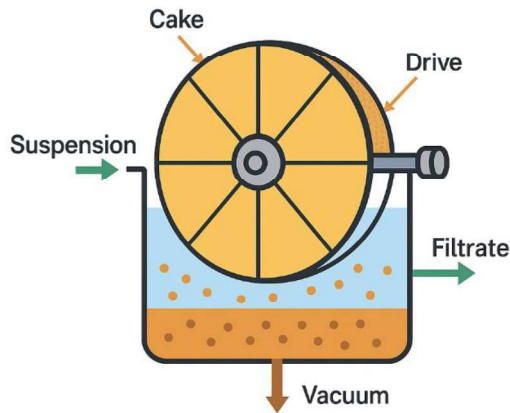
Filtration (Figure II-1-3) involves separating solids from liquids using a porous medium that allows the fluid to pass through while retaining the particles. Filtration can be pressure-driven or vacuum-assisted. Common equipment includes filter presses, rotary vacuum filters, and belt filters.

The governing equation for filtration through a compressible cake is given by Darcy's law:

$$Q = \frac{\Delta P \cdot A}{\mu \cdot R_t}$$

where  $Q$  is the filtrate flow rate,  $\Delta P$  is pressure drop,  $A$  is filter area,  $\mu$  is fluid viscosity, and  $R_t$  is the total resistance (sum of medium resistance and cake resistance).

Washing of the filter cake is often performed to recover trapped metals in the interstitial liquid. Industrial filtration is used in copper, zinc, and nickel hydrometallurgy to clarify leach liquors.



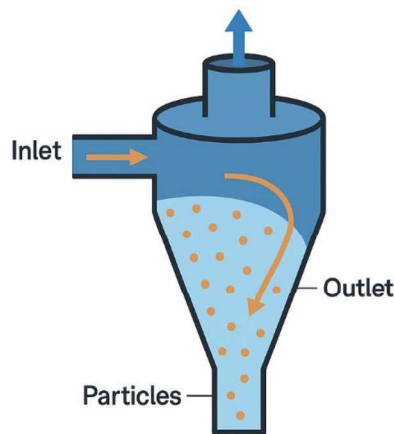
**Figure II-1-3: Disk Vacuum Filter Used in Metallurgy**

### 1. 1.6 Centrifugation

Centrifugation (Figure I-1-4) separates solids and liquids by applying centrifugal force. A rotating drum or bowl generates a field much stronger than gravity, rapidly accelerating particle settling. This method is particularly effective for fine or colloidal suspensions where gravity settling is slow.

The separation efficiency depends on the rotation speed, particle size, and density difference. Decanter centrifuges and solid-bowl centrifuges are widely used in metallurgical processes for thickening, clarification, and dewatering of residues.

Although centrifugation provides rapid and clean separation, it involves high maintenance and operational costs. Therefore, it is typically reserved for specific cases where sedimentation or filtration is insufficient.



**Figure II-1-4: Simplified Diagram of a Cyclone**

### 1.1.7 Industrial Applications

Solid–liquid separation after leaching plays a vital role in the efficiency and economics of hydrometallurgical processes. The selection of a proper technique—flotation, sedimentation, filtration, or centrifugation—depends on the characteristics of the pulp, required product purity, and downstream process requirements.

In industrial practice, these techniques are often combined: thickening followed by filtration, or centrifugation after flocculation. Optimizing these steps contributes to higher metal recovery, lower reagent losses, and reduced environmental impact.

## 1.2.- Operations for solid/solid separation

### 1.2.1 General Introduction

Solid/solid separation operations play an essential role in mineral processing, metallurgy, and the chemical industry. Their main objective is to separate different solids according to their physical or physicochemical properties in order to obtain products of the desired purity and particle size suitable for subsequent process stages.

These operations are involved in many fields: ore preparation, recycling, material purification, and industrial product quality control. Therefore, their understanding and implementation are essential for engineers and technicians working in process engineering.

### 1.2.2 Fundamental Principles

Solid/solid separations rely on differences in particle characteristics. These characteristics may be physical (size, density, shape, conductivity, magnetism) or surface-related (chemical affinity, electric charge).

The choice of method depends on the nature of the material, the particle size distribution, and the purpose of the separation—whether enrichment, impurity removal, or preparation of a homogeneous raw material.

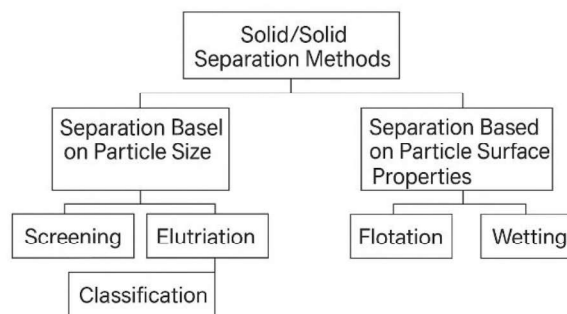


Figure II-1-5 – Classification of Solid/Solid Separation Methods

### 1.2.3 Particle Size Separation

Separation by particle size (screening or sieving) is one of the oldest and most widespread methods. It consists of passing a particle mixture through a perforated surface or a vibrating screen.

Particles smaller than the openings pass through the screen, while larger ones are retained. This method enables effective particle size classification for both dry and wet materials.

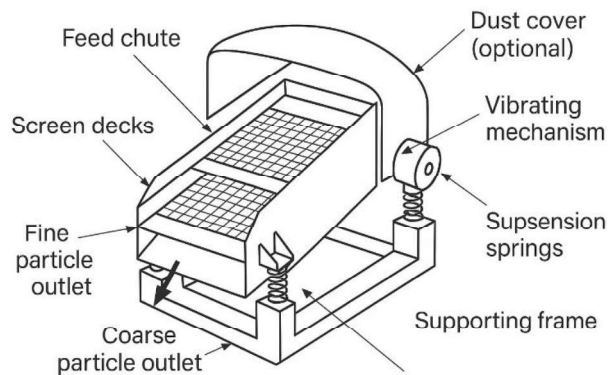


Figure II-1-6 – Diagram of an Industrial Vibrating Screen

### 1.2.4 Gravity Separation

Gravity separation is based on the difference in density between solid particles. Under the action of gravity or a centrifugal field, heavier particles settle faster than lighter ones.

Equipment used includes shaking tables, spirals, jigs, and air classifiers. These techniques are widely used for processing heavy minerals (coal, gold, cassiterite).

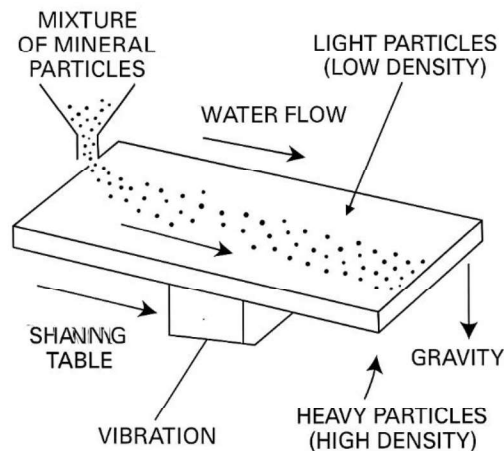


Figure II-1-7 – Principle of Gravity Separation on a Shaking Table

### 1.2.5 Magnetic Separation

This method exploits the difference in magnetic susceptibility between particles. Ferromagnetic materials are attracted by magnetic fields, while non-magnetic materials are not.

Magnetic drum, belt, or roll separators are used to extract iron from ores or to purify non-ferrous materials.

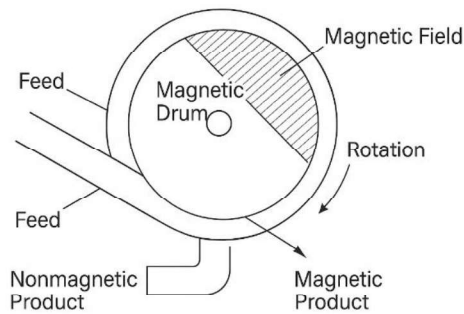


Figure II-1-8 – Diagram of a Rotating Drum Magnetic Separator

### 1.2.6 Electrostatic Separation

Electrostatic separation is based on differences in the electrical conductivity of solid particles. Under an electric field, conductive particles become charged and are attracted to the opposite electrode, while non-conductive ones remain suspended or fall separately.

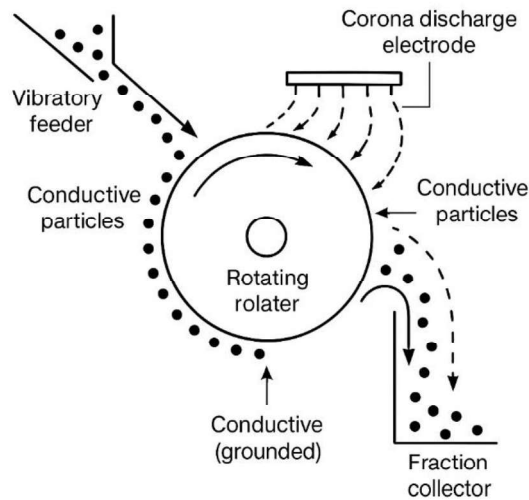


Figure II-1-9 – Roller-Type Electrostatic Separator

### 1.2.7 Flotation

Flotation is a separation technique based on the surface properties of particles. Hydrophobic particles attach to air bubbles and rise to the surface to form a froth, while hydrophilic particles remain in the liquid phase.

This method is widely used in the processing of sulfide ores such as galena (PbS), sphalerite (ZnS), or chalcopyrite (CuFeS<sub>2</sub>).

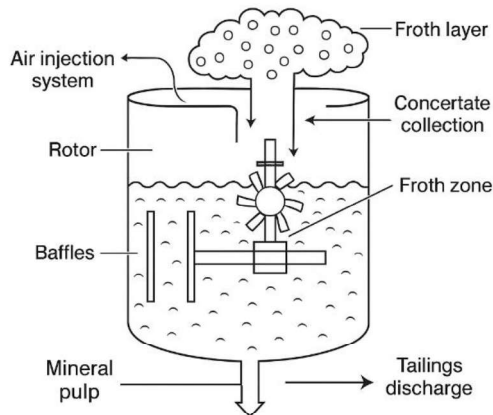


Figure II-1-10 – Industrial Flotation Cell

### 1.2.8 Industrial Applications

In industry, several solid/solid separation methods are often combined to optimize the quality of the final product. Processing circuits generally include stages of crushing, grinding, classification, and concentration.

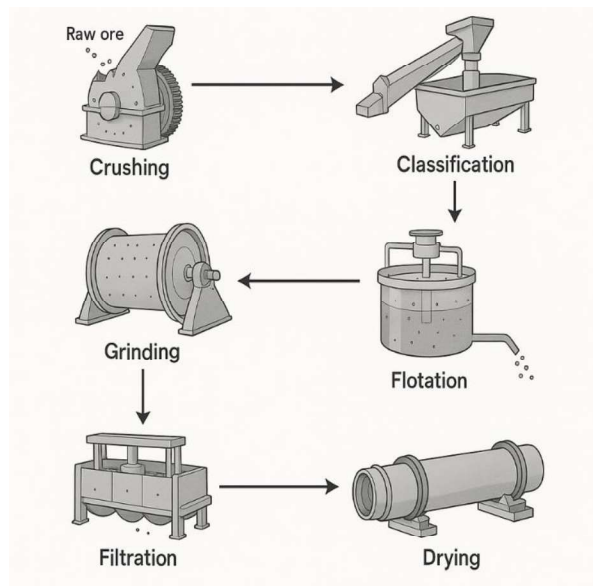


Figure II-1-11 – Diagram of an Industrial Mineral Processing Circuit

Applications cover the mining, metallurgical, recycling, and environmental industries, where energy efficiency and solid waste recovery have become major priorities.

## **Glossary**

**Screening:** Separation operation based on particle size.

**Flotation:** Separation using air bubbles and surface properties.

**Magnetic:** Related to attraction by a magnetic field.

**Electrostatic:** Technique based on the electrical conductivity of solids.

**Gravitational (Gravity):** Separation using density differences.

## **2 – Fluid Phase Separation Operations**

### **2.1 Introduction**

Fluid phase separation operations constitute a fundamental category of unit operations in metallurgical and chemical processes. These operations are primarily based on phase transition phenomena—condensation, sublimation, liquation, and distillation. They are essential for purifying metals, separating volatile components, and recovering solvents or by-products from process streams.

In extractive metallurgy, especially in pyrometallurgy and hydrometallurgy, fluid phase separations enable the transformation of gaseous or vaporized metal compounds into condensed or purified forms. Understanding the thermodynamics of vapor–liquid and solid–vapor equilibria is crucial to optimizing these processes.

### **2.2 Condensation**

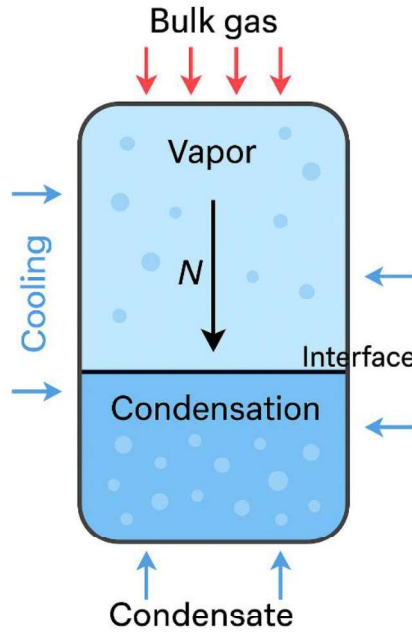
Condensation (Figure II-2-1) refers to the transformation of a vapor into a liquid when its temperature drops below the saturation point at a given pressure. In metallurgical systems, condensation is used for the recovery of volatile metals such as zinc, cadmium, and mercury, as well as for reclaiming solvent vapors in hydrometallurgical operations.

The driving force for condensation is the difference between the actual vapor pressure and the equilibrium vapor pressure at the surface. The latent heat of condensation must be removed efficiently to maintain the process rate. This can be achieved through surface condensers (filmwise or dropwise) or direct-contact condensers.

The mass transfer rate in condensation can be expressed as:

$$N = k_y(\rho_v - \rho_s)$$

where  $N$  is the molar flux of vapor condensing ( $\text{mol}/\text{m}^2\cdot\text{s}$ ),  $k_y$  is the mass transfer coefficient,  $\rho_v$  is the bulk vapor pressure, and  $\rho_s$  is the saturation pressure at the condensing surface.



**Figure II-2-1: Diagram of a Condensation Process**

### 2-3 Sublimation

Sublimation (Figure II-2-2) is the direct phase transition from the solid state to the gaseous state without passing through the liquid phase. It occurs under specific temperature and pressure conditions, usually below the triple point of the substance. The process is endothermic, requiring the absorption of latent heat.

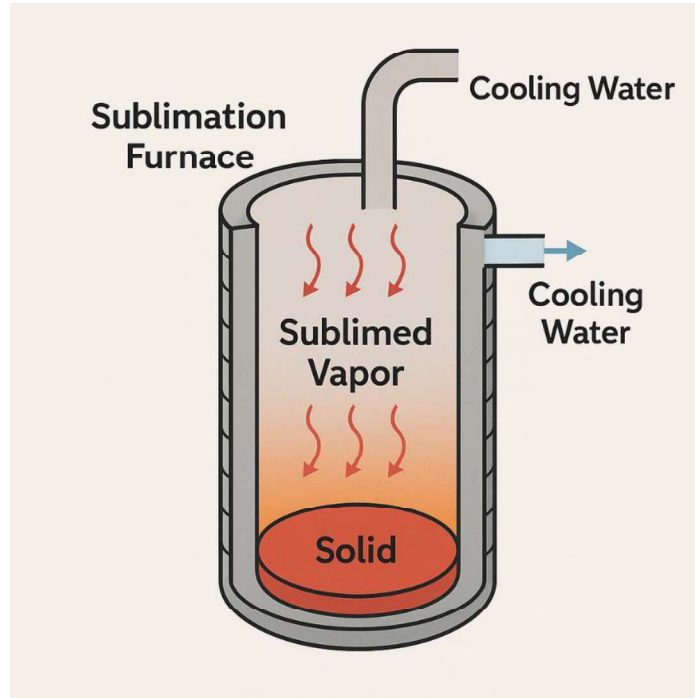
In metallurgy, sublimation is utilized in processes such as the refining of zinc, cadmium, and iodine, where metal compounds with high vapor pressures are vaporized and subsequently condensed into high-purity products.

The equilibrium vapor pressure over a solid can be described by the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{sup}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where  $\Delta H_{\text{sub}}$  is the enthalpy of sublimation (J/mol),  $R$  is the universal gas constant, and  $T_1$ ,  $T_2$  are absolute temperatures (K).

Industrial sublimation furnaces are designed to control the heating rate, vacuum level, and condensation surfaces to achieve high separation efficiency.



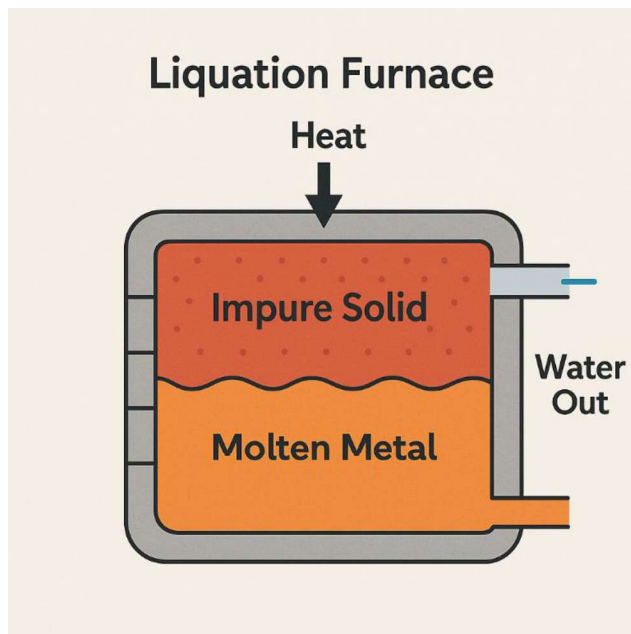
**Figure II-2-2: Schematic Diagram of Sublimation Furnace**

## 2.4 Liquefaction

Liquefaction (Figure II-2-3) is a metallurgical separation process based on differences in melting points of metals or alloys. When a mixture containing metals with distinct melting points is heated, the lower-melting component liquefies first and can be drained off, while the higher-melting component remains solid.

Historically, liquefaction was used to separate lead and tin, or to remove antimony from lead–silver alloys. Although largely replaced by electrorefining and solvent extraction, liquefaction remains an important pedagogical example of thermal separation driven by phase equilibria.

The success of liquefaction depends on temperature control, alloy composition, and gravity effects. The liquated metal must be collected carefully to avoid contamination with the unmelted residue.



**Figure II-2-3: Diagram of a Liquefaction Furnace**

### 2.5 Distillation

Distillation (Figure II-2-4) is a thermal separation process based on the difference in volatility between components of a mixture. When a liquid mixture is heated, the component with higher vapor pressure evaporates preferentially, and the vapor is subsequently condensed to obtain the purified component.

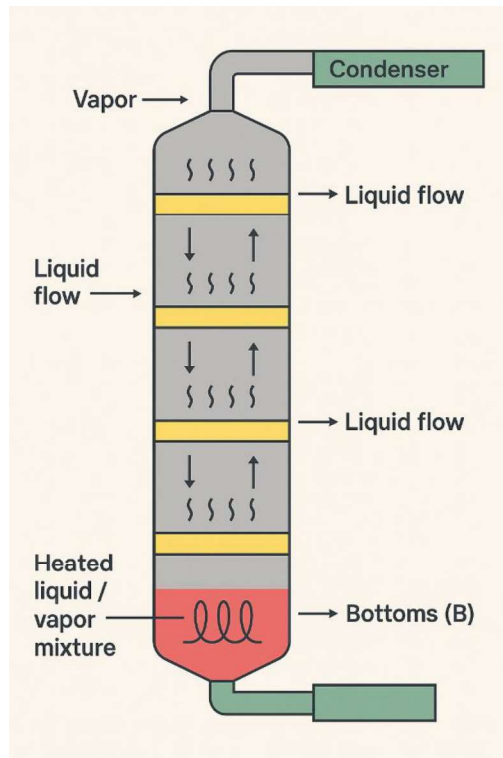
In metallurgical applications, distillation is used to separate metals such as zinc, magnesium, and mercury from impurities. For example, in zinc refining, impure zinc vapor is distilled and condensed to achieve high-purity zinc.

The separation efficiency in distillation depends on relative volatility ( $\alpha$ ), defined as:

$$\alpha = \frac{y_A/x_A}{y_B/x_B}$$

where  $x_i$  and  $y_i$  represent the liquid and vapor phase mole fractions of components A and B, respectively.

Fractional distillation uses a column with multiple stages or trays to improve separation by successive vapor–liquid equilibria. Each tray acts as a theoretical stage where vapor and liquid reach equilibrium.



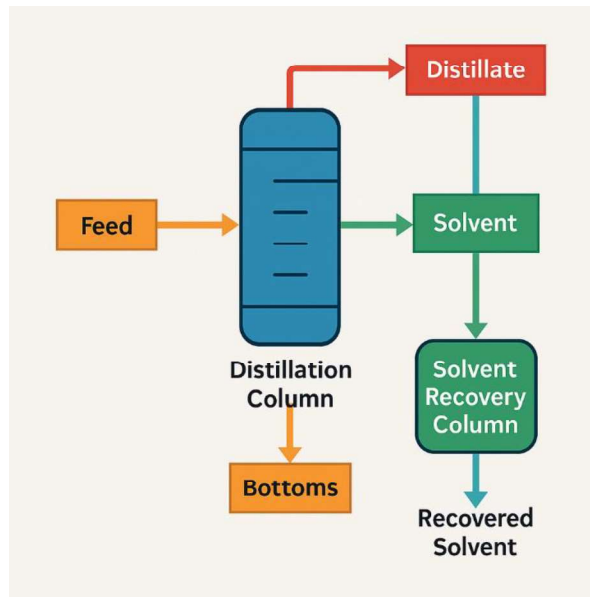
**Figure II-2-4: Fractional Distillation Column Diagram**

## 2.6 Extractive Distillation

Extractive distillation (Figure II-2-5) enhances the volatility difference between two components in a mixture by adding a third component (the entrainer) that selectively interacts with one of the constituents. Unlike azeotropic distillation, the entrainer does not form an azeotrope with the main components.

This process can be homogeneous (no phase separation) or heterogeneous (with partial immiscibility). Homogeneous extractive distillation is used for systems such as ethanol–water with ethylene glycol as entrainer. Heterogeneous extractive distillation may induce two liquid phases, facilitating the recovery of target components.

In metallurgical and chemical applications, extractive distillation is employed for solvent recovery, purification of electrolytes, and dehydration of process streams.



**Figure II-2-5: Typical Flow Diagram of Extractive Distillation Process**

### 2.7 Industrial Applications

Fluid phase separation processes are widely used in both hydrometallurgical and pyrometallurgical operations. Examples include:

- Condensation of zinc and cadmium vapors during roasting and smelting.
- Sublimation of iodine in titanium purification.
- Liquation of tin–lead alloys in recycling industries.
- Distillation of zinc and magnesium in vacuum refining.
- Extractive distillation in electrolyte purification units.

Each of these methods exploits thermodynamic equilibria and phase transitions to achieve selective separation and purification. Process optimization requires balancing energy consumption, recovery rate, and environmental considerations.

Fluid phase separation operations are crucial to metallurgical process efficiency. Understanding vapor–liquid–solid equilibria, heat transfer, and mass transfer mechanisms allows engineers to design more effective separation units. As energy-intensive operations, they require careful thermal management and system integration to ensure sustainability.

### 3- Chemical Unit Operations and Reactors in Pyrometallurgy

#### 3.1 Introduction

Pyrometallurgy involves high-temperature processes for extracting and refining metals. Chemical unit operations in pyrometallurgy include roasting, smelting, converting, and refining. The efficiency of these processes relies heavily on the design and operation of reactors where solid, liquid, and gaseous phases interact under extreme thermal conditions.

This part focuses on the types of reactors used in pyrometallurgical operations, such as gas–solid contactors, electric furnaces, and converters. The choice of reactor depends on temperature requirements, feed composition, desired reaction kinetics, and energy source. These systems are fundamental for the recovery of metals like iron, copper, nickel, lead, zinc, and ferroalloys.

#### 3.2 Gas–Solid Reactors

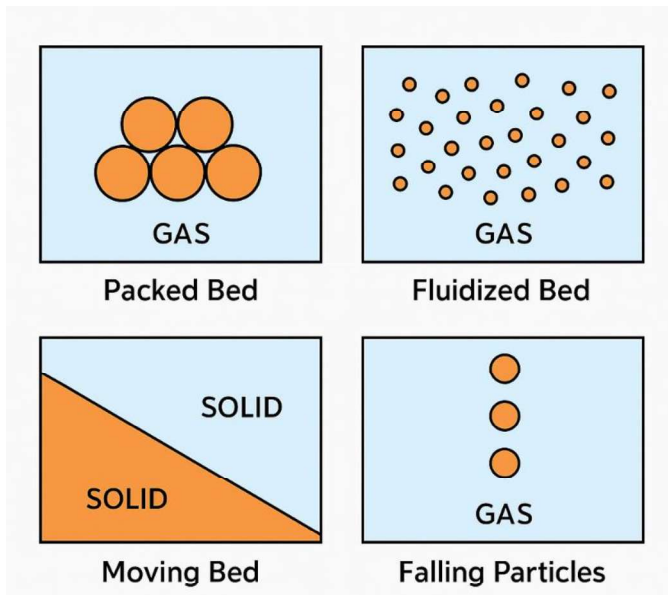
Gas–solid reactors are the cornerstone of pyrometallurgical operations. They facilitate reactions between gaseous reactants and solid feed materials. Examples include oxidation, reduction, chlorination, and sulfation reactions. Depending on the gas flow rate and particle size, various reactor configurations are employed, such as fixed beds, moving beds, fluidized beds, and entrained flow reactors.

The performance of gas–solid reactors depends on effective mass transfer, heat transfer, and reaction kinetics. The conversion rate ( $X$ ) for a gas–solid reaction can be modeled using the shrinking core model:

$$1 - (1 - X)^{1/3} = k_g t + k_r t$$

where  $k_g$  and  $k_r$  represent the rate constants for external mass transfer and chemical reaction, respectively. This equation assumes spherical particles reacting under steady-state conditions.

Fixed-bed reactors are suitable for coarse particles and slow reactions, while fluidized-bed reactors offer high heat and mass transfer rates. Cyclone and entrained flow reactors are preferred for fine particles and high-temperature operations.



**Figure II-3-1: Modes of Contact between Solid and Gaseous Phases**

### 3.3 Electric Arc Furnaces

Electric Arc Furnaces (EAF) (Figure II-3-2) are electrothermal reactors that generate heat through electric arcs formed between graphite electrodes and the metallic charge. The temperature in the arc zone can exceed 3500°C, allowing rapid melting and refining of various metals and alloys.

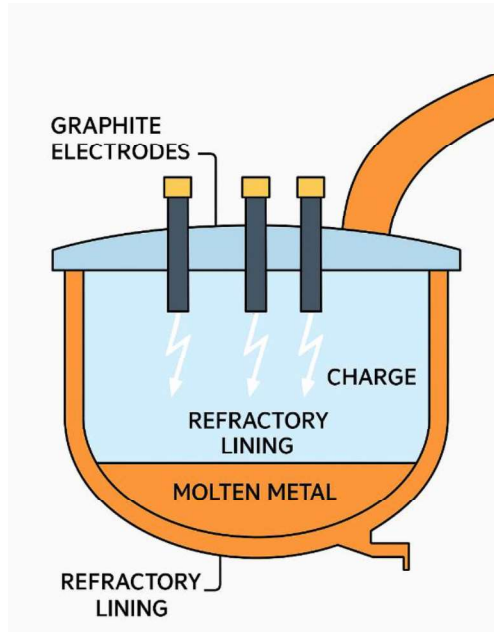
Two main types of EAFs exist: alternating current (AC) and direct current (DC). In AC furnaces, three electrodes form arcs in a three-phase configuration, typically used in steelmaking. In DC furnaces, one or two electrodes are connected to rectifiers, providing a stable arc and uniform heating.

The main reactions in an EAF include oxidation of impurities, slag formation, and gas evolution. The furnace atmosphere can be controlled to enhance metal purity and minimize oxidation losses. EAFs are used in steelmaking, ferroalloy production, and recycling.

The thermal power of an EAF can be estimated using:

$$P = V \cdot I \cdot \eta$$

where P is power (kW), V is voltage (V), I is current (A), and  $\eta$  is the electrical efficiency.



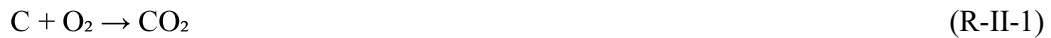
**Figure II-3-2: Schematic of an Electric Arc Furnace**

### 3.4 Converters

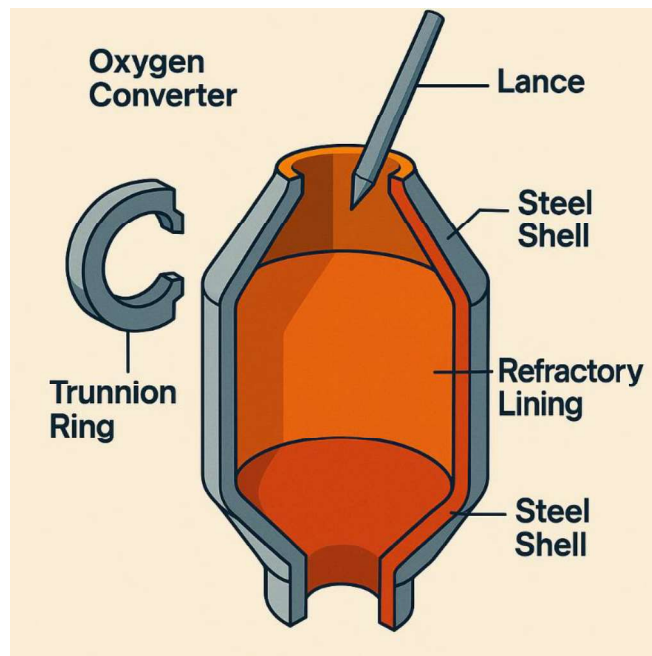
Converters (Figure II-3-3) are metallurgical reactors used to oxidize impurities from molten metal or matte. They operate by blowing air or oxygen through tuyeres into the molten bath, promoting oxidation of unwanted elements such as carbon, sulfur, and phosphorus.

There are three major types of converters: Bessemer, Thomas, and oxygen (LD) converters. The Bessemer process uses an acid refractory lining, suitable for low-phosphorus iron. The Thomas converter uses a basic lining of dolomite, ideal for high-phosphorus iron ores. Oxygen converters employ pure oxygen jets to refine the molten iron into steel efficiently.

In oxygen steelmaking, the oxidation reactions can be represented as:



These exothermic reactions provide the heat required to maintain the molten state of the metal. Converters are designed to allow easy tilting and slag removal. Gas cleaning systems capture CO and CO<sub>2</sub> emitted during operation.



**Figure II-3--3: Exploded View of an Oxygen Converter**

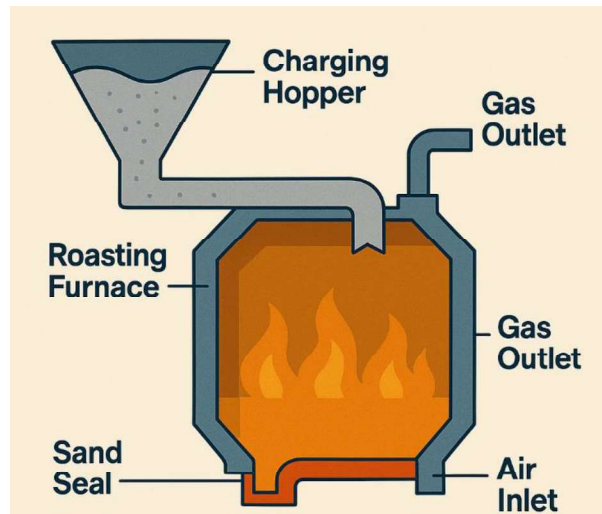
### 3.5 Roasting Furnaces

Roasting (Figure II-3-4) is a gas–solid reaction process in which sulfide ores are oxidized to produce oxides or sulfates. It is a preparatory step before smelting or leaching. Typical reactions include oxidation of zinc sulfide and copper sulfide:



Roasting can be carried out in multiple furnace types: multiple-hearth furnaces, fluidized-bed roasters, and rotary kilns. Fluidized-bed roasting provides high throughput and uniform temperature distribution, while multiple-hearth furnaces are used for ores requiring precise temperature control.

Modern roasting systems are equipped with gas scrubbers and sulfur recovery units to minimize environmental impact.



**Figure III-4: Typical Roasting Furnace Configuration**

### 3.6 Industrial Applications

Pyrometallurgical reactors are employed across a wide range of metal extraction and refining industries. Examples include:

- Copper production (flash smelting and converting)
- Nickel extraction (rotary kiln and electric furnace)
- Iron and steel manufacturing (blast furnace and basic oxygen converter)
- Lead and zinc production (roasting and reduction smelting)
- Ferroalloy and silicon carbide synthesis in electric furnaces

The choice of reactor is dictated by thermodynamics, kinetics, and economics. Energy recovery and emission control are integral parts of modern pyrometallurgical plant design.

Chemical unit operations in pyrometallurgy are crucial for the transformation of raw ores into refined metals. Reactor design must ensure efficient heat transfer, mass transfer, and reaction control under high-temperature conditions. The integration of modern control systems, advanced refractories, and environmental protection technologies continues to enhance the sustainability and efficiency of pyrometallurgical operations.

## 4 – Chemical Unit Operations and Reactors in Hydrometallurgy

### 4.1 Introduction

Hydrometallurgy is a branch of extractive metallurgy that uses aqueous chemistry to extract metals from ores, concentrates, and recycled or residual materials. Chemical unit operations in hydrometallurgy involve a sequence of leaching, solution concentration and purification, and metal recovery processes. The success of these operations depends heavily on the type and performance of reactors where dissolution, precipitation, and solvent extraction take place.

This part discusses the most common hydrometallurgical reactors and their operational principles, including leaching reactors, precipitation systems, and liquid–liquid extraction units such as mixer–settlers. Emphasis is placed on mass transfer, reaction kinetics, equipment design, and industrial applications.

### 4.2 Leaching Reactors

Leaching (Figure II-4-1) is the process of dissolving valuable metals from solid materials into a liquid phase. Depending on temperature, pressure, and solution chemistry, leaching can be carried out under atmospheric conditions or in high-pressure autoclaves. The choice of leaching technique depends on ore type, mineralogy, and target metal.

The general reaction for metal dissolution can be expressed as:

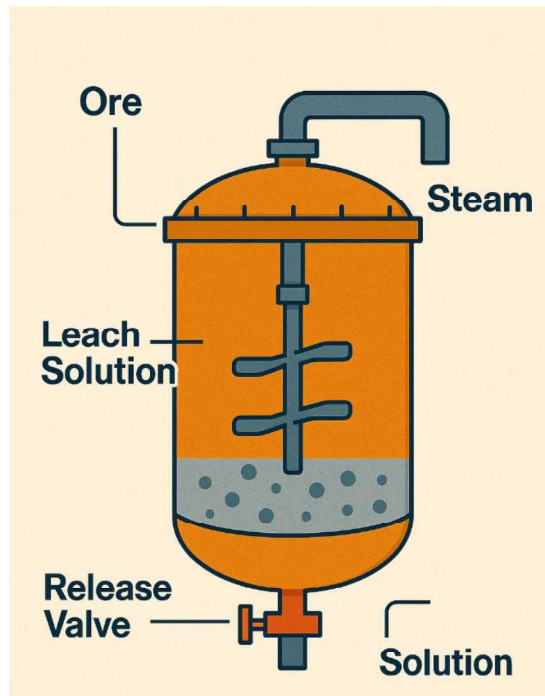


where M represents the metal and A represents the anionic component of the mineral.

Types of leaching reactors include:

- **Agitated Tanks:** Stirred vessels equipped with impellers for continuous operation.
- **Percolation Leaching:** Static beds where leach solution percolates through crushed ore.
- **Heap Leaching:** Large outdoor heaps irrigated by leach solution, commonly used for copper and gold.
- **Pressure Leaching (Autoclaves):** Closed vessels operating at elevated temperatures (up to 250°C) and pressures (up to 5 MPa).

Kinetic control of leaching depends on diffusion through product layers and chemical reaction at the solid surface. Autoclaves provide enhanced reaction rates and selectivity, while maintaining environmental safety through containment of gases.

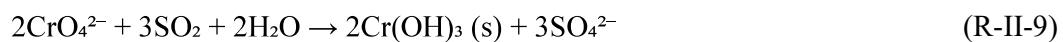
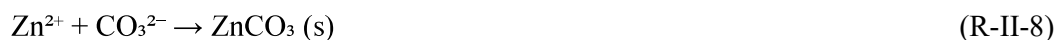


**Figure II-4-1: Leaching Reactor or Autoclave System**

### 4.3 Precipitation Systems

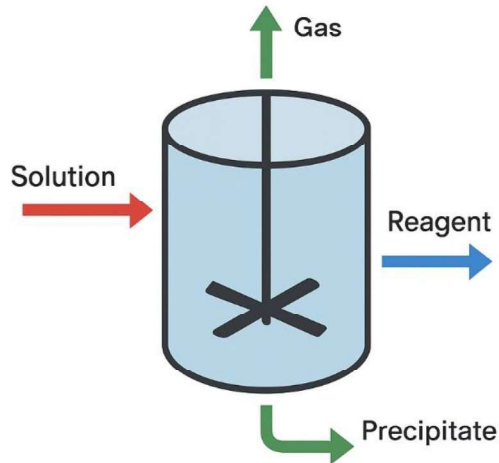
Precipitation (Figure II-4-2) is a key hydrometallurgical step where dissolved metals are recovered from solution by chemical or electrochemical means. Precipitation may involve neutralization, hydrolysis, or reduction reactions that convert dissolved ions into insoluble solids.

Examples of precipitation reactions include:



Precipitation reactors are designed to promote uniform mixing, maintain pH control, and prevent excessive particle growth or agglomeration. Common reactor types include continuous stirred-tank reactors (CSTRs) and plug-flow reactors (PFRs).

Particle size distribution, temperature, and residence time are critical parameters. Industrial systems may include cascade tanks or series of reactors for multistage precipitation and washing.



**Figure II-4-2: Precipitation Reactor Diagram**

#### 4.4 Mixer–Settlers

Mixer–settlers (Figures II-4-3 to II-4-6) are liquid–liquid extraction units used to separate and purify metals from leach solutions. They operate based on the immiscibility of aqueous and organic phases, enabling selective transfer of target metal ions between the two phases.

The system typically consists of a mixing chamber where the aqueous and organic phases are vigorously agitated to ensure droplet dispersion, followed by a settling chamber where the phases separate under gravity. The organic phase, loaded with the target metal, is then transferred to the stripping section for metal recovery.

The performance of a mixer–settler is influenced by factors such as:

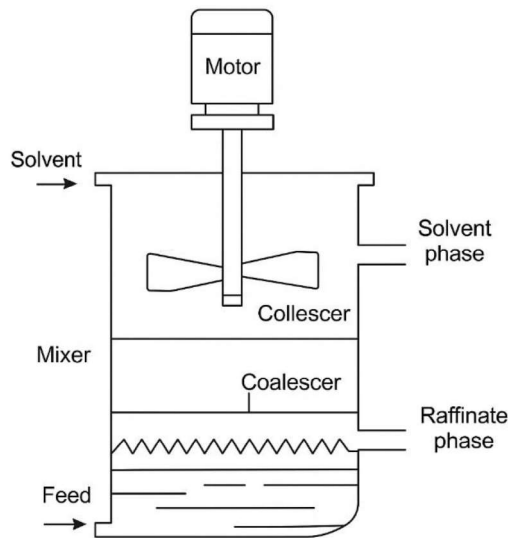
- Interfacial tension and droplet size
- Agitation speed and mixing time
- Phase ratio (organic/aqueous)
- Temperature and viscosity
- Mass transfer coefficient and diffusion rates

The governing equation for mass transfer in extraction is expressed as:

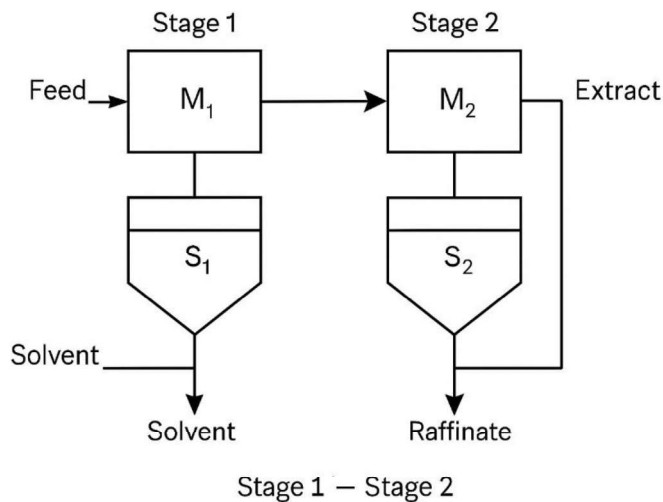
$$N = k_L a (C_A^* - C_A)$$

where  $N$  is the mass transfer rate ( $\text{mol}/\text{m}^2 \cdot \text{s}$ ),  $K_L$  is the overall mass transfer coefficient,  $a$  is the interfacial area,  $C_A^*$  is the equilibrium concentration, and  $C_A$  is the bulk concentration of solute.

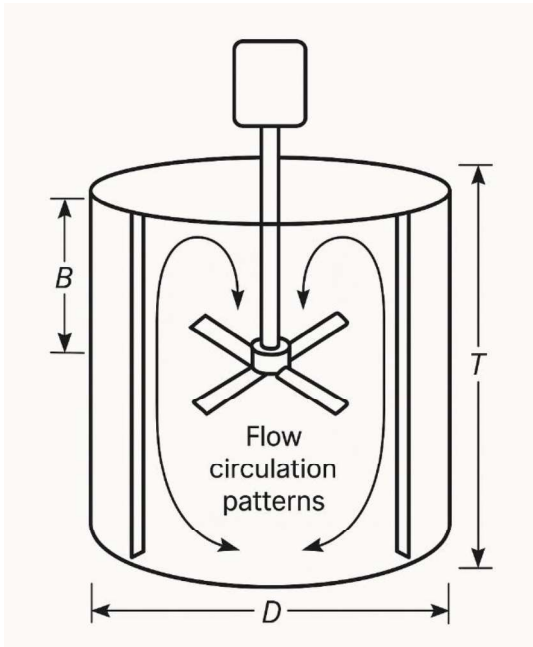
Industrial mixer-settlers are used for the extraction of copper, uranium, cobalt, and rare earth elements. They offer high selectivity and can be arranged in counter-current cascades to maximize efficiency.



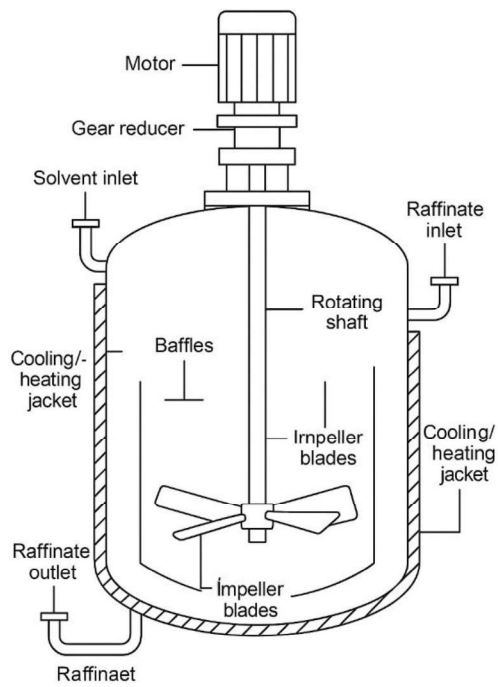
**Figure II-4-3: Mixer-Settler Unit**



**Figure II-4-4: Two-Stage Mixer-Settler System**



**Figure II-4-5: Mixer with Baffles**



**Figure II-4-6: Industrial Agitator for Liquid–Liquid Extraction**

#### **4.5 Reactor Design Considerations**

Designing hydrometallurgical reactors requires balancing reaction kinetics, heat transfer, and mass transfer efficiency. Agitation ensures uniform distribution of solids and reagents, while temperature and pH control stabilize chemical equilibria. Material selection is crucial since aggressive leach solutions can corrode reactor walls; common materials include titanium, rubber-lined steel, and polymer composites.

Scale-up from laboratory to industrial operation must consider geometric similarity, Reynolds number scaling, and mixing energy requirements. Computational fluid dynamics (CFD) is increasingly used to model hydrodynamics and optimize reactor performance.

#### **4.6 Industrial Applications**

Hydrometallurgical reactors are used in numerous industrial operations, including:

- Pressure leaching of zinc concentrates (Jarosite process)
- Nickel laterite leaching (High Pressure Acid Leach, HPAL)
- Copper oxide leaching (Heap and dump leaching)
- Uranium recovery from low-grade ores
- Solvent extraction of cobalt and rare earth elements

The integration of these reactors into closed-loop systems minimizes waste generation and allows for efficient water and reagent recycling, aligning with modern sustainable metallurgical practices.

Hydrometallurgical unit operations rely on precise control of chemical and physical phenomena. Leaching, precipitation, and solvent extraction remain the three pillars of aqueous metal recovery. The efficiency of these operations depends on reactor design, flow dynamics, and mass transfer mechanisms.

Modern developments in reactor technology—such as intensified mixing, continuous flow operation, and process automation—have significantly improved metal recovery yields, reduced reagent consumption, and enhanced environmental performance. As hydrometallurgy continues to evolve, reactor innovation will remain central to sustainable resource extraction.

## **Chapter III: Thermodynamics of Pyrometallurgical Transformations: Transformations of Solid Particles**

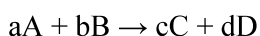
### **1- Thermodynamic data on oxide formation reactions**

#### **1.1 Introduction to Oxide Formation Thermodynamics**

The formation of metal oxides represents one of the most fundamental chemical transformations in pyrometallurgical systems. It determines the oxidation state and stability of metallic elements during high-temperature processes such as roasting, smelting, and refining. The thermodynamic analysis of oxide formation enables prediction of equilibrium conditions, reaction direction, and temperature limits for oxidation or reduction. Thermodynamics provides quantitative tools to assess the feasibility of oxidation reactions through key parameters such as enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), and Gibbs free energy ( $\Delta G$ ). The balance between these quantities determines whether a reaction is spontaneous at a given temperature and pressure.

#### **1.2 Fundamental Thermodynamic Quantities**

For a general chemical reaction:



the Gibbs free energy change is expressed as:

$$\Delta G = \Delta H - T\Delta S$$

where  $\Delta H$  is the change in enthalpy,  $T$  the absolute temperature, and  $\Delta S$  the change in entropy. A negative value of  $\Delta G$  indicates that the reaction proceeds spontaneously under constant temperature and pressure.

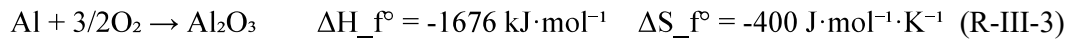
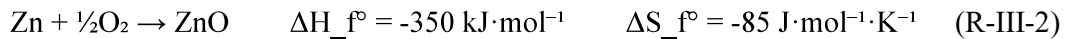
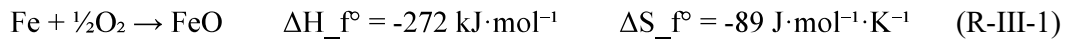
At equilibrium, the relationship between Gibbs free energy and the equilibrium constant ( $K$ ) is given by:

$$\Delta G^\circ = -RT \ln K$$

where  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). This relationship forms the basis of predicting the equilibrium composition of gas–solid systems in metallurgical processes.

### 1.3 Enthalpy and Entropy of Oxide Formation

The enthalpy of formation ( $\Delta H_f^\circ$ ) and entropy of formation ( $\Delta S_f^\circ$ ) are standard thermodynamic properties used to calculate the stability of oxides. These values are typically tabulated at 298 K for numerous metal oxides. For example:



The magnitude of  $\Delta H_f^\circ$  reflects the bond strength between metal and oxygen atoms, while  $\Delta S_f^\circ$  accounts for the decrease in randomness when gaseous oxygen reacts to form a condensed oxide phase.

### 1.4 Gibbs Free Energy and Oxide Stability

The Gibbs free energy change for oxide formation is the primary indicator of oxide stability. At constant pressure, it can be expressed as a linear function of temperature:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The slope of this relationship ( $-\Delta S^\circ$ ) represents the temperature dependence of stability, while the intercept ( $\Delta H^\circ$ ) reflects the heat effect of the reaction. Plotting  $\Delta G^\circ$  versus temperature provides valuable insight into the relative stability of oxides under various conditions.

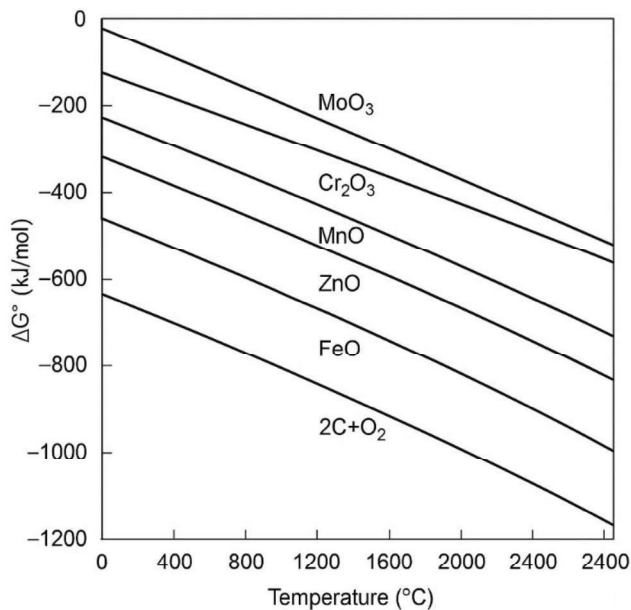


Figure III-1-1 – Standard Gibbs Free Energy vs. Temperature for Metal Oxides

### 1.5 The Ellingham Diagram

Ellingham diagrams (Figure III-1-2) are graphical representations of the standard Gibbs free energy change ( $\Delta G^\circ$ ) for the formation of oxides as a function of temperature. Each metal–oxygen system is represented by a straight line whose slope and position indicate the oxide's thermodynamic stability.

The diagram allows direct comparison of metals, helping identify which metals can reduce others' oxides. For instance, a metal whose line lies below another metal's oxide line can thermodynamically reduce that oxide. For example, aluminum, whose oxide line lies low on the diagram, can reduce many metal oxides such as  $\text{Fe}_2\text{O}_3$  and  $\text{CuO}$ .

The general reaction for oxide formation is:



The corresponding Gibbs free energy is calculated using tabulated values of  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$ .

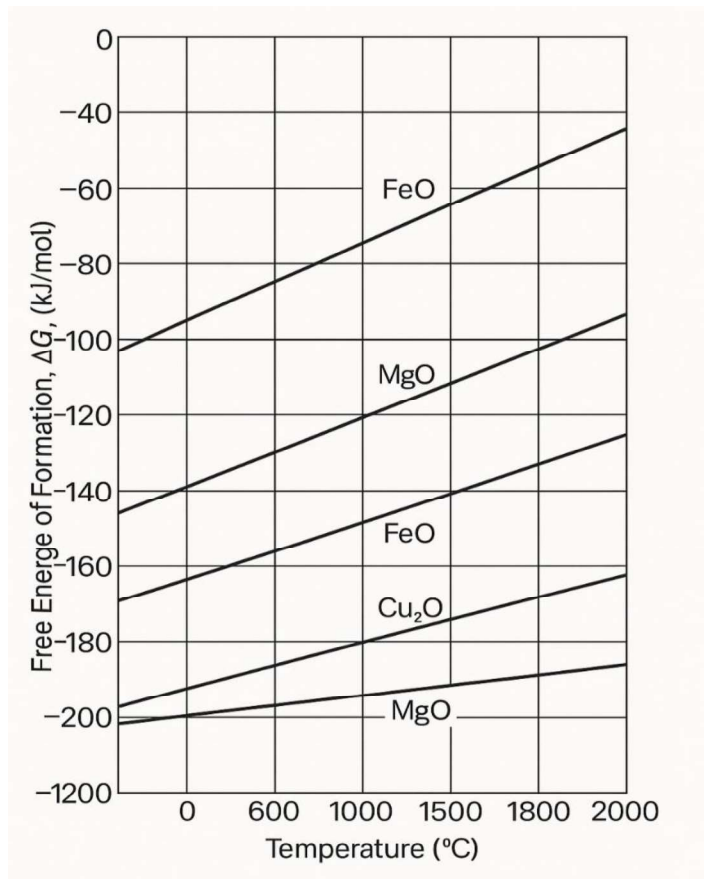


Figure III-1-2 – Typical Ellingham Diagram for Oxide Stability

## 1.6 Effect of Temperature and Oxygen Partial Pressure

The equilibrium between metal, oxide, and oxygen can be described by the reaction:



At equilibrium, the oxygen partial pressure ( $p_{O_2}$ ) corresponding to this reaction is obtained from the relation:

$$\Delta G^\circ = RT \ln(1/p_{O_2})$$

or rearranged as:

$$p_{O_2} = \exp(\Delta G^\circ / RT)$$

This expression allows calculation of the minimum oxygen pressure required to maintain oxide stability at a given temperature. As temperature increases,  $\Delta G^\circ$  becomes less negative for most oxides, leading to decreased oxide stability and easier reduction.

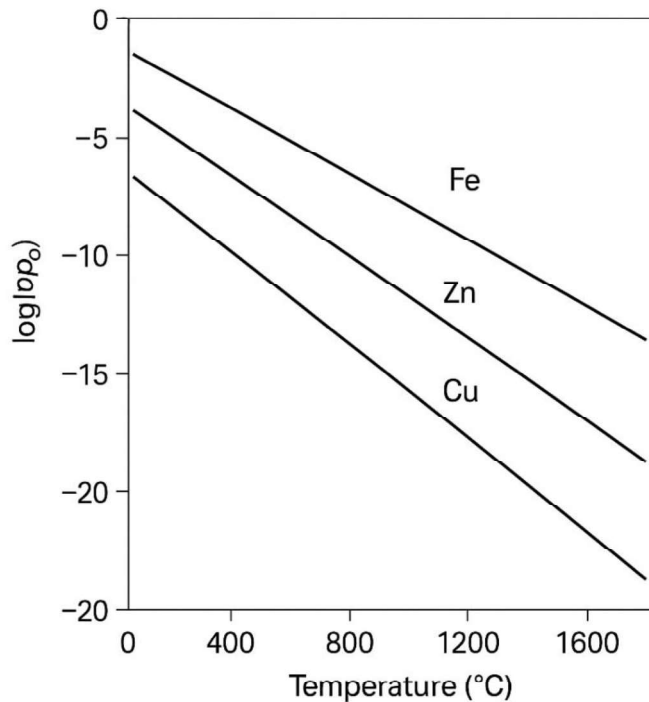


Figure III-1-3 – Variation of Equilibrium Oxygen Pressure with Temperature

### 1.7 Example: Iron Oxide Formation

For the reaction  $\text{Fe} + \frac{1}{2}\text{O}_2 \rightarrow \text{FeO}$ , the standard Gibbs free energy change is approximated by:

$$\Delta G^\circ = -272000 + 89T \text{ (J}\cdot\text{mol}^{-1}\text{)}$$

$$\text{At } 1000 \text{ K, } \Delta G^\circ = -272000 + 89(1000) = -183000 \text{ J}\cdot\text{mol}^{-1}$$

Since  $\Delta G^\circ < 0$ , FeO formation is spontaneous at 1000 K. At higher temperatures,  $\Delta G^\circ$  becomes less negative, indicating that FeO may decompose, especially under reducing atmospheres.

Similarly, for  $\text{Al}_2\text{O}_3$ ,  $\Delta G^\circ$  remains highly negative even at 2000 K, showing that aluminum oxide is extremely stable and difficult to reduce thermally.

### 1.8 Thermodynamic Data Tables

The following table summarizes typical thermodynamic data used in pyrometallurgical calculations for oxide formation reactions:

**Table III- 1- Thermodynamic Data Tables**

Metal	Reaction	$\Delta H_f^\circ$ (kJ/mol O <sub>2</sub> )	$\Delta S_f^\circ$ (J/mol·K)	$\Delta G^\circ$ (kJ/mol O <sub>2</sub> at 1000 K)
Fe	$2\text{Fe} + \text{O}_2 \rightarrow 2\text{FeO}$	-544	-178	-366
Zn	$2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$	-700	-170	-530
Al	$4\text{Al} + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3$	-3352	-800	-2550
Cu	$2\text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}_2\text{O}$	-320	-90	-230
Ni	$2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$	-480	-160	-320

### 1.9 Importance in Pyrometallurgical Processes

Understanding the thermodynamics of oxide formation is crucial for process design in pyrometallurgy. Roasting, smelting, and reduction reactions all depend on controlling oxygen potential and temperature. The thermodynamic stability of oxides determines whether a particular metal can be reduced using carbon, carbon monoxide, hydrogen, or another metal as a reducing agent.

For instance, in the production of metallic iron, reduction of  $\text{Fe}_2\text{O}_3$  to Fe occurs through sequential stages ( $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ ). Each transition corresponds to a specific equilibrium oxygen pressure, as derived from thermodynamic data.

Thermodynamic data on oxide formation reactions provide the foundation for understanding and predicting the behavior of metal–oxygen systems in pyrometallurgy. The Gibbs free energy and Ellingham diagrams remain essential tools for determining oxide stability, evaluating reduction conditions, and optimizing metallurgical furnace operations.

The quantitative approach enables engineers to design efficient, energy-saving, and environmentally responsible metallurgical processes.

## **2-Reduction of Oxides**

### **2.1 Introduction to the Reduction of Metal Oxides**

The reduction of metal oxides is one of the most important processes in pyrometallurgy. It is the fundamental step in converting oxide minerals or roasted products into pure metals. The process involves the removal of oxygen from metal oxides through reaction with a reducing agent such as carbon, carbon monoxide, hydrogen, or another metal. The thermodynamics of oxide reduction govern the choice of reductant, temperature range, and process conditions.

The feasibility of reduction is determined primarily by the Gibbs free energy change ( $\Delta G$ ) associated with the reaction. If  $\Delta G$  is negative at the operating temperature, the reduction proceeds spontaneously. Ellingham diagrams are essential tools for predicting reduction behavior, comparing the relative stability of oxides, and identifying feasible reduction routes.

### **2.2 Thermodynamic Basis of Reduction**

The general reaction for the reduction of a metal oxide (MO) can be expressed as:



where R is the reducing agent. The change in Gibbs free energy is given by:

$$\Delta G = \Delta H - T\Delta S$$

If  $\Delta G < 0$ , the reaction proceeds spontaneously. The stability of oxides and the ease of their reduction depend on the standard Gibbs free energy of formation of the oxide and the thermodynamic potential of the reducing agent.

For gaseous systems, the equilibrium between the oxide and reducing gas is described by:



The equilibrium constant (K) for this reaction is expressed as:

$$K = (p_{\text{CO}_2} / p_{\text{CO}})$$

and the Gibbs energy is related by:

$$\Delta G^\circ = -RT \ln K = RT \ln(p_{\text{CO}} / p_{\text{CO}_2})$$

### 2.3 The Ellingham Diagram for Reduction

The Ellingham diagram provides a graphical representation of the thermodynamic stability of oxides and the corresponding reducing power required. The reduction of a metal oxide by carbon or CO becomes possible when the line representing the oxide formation reaction lies above the line representing the oxidation of the reducing agent.

The CO/CO<sub>2</sub> ratio required for reduction at equilibrium can be calculated using the relation:

$$\log(p_{\text{CO}} / p_{\text{CO}_2}) = \Delta G^\circ / (2.303RT)$$

Thus, at a given temperature, only mixtures with a CO/CO<sub>2</sub> ratio higher than the equilibrium value can reduce the oxide.

For example, the reduction of FeO by CO follows:



At 1000 K, the equilibrium ratio ( $p_{\text{CO}} / p_{\text{CO}_2}$ )  $\approx$  1.6, indicating that a gas mixture richer in CO promotes reduction.

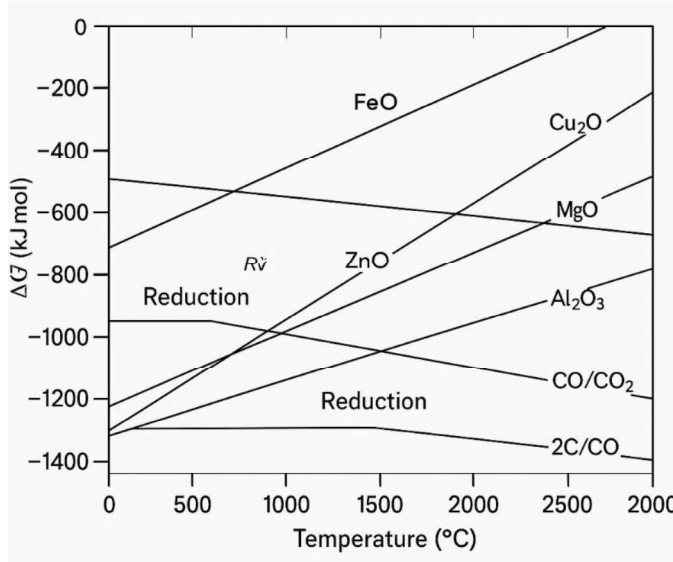
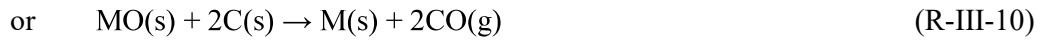


Figure III-2-1 – Ellingham Diagram Showing Reduction Zones for Oxides

## 2.4 Reduction by Carbon (Solid–Solid Reaction)

Reduction by carbon involves direct reaction between solid carbon and the metal oxide:



This reaction typically occurs at high temperatures, where carbon monoxide is generated in situ and serves as the primary reducing species. The process is therefore a combination of solid–solid and gas–solid reactions.

The thermodynamic feasibility of reduction by carbon can be represented by the intersection of the metal oxide line and the C/CO or CO/CO<sub>2</sub> lines in the Ellingham diagram. For instance, carbon can reduce Fe<sub>2</sub>O<sub>3</sub>, CuO, and NiO at moderate temperatures, but not Al<sub>2</sub>O<sub>3</sub> or MgO, which have much lower  $\Delta G^\circ$  values.

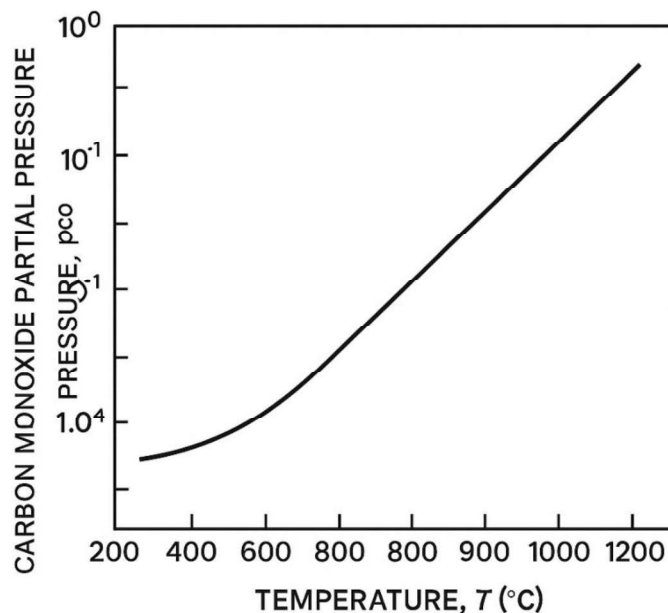
At equilibrium, the carbon gasification reaction is given by the Boudouard equation:



The equilibrium constant is:

$$K = (p_{\text{CO}}^2 / p_{\text{CO}_2}) = \exp(-\Delta G^\circ / RT)$$

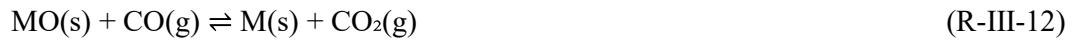
This equation governs the composition of the reducing gas in contact with the solid carbon.



**Figure III-2-2 – Reduction of Metal Oxides by Solid Carbon: Boudouard Equilibrium**

## 2.5 Reduction by Carbon Monoxide

Reduction by carbon monoxide is the most common mechanism in blast furnaces and shaft furnaces. It occurs via gas–solid reactions that are fast and efficient due to high diffusion rates. The typical reaction is:



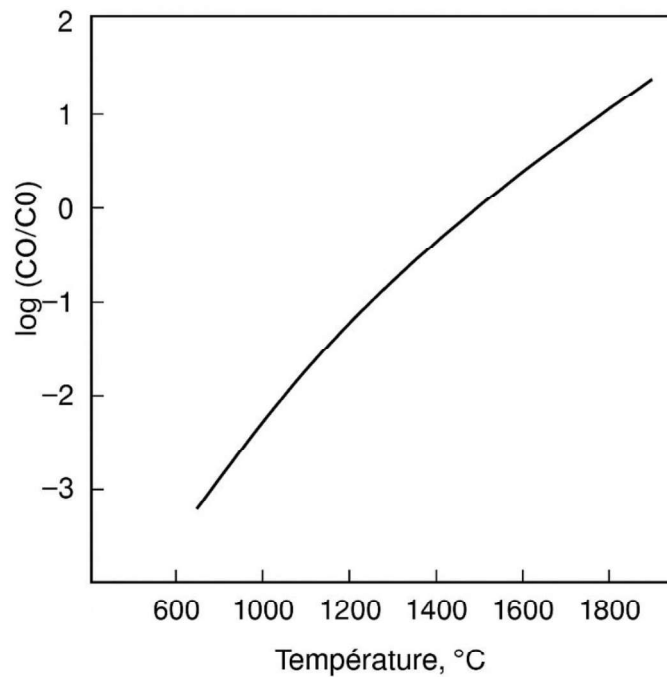
The equilibrium constant (K) and Gibbs free energy are expressed as:

$$K = (p_{\text{CO}_2} / p_{\text{CO}})$$

$$\Delta G^\circ = RT \ln(p_{\text{CO}} / p_{\text{CO}_2})$$

A high CO/CO<sub>2</sub> ratio favors reduction. At lower temperatures, the reaction may be limited by kinetics rather than thermodynamics.

Industrial examples include the reduction of iron oxides in blast furnaces and nickel oxides in rotary kilns.



**Figure III-2-3 – Equilibrium Relationship Between CO/CO<sub>2</sub> Ratio and Temperature**

## 2.6 Reduction by Hydrogen

Hydrogen is an effective reducing agent, particularly in processes requiring low impurity levels. The reduction reaction proceeds as:



The equilibrium constant is:

$$K = (p_{\text{H}_2\text{O}} / p_{\text{H}_2})$$

and the Gibbs energy change is given by:

$$\Delta G^\circ = RT \ln(p_{\text{H}_2} / p_{\text{H}_2\text{O}})$$

Hydrogen reduction is particularly attractive for oxides of iron, nickel, and tungsten. It produces only water vapor as a by-product, making it environmentally cleaner than carbon-based reduction.

The feasibility of hydrogen reduction depends on temperature and water vapor partial pressure. Hydrogen is more effective than CO at low temperatures, but requires higher energy input for large-scale applications.

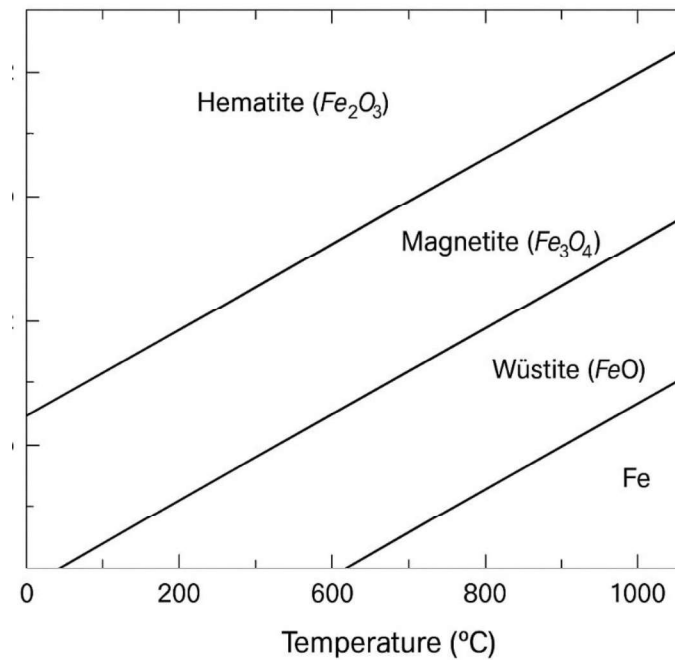


Figure III-2-4 – Reduction of Iron Oxide by Hydrogen: Thermodynamic Behavior

## 2.7 Metallothermic Reduction

Metallothermic reduction involves the use of a reactive metal as the reducing agent. Common examples include aluminum (aluminothermy), magnesium (magnesiothermy), and calcium (calciothermy). The reaction is highly exothermic, often producing molten metal directly.

A typical aluminothermic reaction is:



The Gibbs free energy for this reaction is highly negative even at elevated temperatures, demonstrating strong reducing power of aluminum.

Metallothermic reductions are used for producing metals with very stable oxides, such as chromium, titanium, and vanadium. They are typically carried out in refractory-lined crucibles or molds due to the intense heat generated.

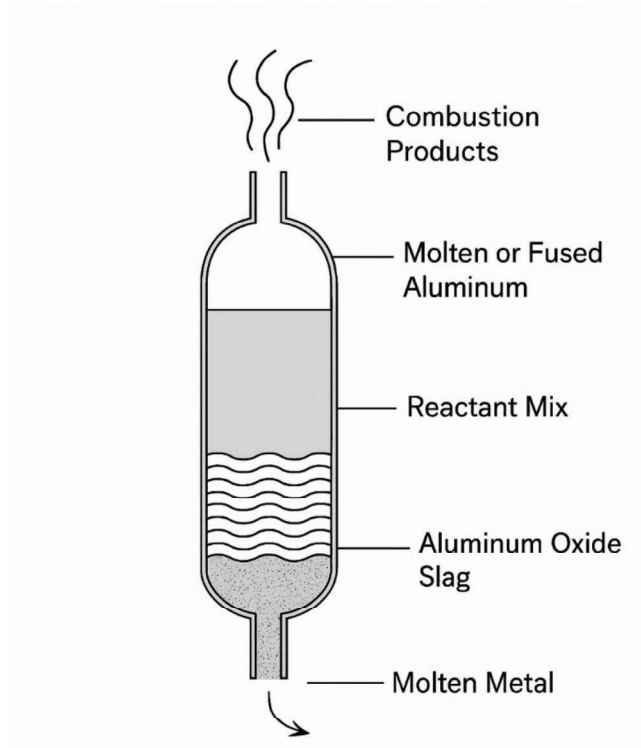


Figure III-2-5 – Schematic Diagram of an Aluminothermic Reactor

## 2.8 Stepwise Reduction of Iron Oxides

The reduction of iron oxides provides a classical example of stepwise transformation governed by thermodynamics. The overall process proceeds through successive stages:



Each reaction has its own equilibrium temperature and CO/CO<sub>2</sub> ratio, determined from Ellingham data. The first steps occur at lower temperatures (~500–700 °C), while the final reduction of FeO to Fe requires higher temperatures (>800 °C).

The global process efficiency depends on maintaining an adequate reducing atmosphere and minimizing back-oxidation of metallic iron.

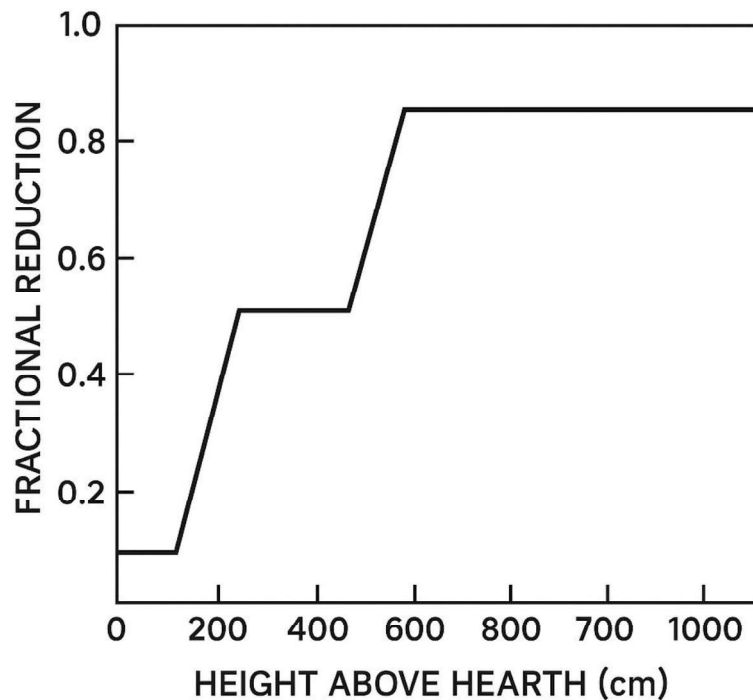


Figure III-2-6 – Stepwise Reduction of Iron Oxides in a Blast Furnace

## 2.9 Industrial Reduction Processes

Reduction of oxides forms the basis of many metallurgical operations, including:

- **Blast furnace ironmaking:** Reduction of hematite using CO and C.
- **Direct reduction of iron (DRI):** Gas-based reduction using CO and H<sub>2</sub>.
- **Zinc production:** Carbothermic reduction of ZnO to Zn vapor.
- **Nickel extraction:** Reduction roasting followed by magnetic separation.
- **Titanium production:** Magnesiothermic reduction of TiCl<sub>4</sub> or TiO<sub>2</sub>.

Thermodynamic data enable engineers to select appropriate reductants, temperatures, and reactor types to achieve high metal recovery.

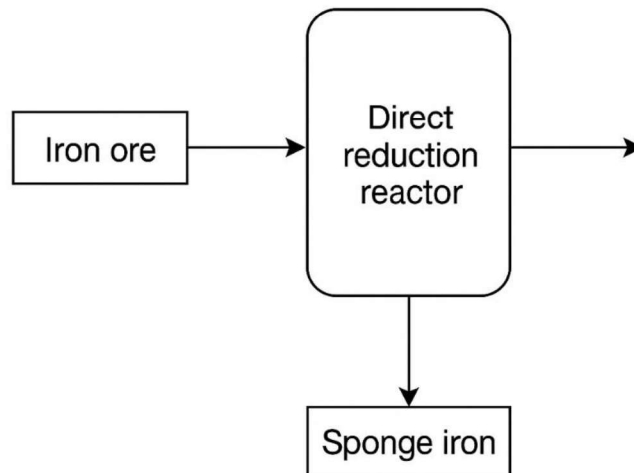


Figure III-2-7 – Flow Diagram of a Direct Reduction Process

### 2.10 Example Calculation: Reduction of ZnO by CO

Consider the reaction:



At 1000 K, the standard Gibbs free energy change is given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (-350000) - (1000 \times -150) = -200000 \text{ J/mol}$$

Thus, the reaction is thermodynamically favorable at 1000 K. Zinc vapor can then be condensed to recover metallic zinc.

This calculation illustrates the principle that increasing temperature generally favors reduction for endothermic reactions.

The reduction of oxides is a thermodynamically controlled process that forms the foundation of pyrometallurgy. Depending on the metal oxide and reductant, reduction may proceed via carbon, CO, hydrogen, or other metals. Ellingham diagrams provide invaluable insight into the feasibility and temperature range for reduction. Understanding these principles is essential for designing efficient and sustainable metallurgical processes.

### 3 Roasting of Sulfides

#### 3.1 Introduction to Roasting

Roasting is one of the oldest and most important pyrometallurgical operations. It consists of the controlled oxidation of metal sulfides to produce oxides, sulfates, or elemental metals, depending on temperature and gas composition. This process serves as a preparatory step before smelting or leaching, as it removes sulfur and converts the mineral into a form more amenable to subsequent processing.

The thermodynamics of roasting reactions dictate the extent of oxidation, the temperature of transformation, and the partial pressure of oxygen or sulfur dioxide in the gas phase. Roasting can be classified as oxidizing, reducing, chloridizing, or sulfating, depending on the gaseous environment and process objectives.

#### 3.2 Thermodynamic Principles of Sulfide Oxidation

The general oxidation reaction of a metal sulfide is represented as:



The Gibbs free energy change ( $\Delta G^\circ$ ) for this reaction determines whether oxidation proceeds spontaneously under given conditions. The equilibrium constant ( $K$ ) is expressed as:

$$K = p_{\text{SO}_2} / p_{\text{O}_2}^{3/2}$$

A negative value of  $\Delta G^\circ$  implies spontaneous oxidation, while a positive value indicates that the reaction requires external energy input or a higher oxygen potential.

The temperature dependence of oxide and sulfate formation is analyzed using standard thermodynamic data ( $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$ ), which are often represented graphically in predominance diagrams or temperature–partial pressure plots.

#### 3.3 Types of Roasting Processes

Depending on the objective, roasting operations can be categorized as follows:

- **Oxidizing Roasting:** Converts sulfides into oxides by complete oxidation of sulfur to  $\text{SO}_2$ .

- **Sulfating Roasting:** Produces sulfates at moderate temperatures in the presence of excess SO<sub>2</sub> and limited O<sub>2</sub>.

- **Partial Roasting:** Involves incomplete oxidation, forming a mixture of sulfide and oxide phases.

- **Reducing Roasting:** Employs CO or H<sub>2</sub> to reduce oxides or sulfates to lower oxidation states.

- **Chloridizing Roasting:** Introduces Cl<sub>2</sub> or chlorides to convert oxides into volatile chlorides.

Each roasting type requires a precise balance of temperature, oxygen potential, and gas composition to achieve the desired chemical transformation.

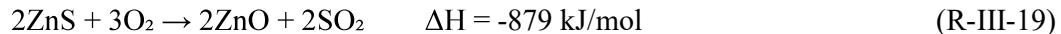
### 3.4 Oxidizing Roasting

Oxidizing roasting (Figure III-3-1) is the most common industrial roasting process. It converts metal sulfides into oxides or metals by reacting with oxygen or air. The general reaction is:

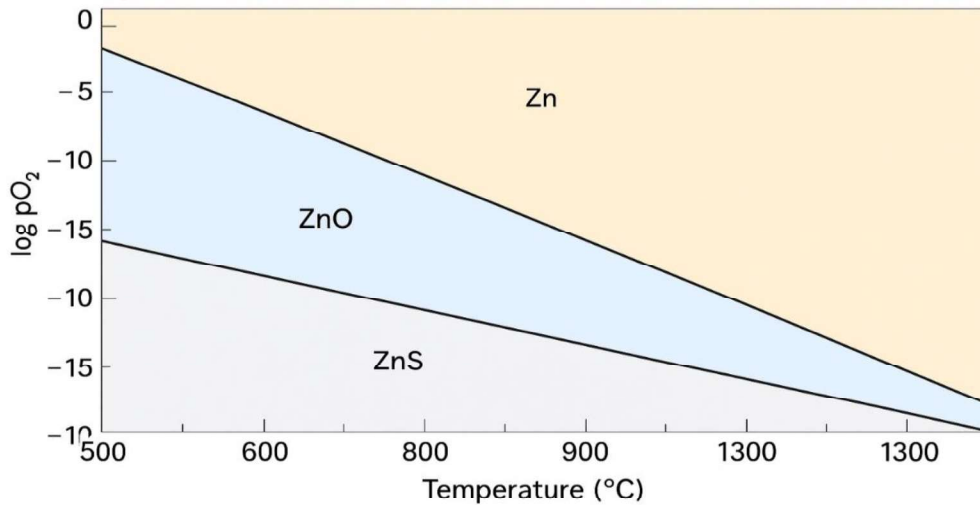


The thermodynamics of this process depend on the Gibbs free energy of oxide and SO<sub>2</sub> formation. Metals with more stable oxides (e.g., Fe, Zn, Ni) readily form oxides, whereas noble metals such as Cu and Pb may form intermediate sulfates or sub-oxides under certain conditions.

An example is the oxidation of zinc sulfide:



This reaction is highly exothermic and self-sustaining once initiated. Control of temperature and airflow is essential to prevent sintering and melting of particles.



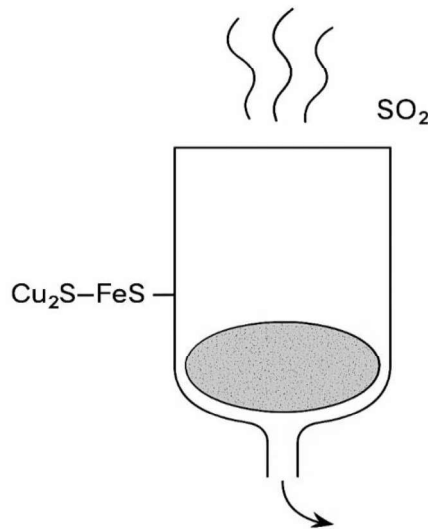
**Figure III-3-1 – Temperature–Partial Pressure Diagram for ZnS Roasting**

### 3.5 Partial Roasting

Partial roasting (Figure III-3-2) is carried out when it is desirable to retain part of the sulfide in the roasted product. This occurs when the objective is to produce a mixed sulfide–oxide material for subsequent reduction or smelting. For example:



Partial roasting is used in copper metallurgy to produce matte with the desired sulfur content before smelting. The temperature and oxygen partial pressure must be carefully controlled to maintain equilibrium between sulfide and oxide phases.



**Figure III-3-2 – Schematic Representation of Partial Roasting in Cu–Fe–S System**

### 3.6 Sulfating Roasting

Sulfating roasting is performed at lower temperatures (600–800 °C) in an atmosphere containing SO<sub>2</sub> and limited O<sub>2</sub>. The aim is to convert metal oxides or sulfides into soluble sulfates suitable for hydrometallurgical leaching. A typical reaction is:



Thermodynamically, the process requires moderate oxygen potentials to prevent decomposition of the sulfate. Sulfating roasting is applied in the treatment of copper, nickel, and cobalt concentrates to enhance metal recovery.

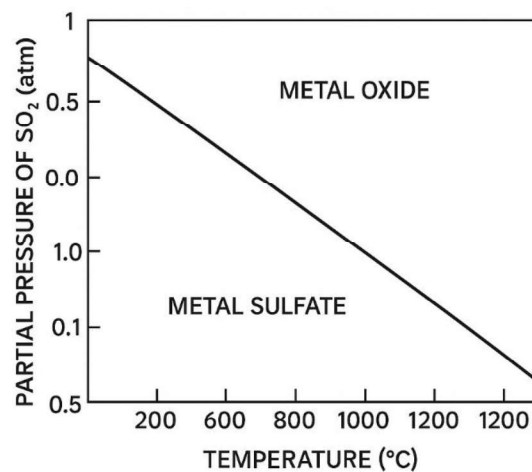


Figure III-3-3 – Equilibrium Diagram for Sulfate Formation from Metal Oxides

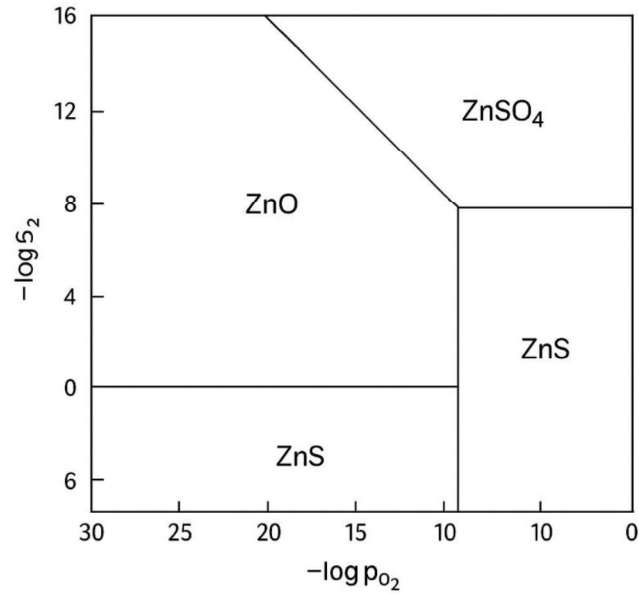
### 3.7 Predominance Area Diagrams

Predominance area diagrams (Figure III-3-4) are useful for understanding the stability regions of sulfide, oxide, and sulfate phases as a function of temperature and oxygen partial pressure. The boundaries between these regions correspond to equilibrium conditions derived from thermodynamic data.

For the Zn–S–O system, the following equilibria can be represented:



Plotting  $\log(p_{\text{SO}_2}/p_{\text{O}_2})$  versus temperature provides insight into the transitions between oxide, sulfide, and sulfate stability zones.



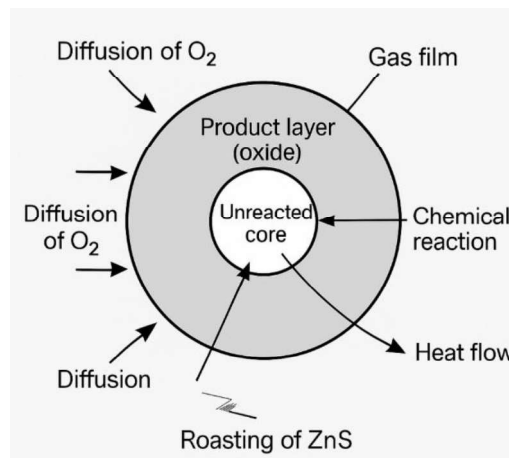
**Figure III-3-4 – Predominance Area Diagram for Zn–S–O System**

### 3.8 Kinetics of Roasting Reactions

Although roasting is thermodynamically favorable for most sulfides, the rate of reaction depends on kinetics and diffusion. The process involves successive steps:

1. Diffusion of oxygen through the gas film to the solid surface.
2. Chemical reaction at the gas–solid interface.
3. Diffusion of SO<sub>2</sub> through the porous product layer.

The overall rate is often controlled by diffusion through the oxide layer. The shrinking core model is commonly used to describe these mechanisms, where the unreacted core decreases progressively as oxidation proceeds.



**Figure III-3-5 – Schematic Representation of the Shrinking Core Model in Roasting**

### 3.9 Industrial Roasting Furnaces

Several furnace types are employed for industrial roasting, depending on feed properties and process requirements:

- **Multiple-hearth furnaces:** Suitable for fine concentrates and controlled oxidation.
- **Fluidized-bed roasters:** Provide excellent heat and mass transfer; ideal for sulfide ores like ZnS and NiS.
- **Rotary kilns:** Used for coarse materials or where longer residence time is required.
- **Flash roasters:** Operate at high temperatures with short contact times, enabling continuous oxidation of fine particles.

Fluidized-bed roasters are particularly popular for their high efficiency and uniform temperature control. They operate at temperatures between 900 and 1000 °C and can process large quantities of concentrate continuously.

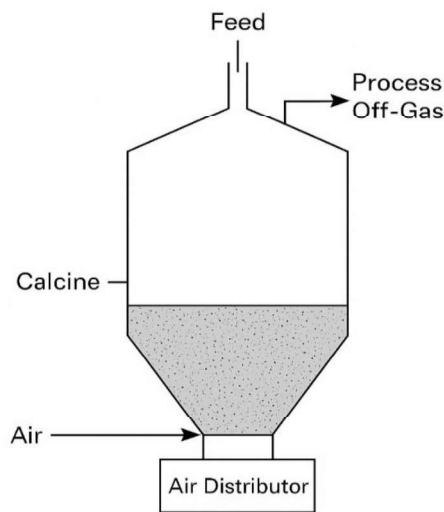


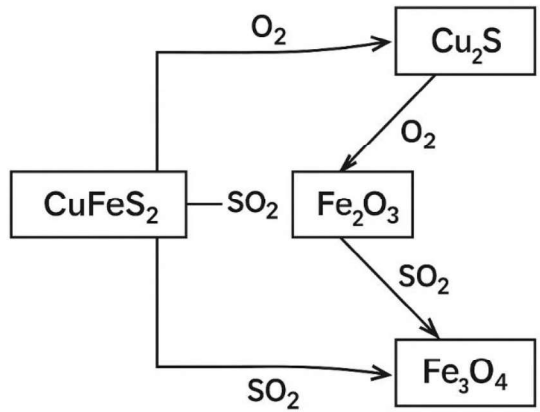
Figure III-3-6 – Typical Design of a Fluidized-Bed Roaster

### 3.10 Example: Roasting of Copper Concentrates

Copper sulfide concentrates primarily contain chalcopyrite ( $\text{CuFeS}_2$ ). The roasting process partially oxidizes the mineral to form copper sulfide matte and iron oxide, with sulfur evolving as  $\text{SO}_2$  gas. The reaction sequence is:



The roasting process is carefully controlled to maintain the desired sulfur level in the matte for the subsequent smelting stage.



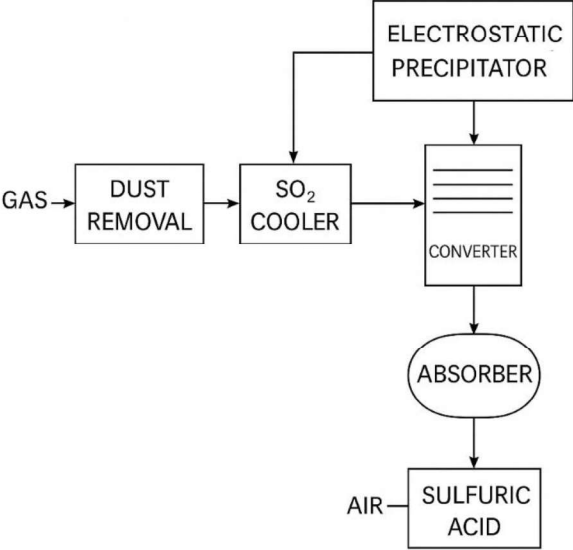
**Figure III-3-7 – Reaction Pathway for CuFeS<sub>2</sub> Roasting**

**3.11 Environmental Aspects of Roasting**

Roasting generates large quantities of sulfur dioxide (SO<sub>2</sub>), which must be treated before release to the atmosphere. Modern metallurgical plants employ gas capture and sulfur recovery systems to convert SO<sub>2</sub> into sulfuric acid. The overall reaction for acid production is:



These integrated systems greatly reduce environmental pollution and allow recovery of valuable by-products. Process optimization ensures minimal emission of particulates and unreacted gases.



**Figure III-3-8 – Sulfur Dioxide Recovery and Acid Plant Flow Diagram**

Roasting of sulfides plays a crucial role in the preparation of ores for further pyrometallurgical or hydrometallurgical treatment. Thermodynamic data enable prediction of oxidation equilibria, while kinetic considerations determine process rates. Modern roasting technologies, including fluidized and flash roasters, provide efficient and environmentally sustainable solutions for large-scale metal production.

## 4 Chlorination of Oxides

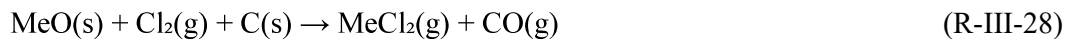
### 4.1 Introduction to Chlorination in Pyrometallurgy

Chlorination represents a distinct class of pyrometallurgical processes involving the conversion of metallic oxides, sulfides, or silicates into volatile metal chlorides. These chlorides are then separated, purified, and decomposed to obtain pure metals. The process is of great importance for the extraction of refractory and reactive metals such as titanium, zirconium, uranium, and rare earth elements, which cannot be efficiently reduced by conventional carbon or hydrogen-based methods.

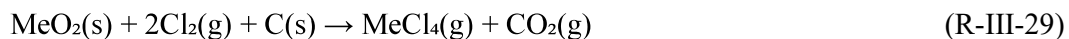
Thermodynamically, chlorination relies on the reaction between a solid oxide and a chlorinating agent ( $\text{Cl}_2$ ,  $\text{HCl}$ , or carbon tetrachloride) under high-temperature conditions. The feasibility of such transformations depends on the Gibbs free energy change ( $\Delta G^\circ$ ), the partial pressures of chlorine and oxygen, and the temperature of operation.

### 4.2 Thermodynamic Basis of Chlorination Reactions

The general reaction for the chlorination of a metal oxide can be expressed as:



or, for higher oxides:



The Gibbs free energy of chlorination ( $\Delta G^\circ$ ) is obtained from standard thermodynamic data using the relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The reaction proceeds spontaneously when  $\Delta G^\circ < 0$ . The standard enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) values for these reactions can be found in thermochemical tables, and their temperature dependence allows determination of the equilibrium conditions.

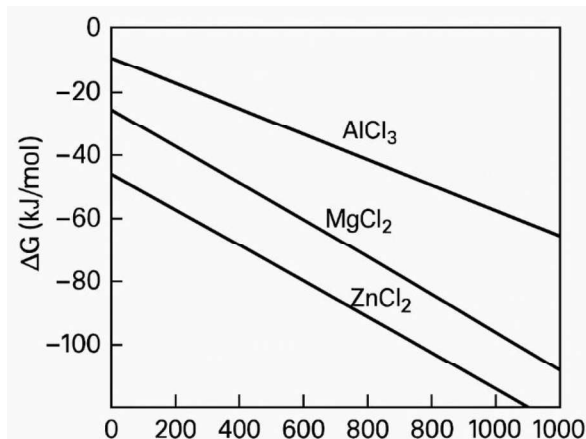


Figure III-4-1 – Ellingham-Type Diagram for Metal Chloride Formation

### 4.3 Chlorinating Agents

Several chlorinating agents are used in industrial and laboratory-scale processes, depending on the reactivity and sensitivity of the metal oxide involved:

- **Chlorine gas (Cl<sub>2</sub>):** The most direct and powerful chlorinating agent; often combined with a reducing agent such as carbon.
- **Hydrogen chloride (HCl):** Used for mild chlorination or in combination with oxidants.
- **Phosgene (COCl<sub>2</sub>):** Applied when moisture-sensitive intermediates must be avoided.
- **Metal chlorides (e.g., FeCl<sub>3</sub>, AlCl<sub>3</sub>):** Used as catalytic chlorination agents for refractory oxides.

In practice, mixtures such as Cl<sub>2</sub> + C or Cl<sub>2</sub> + CO are employed to simultaneously reduce and chlorinate metal oxides, as in the carbochlorination of TiO<sub>2</sub> and ZrO<sub>2</sub>.

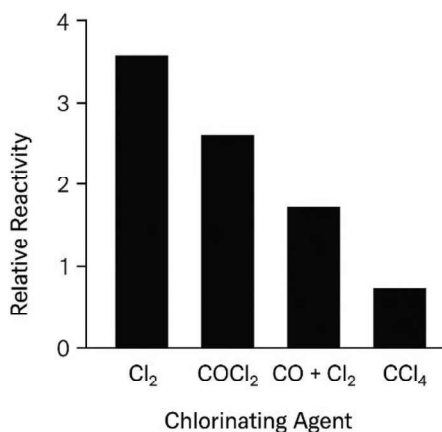
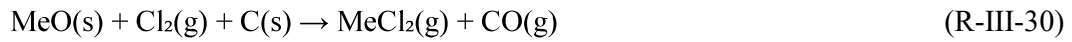


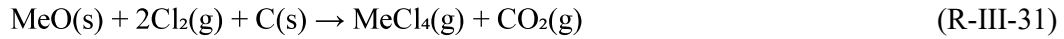
Figure III-4-2 – Comparative Reactivity of Different Chlorinating Agents

#### 4.4 Carbochlorination of Metal Oxides

Carbochlorination involves the simultaneous use of carbon and chlorine to convert metal oxides into volatile chlorides. The overall reaction can be represented as:

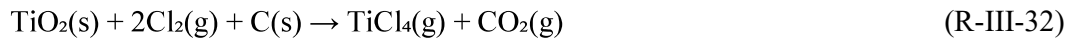


or, in cases where  $\text{CO}_2$  is formed:

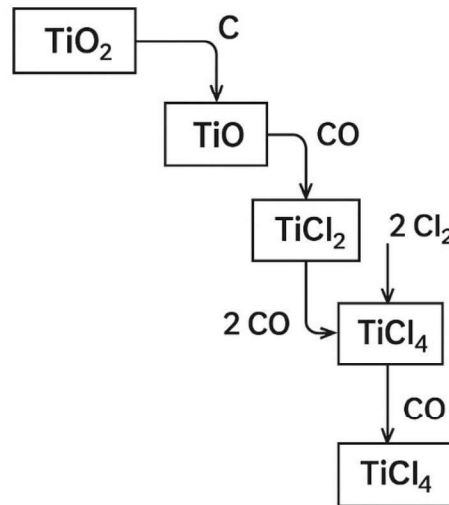


This process is exothermic for most transition metals. The presence of carbon enhances the reaction by reducing the oxide and consuming oxygen, thereby shifting the equilibrium toward chloride formation.

An example is the carbochlorination of titanium dioxide, which forms titanium tetrachloride:



$$\Delta G^\circ_{1000\text{K}} = -200 \text{ kJ/mol}$$



**Figure III-4-3 – Carbochlorination Mechanism of  $\text{TiO}_2$  at High Temperature**

#### 4.5 Thermodynamic Evaluation of Chlorination

The stability of metal chlorides relative to oxides can be analyzed using Gibbs free energy diagrams similar to Ellingham plots. For instance, the reaction:

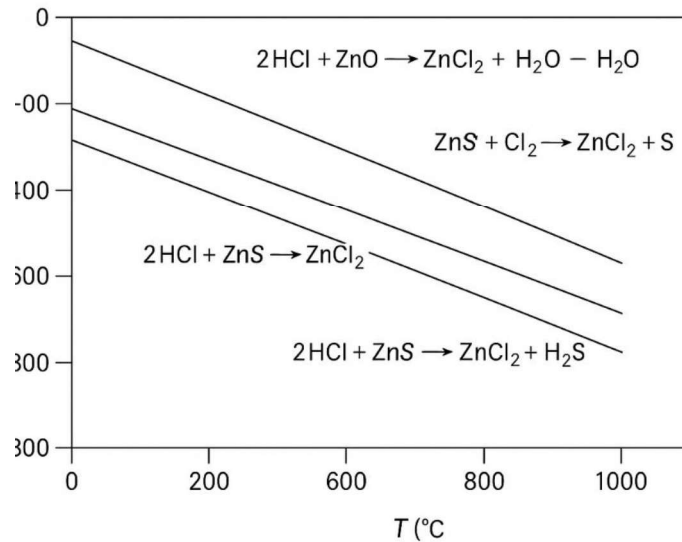


is governed by the relation:

$$\Delta G^\circ = -RT \ln\left[\frac{p_{\text{MeCl}_2} \times p_{\text{O}_2}^{1/2}}{p_{\text{Cl}_2}}\right]$$

A negative  $\Delta G^\circ$  implies that the oxide can be converted into the chloride under the given conditions. The equilibrium partial pressures of  $\text{Cl}_2$  and  $\text{O}_2$  determine the selectivity of the reaction and can be used to design chlorination reactors.

The influence of temperature is critical: higher temperatures typically increase volatility of chlorides but may also promote their decomposition. Therefore, optimal operating temperatures must balance these opposing effects.



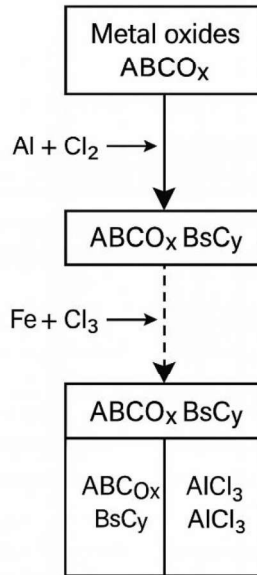
**Figure III-4-4 – Gibbs Free Energy of Chlorination Reactions vs. Temperature**

#### 4.6 Selective Chlorination

Selective chlorination is designed to target one component in a multi-oxide mixture while leaving others unreacted. This approach is especially useful in complex ores or metallurgical residues containing multiple metals.

The principle is based on differences in Gibbs free energy for chloride formation. Metals forming more stable chlorides (e.g., Fe, Al, Ti) chlorinate preferentially, while less reactive metals (e.g., Ni, Cu, Co) remain in oxide form.

Selective chlorination is used in the recovery of valuable metals from slags, fly ash, and red mud, allowing separation of  $\text{FeCl}_3$ ,  $\text{TiCl}_4$ , and  $\text{AlCl}_3$  vapors for further processing.



**Figure III-4-5 – Selective Chlorination Scheme for Multi-Metal Oxides**

#### 4.7 Industrial Chlorination Processes

Several industrial processes utilize chlorination for the extraction of metals. The most notable examples include:

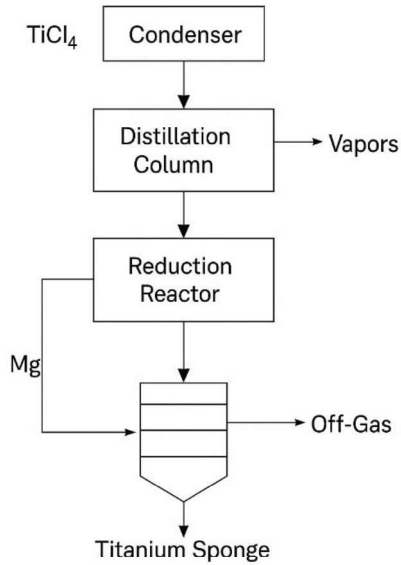
- **The Kroll Process:** Involves chlorination of  $\text{TiO}_2$  to  $\text{TiCl}_4$ , followed by reduction with magnesium.

- **The Van Arkel–de Boer Process:** Produces high-purity zirconium or titanium by thermal decomposition of volatile iodides.

- **Niobium and Tantalum Production:** Carbochlorination of mixed oxides, followed by fractional distillation of chlorides.

- **Uranium Refining:** Chlorination of  $\text{UO}_2$  to volatile  $\text{UCl}_4$ , used in nuclear fuel reprocessing.

These processes combine thermodynamic efficiency with the ability to achieve exceptional purity, especially in metals sensitive to oxygen contamination.



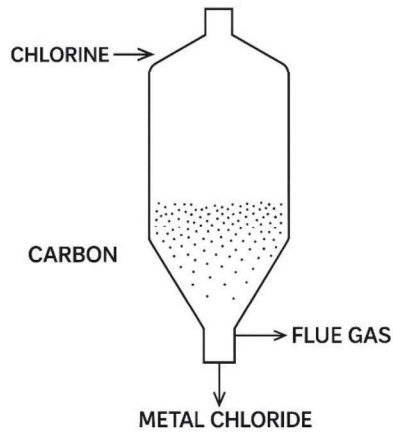
**Figure III-4-6 – Industrial Flow Diagram of the Kroll Process for Titanium**

#### **4.8 Chlorination Reactors and Equipment**

Chlorination reactions are conducted in high-temperature reactors resistant to corrosion by chlorine and metal chlorides. Common reactor types include:

- ***Fluidized-bed reactors:*** For fine powders, ensuring uniform contact between solids and gases.
- ***Rotary kilns:*** Suitable for coarse feed materials and high throughput.
- ***Fixed-bed reactors:*** Used in laboratory and pilot-scale tests.
- ***Plasma-assisted chlorinators:*** Utilize electric arcs or RF plasma to enhance reaction kinetics.

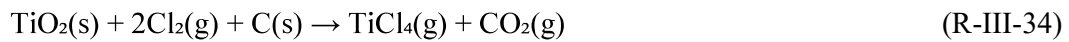
Materials of construction typically include nickel alloys, graphite, and ceramic linings resistant to chloride attack. Precise temperature and gas flow control are essential to maintain selectivity and prevent unwanted corrosion.



**Figure III-4-7 – Schematic Diagram of a Fluidized-Bed Chlorinator**

**4.9 Example: Chlorination of Titanium Dioxide (TiO<sub>2</sub>)**

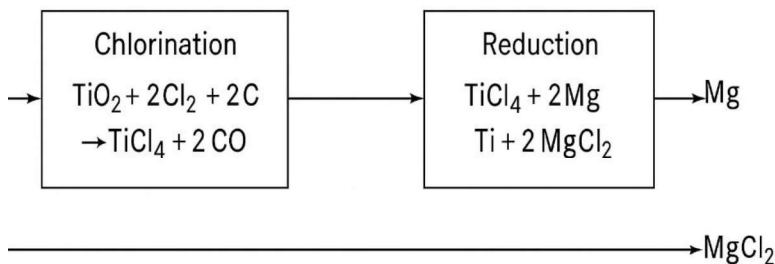
The chlorination of TiO<sub>2</sub> is a key step in the production of metallic titanium through the Kroll process. The reaction proceeds as follows:



TiCl<sub>4</sub> is then condensed, purified, and reduced by molten magnesium to produce titanium sponge:



The process operates at 900–1000 °C under controlled chlorine and carbon feed to maximize TiCl<sub>4</sub> yield. Carbon ensures continuous removal of oxygen and enhances the kinetics of chlorination.

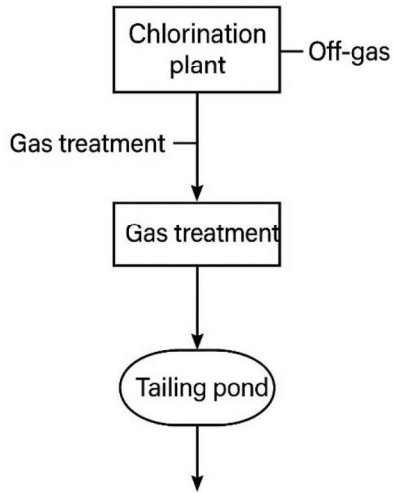


**Figure III-4-8 – Chlorination and Reduction Steps in the Kroll Process**

**4.10 Environmental and Safety Considerations**

Chlorination involves handling toxic and corrosive gases such as Cl<sub>2</sub> and HCl. Therefore, strict safety measures must be applied, including gas scrubbing, neutralization, and containment systems. Waste gases are typically treated through absorption in alkaline solutions to form innocuous salts such as NaCl and Na<sub>2</sub>CO<sub>3</sub>.

The recovery of chlorine from waste streams through electrolysis or catalytic oxidation contributes to process sustainability. In addition, closed-loop chlorination systems are being developed to minimize emissions and improve efficiency.



**Figure III-4-9 – Gas Treatment and Recycling in a Chlorination Plant**

Chlorination of oxides is a powerful thermochemical method for producing volatile metal halides, enabling the extraction and purification of refractory and high-value metals. Thermodynamic principles guide the selection of chlorinating agents, reaction conditions, and process design. Industrial chlorination processes such as the Kroll and Van Arkel–de Boer methods demonstrate the effectiveness of chlorination in modern metallurgical operations.

Understanding the thermodynamics and kinetics of chlorination remains crucial for optimizing efficiency, ensuring environmental compliance, and advancing future metallurgical technologies.

## References

Habashi, F. (1997). Principles of Extractive Metallurgy. Volumes 1–4. Métallurgie et Matériaux, Québec: Metallurgie Extractive Québec.

Biswas, A. K., & Davenport, W. G. (1994). Extractive Metallurgy of Copper (4th ed.). Pergamon Press.

Rosenqvist, T. (2004). Principles of Extractive Metallurgy. Tapir Academic Press.

Gilchrist, J. D. (1989). Extraction Metallurgy. Pergamon Press.

Davenport, W. G., King, M., Schlesinger, M., & Biswas, A. K. (2011). Extractive Metallurgy of Copper (5th ed.). Elsevier.

Gupta, C. K., & Krishnamurthy, N. (1992). Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals. CRC Press.

Habashi, F. (1999). Hydrometallurgy – Textbook and Handbook. Métallurgie Extractive Québec.

Ray, H. S., & Ghosh, A. (2007). Principles of Extractive Metallurgy. New Age International Publishers.

Habashi, F. (2000). A Textbook of Hydrometallurgy. Metallurgie Extractive Québec.

Pletcher, D., & Walsh, F. C. (2018). Industrial Electrochemistry (3rd ed.). Springer.

International Nickel Study Group (2022). World Nickel Statistics. Lisbon.

Ministère de l'Énergie et des Mines (Algérie). Rapport sur le développement du secteur minier national, Alger, 2023.

Begar, A. (2023). Cours de Métallurgie Extractive. Université Mohamed Khider – Biskra, Département de Génie Mécanique.