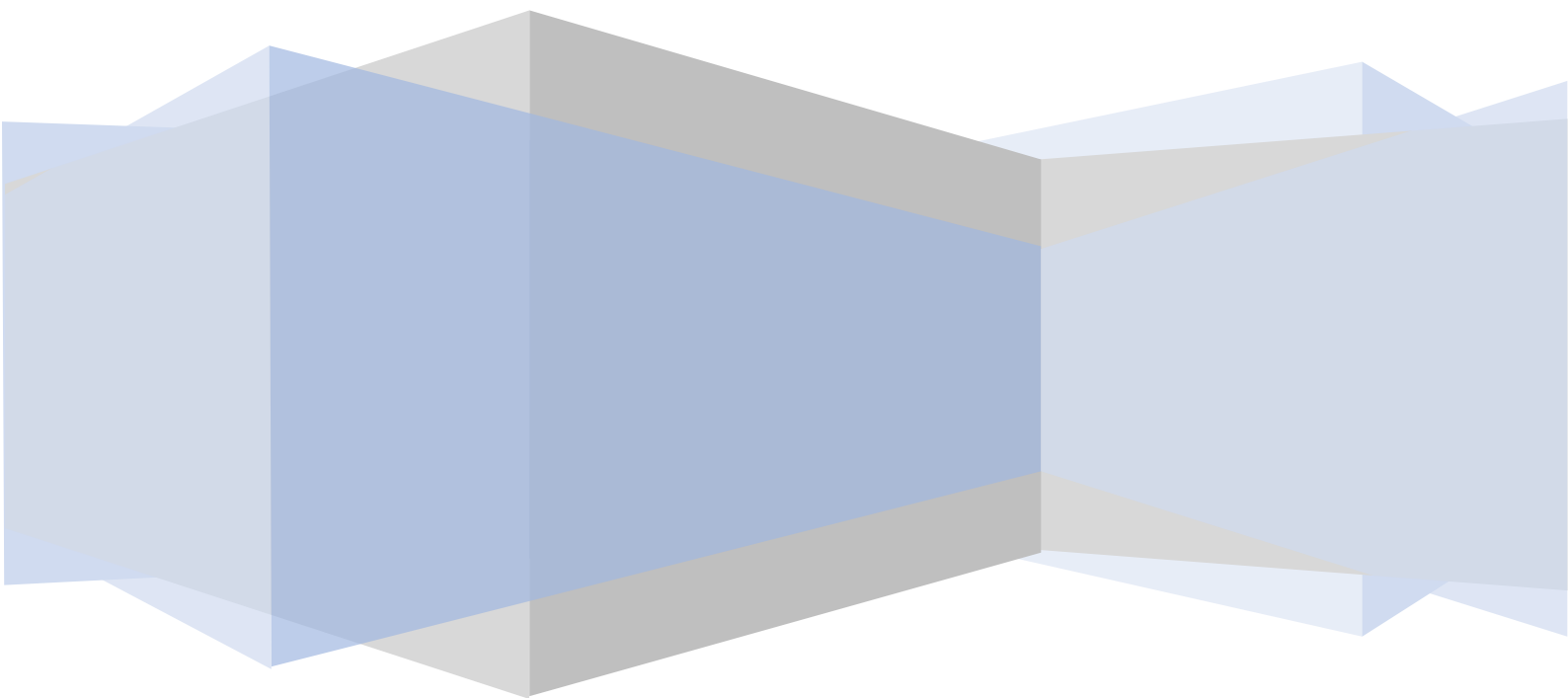


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PROCESS ENGINEERING DEPARTEMENT



Mineral Chemistry



CHAPTER IV: THE MAJOR METALLURGIES

IV.1. INTRODUCTION:

Advances in metalworking have been linked to higher temperatures in melting metals. As we developed methods to achieve higher temperatures, so did our alloying technologies. Metals with lower melting points, like copper and its alloy bronze, were discovered before iron and its alloy steel.

Ancient civilizations identified seven metals: Iron, Tin, Lead, Copper, Mercury, Silver, and Gold. Gold, found naturally in workable form, required no heat for processing. Most other metals are found in ore, which requires heating or other processes. Gold's malleability and ductility made it workable without technology beyond a stone hammer and anvil.

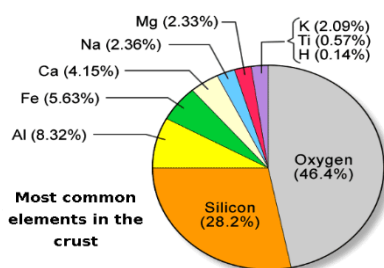
IV.2. DEFINITIONS:

IV.2.1. METALLURGY:

Metallurgy is a branch of materials science and engineering dedicated to exploring the physical and chemical characteristics of metallic elements, along with their inter-metallic compounds and combinations referred to as alloys.

IV.2.1. ORES:

Ore is a naturally occurring material or rock that contains a valuable mineral, metal, or other economically significant substance. It is typically mined and processed to extract the desired element or elements, which may have commercial or industrial value. However, the value of ore is determined by the concentration of valuable minerals and market demand, with higher concentrations being more valuable. Factors like extraction costs, geopolitical conditions, and global economic conditions also impact the



value. Market prices for metals and minerals can fluctuate based on supply and demand dynamics.

The original source of all metal ores is the earth's crust, which generally contains oxides, sulfides, and silicates of native metals that are not commonly concentrated in the earth's crust. The process of ore formation is called ore genesis.

Extracting the "important" element from the ore involves separating the ore from unwanted rocks, separating minerals from the ore, and using additional separation methods due to most minerals being chemical compounds containing metals and other elements.

Minestrone is a solid aggregate formed from crushed ore, with the valuable portion known as **mineral** and the worthless portion as **gangue**, which is then separated.

Group	Member	Formula	Economic Use
Oxides	Hematite	Fe_2O_3	Ore of iron, pigment
	Magnetite	Fe_3O_4	Ore of iron
	Corundum	Al_2O_3	Gemstone, abrasive
	Ice	H_2O	Solid form of water
	Chromite	FeCr_2O_4	Ore of chromium
	Ilmenite	FeTiO_3	Ore of titanium
	Sulfides	Galena	PbS
Sphalerite		ZnS	Ore of zinc
Pyrite		FeS_2	Sulfuric acid production
Chalcopyrite		CuFeS_2	Ore of copper
Bornite		Cu_5FeS_4	Ore of copper
Cinnabar		HgS	Ore of mercury
Sulfates		Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Anhydrite	CaSO_4	Plaster
	Barite	BaSO_4	Drilling mud
Native elements	Gold	Au	Trade, jewelry
	Copper	Cu	Electrical conductor
	Diamond	C	Gemstone, abrasive
	Sulfur	S	Sulfa drugs, chemicals
	Graphite	C	Pencil lead, dry lubricant
	Silver	Ag	Jewelry, photography
	Platinum	Pt	Catalyst
Halides	Halite	NaCl	Common salt
	Fluorite	CaF_2	Used in steelmaking
	Sylvite	KCl	Fertilizer
Carbonates	Calcite	CaCO_3	Portland cement, lime
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$	Portland cement, lime
	Malachite	$\text{Cu}_2(\text{OH})_2\text{CO}_3$	Gemstone
	Azurite	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$	Gemstone
Hydroxides	Limonite	$\text{FeO}(\text{OH}) \cdot n\text{H}_2\text{O}$	Ore of iron, pigments
	Bauxite	$\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$	Ore of aluminum
Phosphates	Apatite	$\text{Ca}_5(\text{F,Cl,OH})(\text{PO}_4)_3$	Fertilizer
	Turquoise	$\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8$	Gemstone

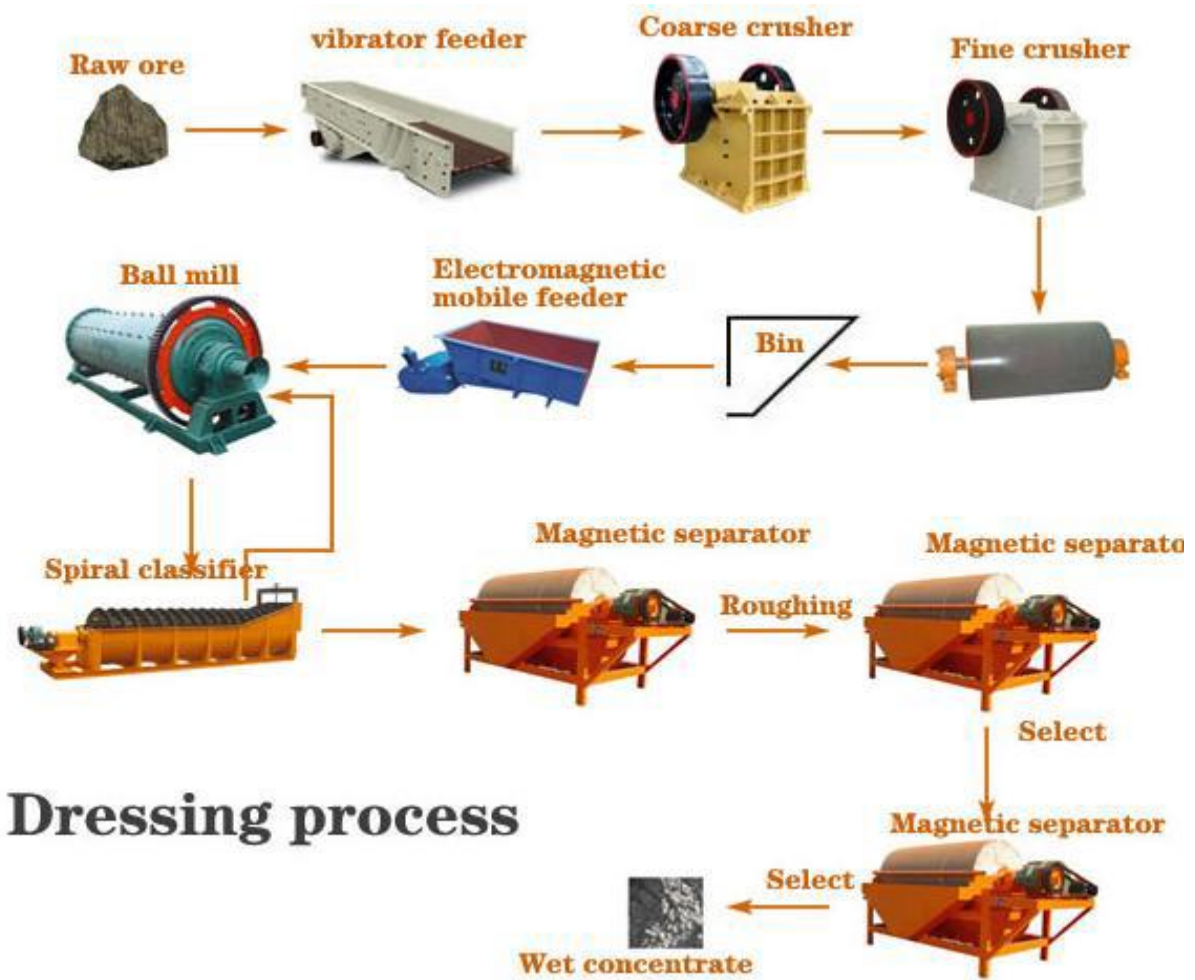
IV.3. SUBJECT OF METALLURGY:

The subject of metallurgy broadly divides itself into:

IV.3.1. MINERAL DRESSING:

The area of **mineral dressing** concerns itself with the starting operations and involves crushing and grinding either for purposes of liberation of the desired substances that are physically entrapped with others or for making them adoptable for further processes. Once liberated, they normally go through such physical beneficiation processes as:

- Magnetic separation.
- Electrostatic separation.
- screening, flotation.



IV.3.2. CHEMICAL METALLURGY:

Chemical metallurgy is a branch of metallurgy that focuses on the extraction, refining, and processing of metals using chemical principles and techniques. It involves the study of the chemical reactions and processes involved in transforming raw materials, often ores or metal-containing compounds, into purified metals or alloys suitable for various industrial applications. This field encompasses a range of activities, including leaching, precipitation, electrolysis, and other chemical methods, to achieve the desired composition and purity of metals for commercial use.

IV.3.3. PHYSICAL METALLURGY:

Physical metallurgy delves into the mechanical, magnetic, electrical, and thermal characteristics of metals, examining them through the lens of solid-state physics. This branch of study involves the investigation of rigid matter, or solids, utilizing methodologies such as quantum mechanics, crystallography, electromagnetism, and metallurgy. The systematic evaluation of the physical properties of metals and alloys is a core aspect of physical

metallurgy, essentially applying the foundational principles of the theory of phase transformation within metallic and alloyed materials.

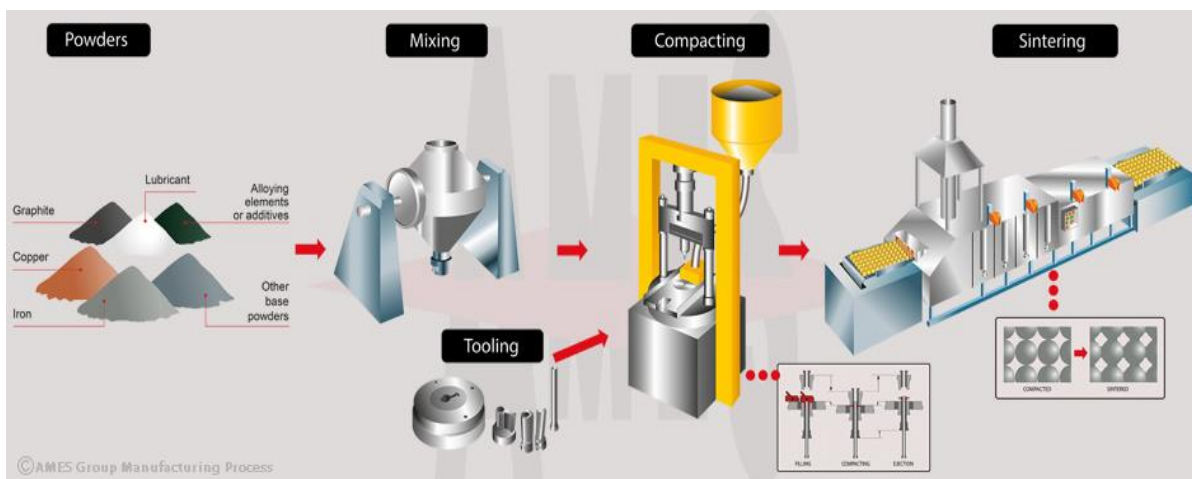
IV.3.4. MECHANICAL METALLURGY:

Metals and alloys are crucial due to their unique mechanical properties, which combine strength with plastic deformation. Their plasticity allows for various mechanical working methods, enhancing their toughness and durability. Mechanical metallurgy examines these properties, designing materials, and predicting performance. It also involves solid state mechanical working processes like rolling, forging, drawing, and extrusion.

IV.3.5. POWDER METALLURGY:

Powder metallurgy is a manufacturing process that involves the production of metal powders and their consolidation into solid objects through various techniques. This method is distinct from traditional methods of metal part production, such as casting or machining. The key steps in powder metallurgy typically include:

1. **Powder Production:** Metal powders are produced through processes like atomization, mechanical comminution (grinding), or chemical methods.
2. **Powder Blending:** Different powders, often comprising different metals or alloying elements, may be blended to achieve the desired composition.
3. **Compaction:** The blended metal powders are pressed or compacted into a desired shape using tools or dies. This stage creates a "green" compact.
4. **Sintering:** The green compact is heated in a controlled atmosphere to a temperature below its melting point. The metal particles fuse together through diffusion, resulting in a denser and stronger product.
5. **Secondary Operations:** Additional processes like heat treatment, machining, or surface finishing may be applied to achieve the final product specifications.



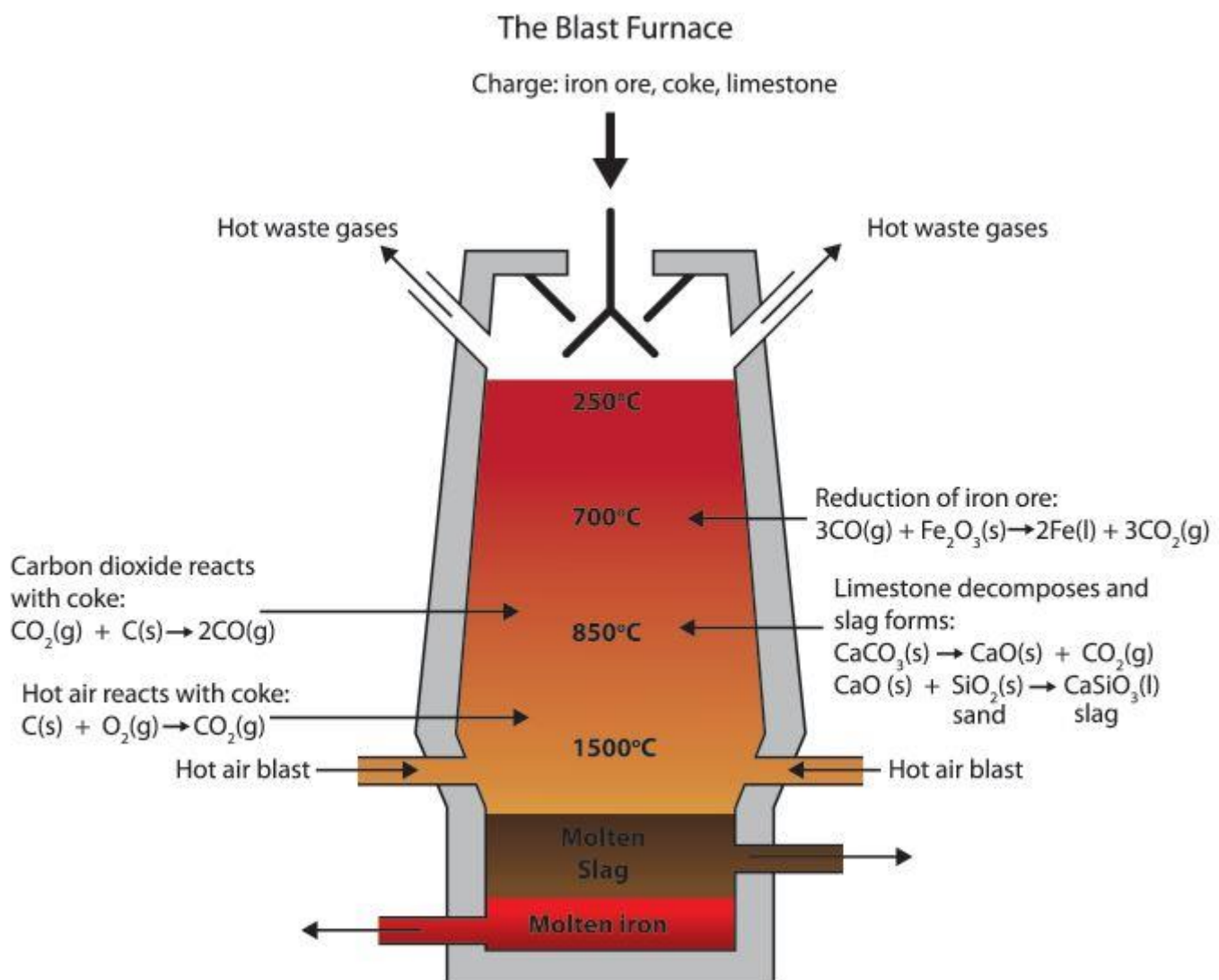
Powder metallurgy is known for its ability to produce complex shapes and parts with high precision. It is commonly used in the manufacturing of components for industries such as

automotive, aerospace, electronics, and medical devices. The technique is particularly advantageous for materials that are difficult to machine or for applications that require specific material properties.

IV.4. THE MAJOR METALLURGY:

IV.4.1. IRON (Fe):

The blast furnace operates as a counter-current gas/solids reactor, where the materials in the descending column of burden (including coke, iron ore, and fluxes/additives) react with the ascending hot gases. This is a continuous process, where raw materials are consistently introduced at the furnace's top, and molten iron and slag are periodically tapped from the bottom of the furnace.



The essential stages of the process are outlined below:

In the upper section of the furnace, free moisture is expelled from the burden materials, and hydrates and carbonates undergo dissociation.

In the lower part of the blast furnace shaft, the indirect reduction of iron oxides by carbon monoxide and hydrogen takes place at temperatures ranging from 700 to 1,000°C.

In the bosh area of the furnace, where the burden begins to soften and melt, direct reduction of iron oxides, along with carbonization by coke, occurs at temperatures between 1,000 and 1,600°C. Molten iron and slag commence dripping through to the bottom of the furnace, known as the hearth.








Between the bosh and the hearth, there are tuyeres (water-cooled copper nozzles) through which the blast, comprising preheated combustion air at 900-1,300°C, often enriched with oxygen, is blown into the furnace. Immediately in front of the tuyeres lies the combustion zone, the hottest part of the furnace at 1,850-2,200°C. Here, coke reacts with oxygen and steam in the blast to produce carbon monoxide, hydrogen, heat, and complete melting of iron and slag.

Molten iron and slag accumulate in the furnace hearth, with the less dense slag floating atop the iron. Both slag and iron are tapped at regular intervals through separate tap holes. In the production of merchant pig iron, the iron is cast into ingots. In integrated steel mills, molten iron or hot metal is transferred in torpedo ladle cars to the steel converters. The slag is conveyed to slag pits for further processing into usable materials, such as raw material for cement production or road construction.

Ferrous metals are metals that contain iron. Ferrous metals appear in the form of cast iron, carbon steel, and tool steel. The various alloys of iron, after undergoing certain processes, are pig iron, gray cast iron, white iron, white cast iron, malleable cast iron, wrought iron, alloy steel, and carbon steel. All these types of iron are mixtures of iron and carbon, manganese, sulfur, silicon, and phosphorous. Other elements are also present, but in amounts that do not appreciably affect the characteristics of the metal. Normally, ferrous metals are magnetic and nonferrous metals are nonmagnetic.

Product	Composition	Characteristics	Domain of use
Pig iron	93% Fe 3-5% C 2-4% other elements	Weak and brittle	cast iron pipe some fittings & valves 90% used for producing steel



Wrought iron	Pure iron <0,08% of C 0,01-0,1% (P, S, Si, Mn)	Low melting point excellent corrosion resistance	outdoor applications such as fencing and furniture and bridges	
Cast iron (gray or white (more of Si))	2-4% C (P, S, Si, Mn) Less of P and S	brittle, but a malleable	Alloying it with Ni, Cr, Mo, Si, or V improves toughness, tensile strength, and hardness	
Ingot iron	99.85% iron.	good ductility and corrosion resistance	The primary use is for galvanized and enamelled sheet.	
Low carbon steel	0.05% - 0.30% C	easily machined by hot or cold methods. It does not respond to heat-treating;	car parts, pipes, construction, and food cans	
Medium carbon steel	0.30% - 0.45% C	high strength, resistance to wear and toughness	railway tracks, train wheels, crankshafts, and gears and machinery parts	
High carbon steel	0.45% - 0.75% C	hardness, tensile strength, and wear resistance	cutting tools, springs, and coils for the manufacturing industry, as well as various washers and fasteners	
Very high-carbon steel	0.75% to 1.70 C	lots of strength and resistance	Parts of machinery which need hard, tough and durability	

The stainless steel:

The single most important property of stainless steels, and the reason for their existence and widespread use, is their corrosion resistance. Martensitic and martensitic-austenitic stainless steels are hardenable, allowing for heat treatment modifications. Precipitation hardening steels, also known as maraging steels, can be hardened through special heat treatment or thermo-mechanical sequences. The



last three categories, ferritic, ferritic-austenitic, and austenitic, are not hardenable but are used in their as-received condition. Austenitic steels are non-magnetic.

Alloying elements and impurities individually impact steel properties, with the combined effect determining the property profile of a specific steel grade.

Table 2. Composition ranges for different stainless steel categories.

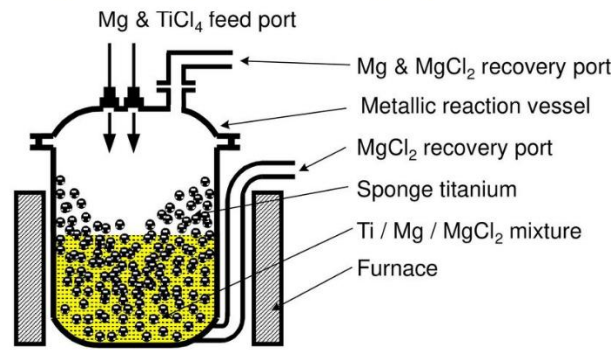
Steel category	Composition (wt%)					Hardenable	Ferro-magnetism
	C	Cr	Ni	Mo	Others		
Martensitic	>0.10	11-14	0-1	-	V	Hardenable	Magnetic
	>0.17	16-18	0-2	0-2			
Martensitic-austenitic	<0.10	12-18	4-6	1-2		Hardenable	Magnetic
Precipitation hardening		15-17 12-17	7-8 4-8	0-2 0-2	Al, Al,Cu,Ti,Nb	Hardenable	Magnetic
Ferritic	<0.08 <0.25	12-19 24-28	0-5 -	<5 -	Ti	Not hardenable	Magnetic
Ferritic-austenitic (duplex)	<0.05	18-27	4-7	1-4	N, W	Not hardenable	Magnetic
Austenitic	<0.08	16-30	8-35	0-7	N,Cu,Ti,Nb	Not hardenable	Non-magnetic

IV.4.2. TITANIUM (Ti):

The world's titanium production is small, with 80% used in aerospace. Car suspension springs could be made of titanium, but it's not available in large quantities or at the required price. The target price needs to be reduced to 30% for mass-market cars.

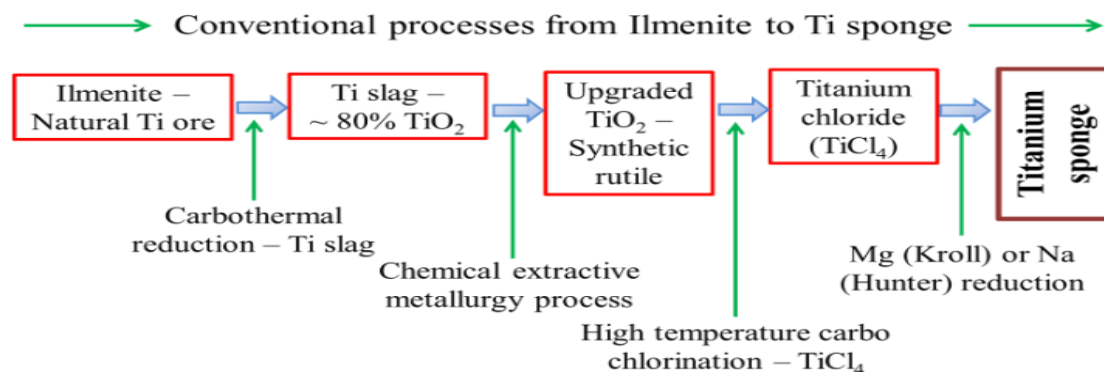
Titanium and its alloys are crucial in aerospace and other industries due to their mechanical properties and low density. However, the Kroll process's complexity and high energy consumption limit their wider application. The main raw material is rutile ore, treated with chlorine and reduced by magnesium.

The Kroll process is utilized to produce pure titanium, involving several thermal post-treatment steps. On an industrial scale, titanium production occurs in stainless-steel reactors of significant volume. The exothermic titanium reduction reaction releases 412 kJ/mol or 686 kJ/mol if magnesium is in a gaseous state. The reactor, once loaded, is maintained at high temperature for several days, followed by cooling and cutting open. The material in the reactor, known as titanium sponge, contains small titanium droplets, reaction products, and unreacted components. The titanium sponge undergoes grinding, sorting, and various postprocessing stages due to different quality regions.

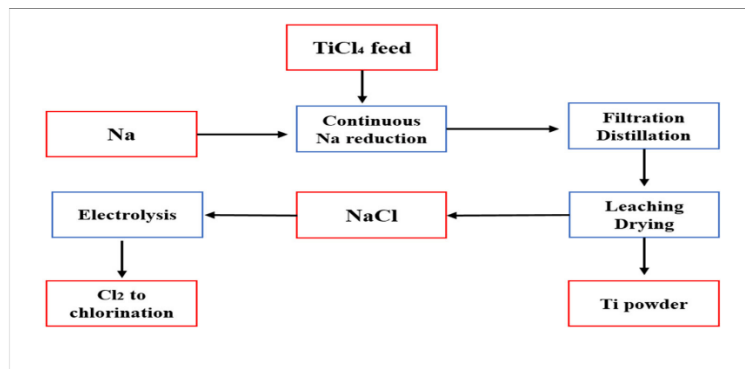


Isolating high-purity metallic titanium from titanium sponge involves several vacuum arc remeltings. While the Kroll process is well-established in industry, not all its steps are fully understood, leading to ongoing research for more effective production technologies. Powder metallurgy is one approach to reducing the cost of titanium extraction from titanium sponge, despite lower material quality.

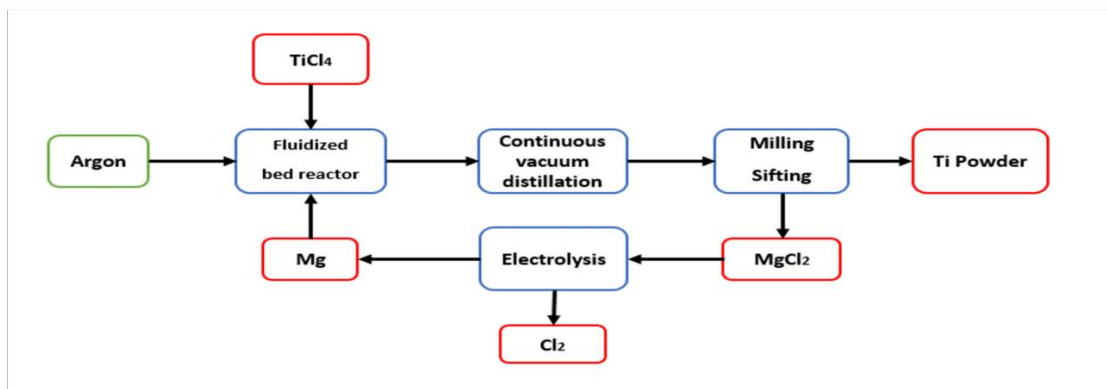
Other ideas include enhanced titanium and reaction product separation in a liquid salt environment and exploring chemical and metallothermic reduction possibilities for producing titanium and its alloys. Hydrometallurgy processes have been developed to upgrade rutile quality by leaching ilmenite (FeTiO_3). However, the decreasing quality of available titanium ore, with rutile content as low as 1%, poses challenges for the industry.



- The Hunter process is a popular thermochemical method for reducing TiCl_4 using Na, similar to the Kroll process. However, it is economically non-competitive due to the need for more Na than Mg.
- The Armstrong process is an advanced method that uses the same reactions as the Hunter process, ensuring continuous operation. It involves pumping molten sodium into a reactor, reacting with TiCl_4 gas, collecting Ti powder, and purifying the product.



- The TiRO Process, developed by CSIRO in Australia, uses gas-solid fluidization in a fluidized bed reactor to increase reaction rate and reduce costs, involving reduction of TiCl_4 with Mg powder and vacuum distillation.



- The MHR process, introduced in 1945, has been used to directly reduce TiO_2 in Russia.
-

Major Uses Of Titanium :

1. In The Aerospace Field
2. In The Automobile Industry
3. In The Medical Industry
4. In The Chemical Industry
5. In The Marine Engineering
6. In Energy Materials

<p>Unalloyed Ti 200X Commercially pure plate, 0.03% iron 732°C (1350°F)/30 Min.; Air Cool (Mill-annealed condition)</p>	<p>Ti-Pd 100X ASTM Grade 7 Sheet 704°C (1300°F)/20 Min.; Air Cool (Mill-annealed condition)</p>	<p>Ti 5Al-2.5Sn 200X Alpha Alloy Hot roll 51mm (2 in.) round bar 816°C (1500°F)/2 Hr.; Air Cool (Mill-annealed condition)</p>

<p>Ti-6Al-2Sn-2Zr-2Mo-2Cr-Si 200X Alpha-beta alloy 1.6mm (.063 in.) sheet 900°C (1650°F)/30 Min.; Air Cool + 510°C (950°F) /10 Hr.; Air Cool (Solution treated and aged)</p>	<p>Ti-4.5Al-3V-2Mo-2Fe (SP700) 500X Alpha-beta alloy 46mm (1.8 in.) plate 788°C (1450°F)/2 Hr.; Air Cool (Mill-annealed condition)</p>	<p>Ti-3Al-8V-6Cr-4Zr-4Mo 100X Beta alloy 16mm (0.625 in.) dia. bar 816°C (1500°F)/30 Min.; Air Cool (Solution treated condition)</p>	<p>Ti-3Al-8V-6Cr-4Zr-4Mo 250X Beta alloy 16mm (0.625 in.) dia. bar 816°C (1500°F)/15 Min.; Air Cool +566°C (1050°F) /6 Hr.; Air Cool (Solution treated and aged condition)</p>

IV.4.3. COPPER (Cu):

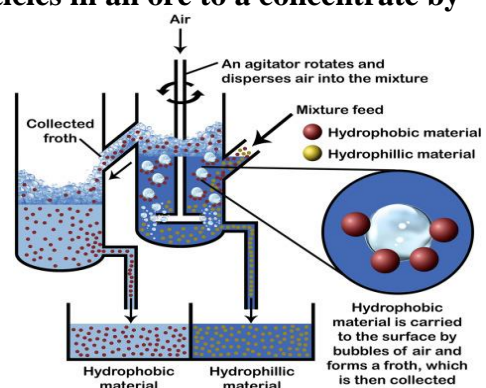
Copper is primarily found in the earth's crust as copper-iron-sulfide and copper sulfide minerals, such as chalcopyrite and chalcocite. It is primarily produced from these ores through concentration, smelting, and refining. Copper also occurs in oxidized minerals, which are processed through leaching, solvent extraction, and electrowinning. Scrap copper and copper alloys are also major sources of copper production.

IV.4.3.1. EXTRACTING COPPER FROM COPPER-IRON-SULFIDE ORES

About 80% of the world's copper-from-ore originates in Cu-Fe-S ores. These minerals are not easily dissolved by aqueous solutions, so the vast majority of copper extraction from these minerals is pyrometallurgical. The extraction entails:

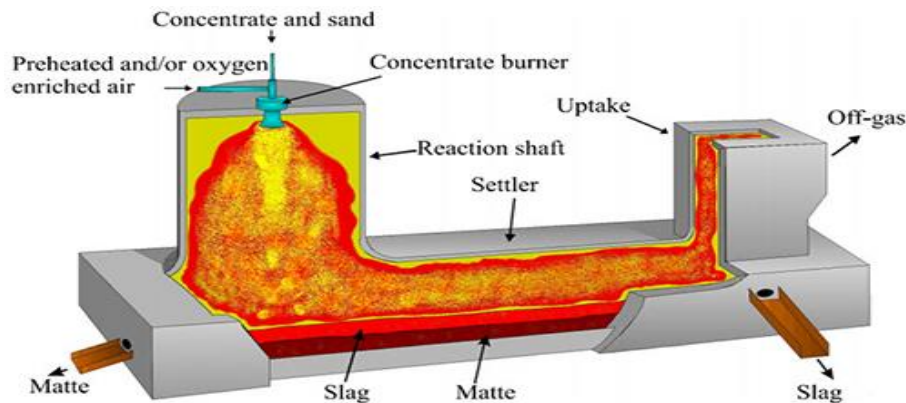
(a) **Isolating the Cu-Fe-S and Cu-S mineral particles in an ore to a concentrate by froth flotation:**

Copper ores are too lean to be smelted directly, but can be isolated into high-Cu concentrate using froth flotation. This process selectively attaches Cu minerals to air bubbles, making them water repellent and allowing them to float on rising bubbles. The floated Cu-mineral

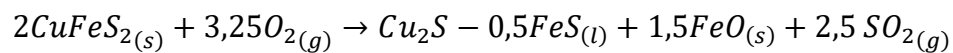


particles overflow the flotation cell, forming a concentrate containing approximately 30% Cu. This method has led to the adoption of efficient smelting processes.

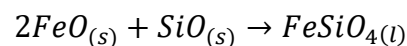
(b) **Smelting this concentrate to molten high-Cu sulfide matte:** Matte smelting oxidizes and melts flotation concentrate in a large, hot (1250 °C) furnace. The objective of the smelting is to oxidize S and Fe from the Cu-Fe-S concentrate to produce a Cu-enriched molten sulfide phase (matte). The oxidant is almost always oxygen-enriched air.



The products of smelting are molten sulfide matte (45-75% Cu) containing most of the copper in the concentrate, and molten oxide slag with as little Cu as possible. The molten matte is subsequently converted (oxidized) in a converting furnace to form impure molten copper. The slag is treated for Cu recovery, then discarded or sold.



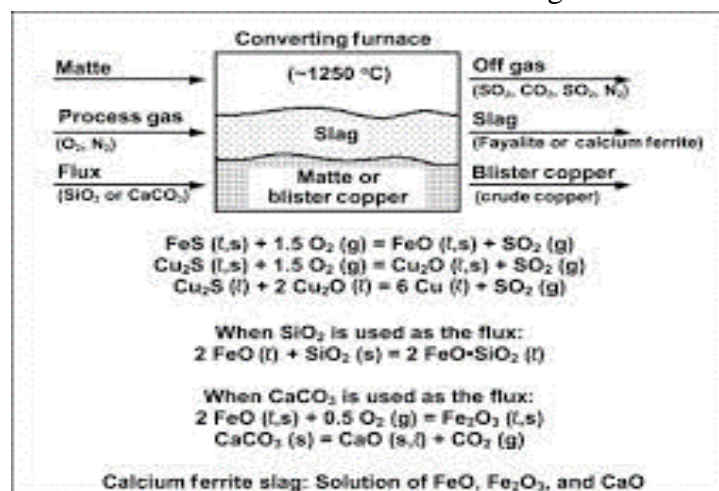
molten matte



in quartz flux molten slag

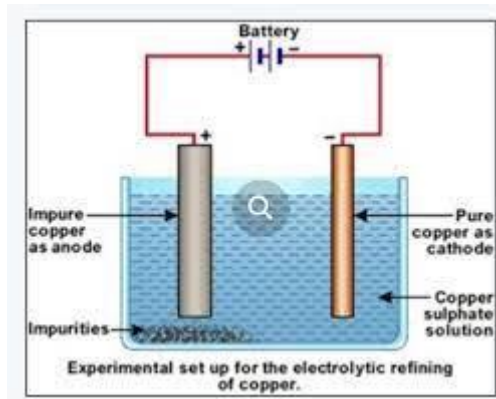
(c) **Converting (oxidizing) this molten matte to impure molten copper:**

Copper converting is an oxidation of the molten matte from smelting with air or oxygen enriched air. It removes Fe and S from the matte to produce crude (99% Cu) molten copper. This copper is then sent to fire-and electrorefining. Converting is mostly carried out in cylindrical Peirce-Smith converters.

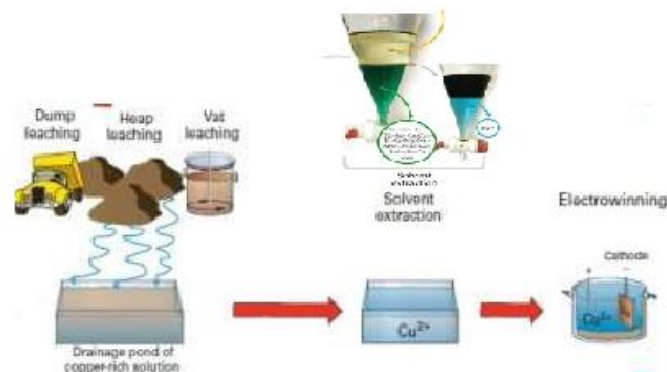


(d) Fire- and electrorefining this impure copper to ultra-pure copper:

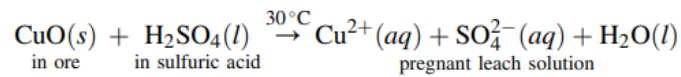
The copper from the above processing is electrochemically refined to high-purity cathode copper. This final copper contains less than 20 ppm undesirable impurities. It is suitable for electrical and almost all other uses. Electrorefining requires strong, flat thin anodes to interleave with cathodes in a refining cell. These anodes are produced by removing S and O from molten blister copper, and casting the resulting fire-refined copper in open, anode shape molds (occasionally in a continuous strip caster). Copper electrorefining entails electrochemically dissolving copper from impure anodes into $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte, and electrochemically plating pure copper (without the anode impurities) from the electrolyte onto stainless steel (occasionally copper) cathodes. Copper is deposited on the cathodes for 7e14 days. The cathodes are then removed from the cell. Their copper is stripped, washed, and sold or melted and cast into useful products.

**IV.4.3.2. HYDROMETALLURGICAL EXTRACTION OF COPPER**

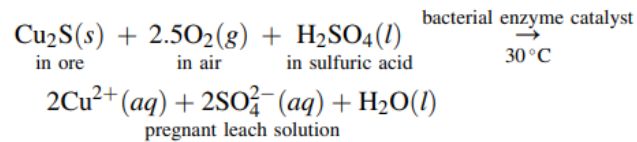
About 80% of copper-from-ore is obtained through flotation, smelting, and refining, while 20% (Most commonly treated ores include oxide copper minerals and chalcocite) is obtained hydrometallurgically. Hydrometallurgical extraction involves:



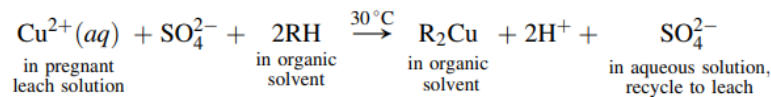
- (a) Leaching sulfuric acid from broken or crushed ore to produce an impure Cu-bearing aqueous solution (his process involves dripping dilute sulfuric acid on broken or crushed ore, requiring several months for efficient extraction. Oxidized minerals are rapidly dissolved by sulfuric acid reactions).



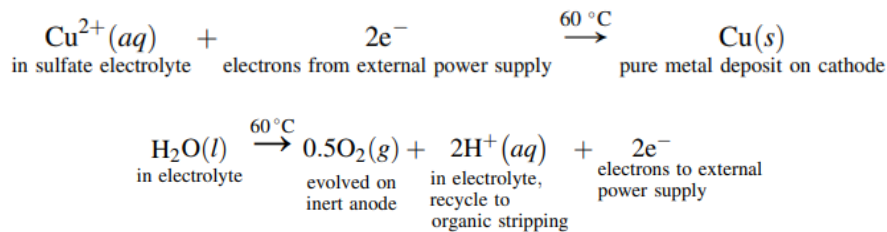
Sulfide minerals, on the other hand, require oxidation, schematically:



- (b) Transferring Cu to a pure, high-Cu electrolyte via solvent extraction (heap leaching solutions contain 1-6 kg Cu/m³ and 0.5-5 kg H₂SO₄/m³, with dissolved impurities like Fe and Mn, making them too dilute for direct copper metal electroplating, necessitating transfer to pure, high-Cu electrolyte).



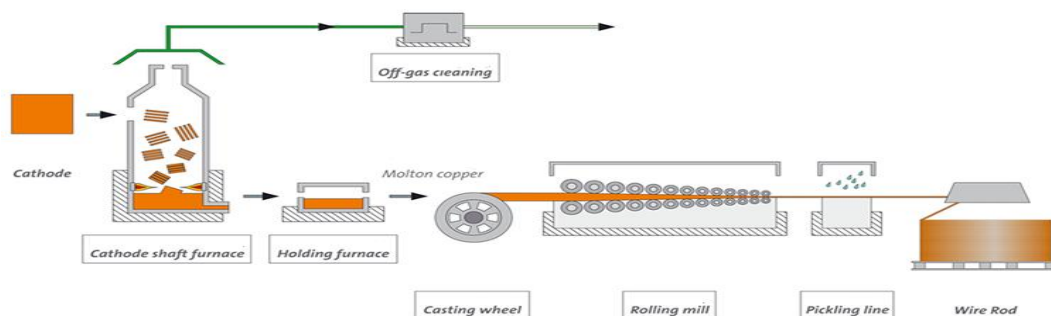
- (c) Electroplating pure cathode copper from this electrolyte (electroplating pure metallic cathode copper is a universal method for recovering Cu in electrolytes, similar to electrorefining but with an inert anode like lead or iridium oxide-coated titanium).



The process requires approximately 2.0 V, producing pure metallic copper at the cathode and gaseous O₂ at the anode.

IV.4.3.3. MELTING AND CASTING CATHODE COPPER

Electro-refined and electrowon copper products are made through melting and casting processes. Melting occurs in vertical shaft furnaces using low-sulfur fuels and reducing flames. The molten copper is cast in continuous casting machines, which then undergo rolling, extrusion, and manufacturing. A significant combination is continuous bar casting/rod rolling, producing a 1 cm diameter rod ready for wire drawing.



IV.4.3.4. RECYCLE OF COPPER AND COPPER-ALLOY SCRAP

Copper and copper-alloy scrap recycling accounts for 10-15% of pre-manufacture copper production, reducing energy consumption, avoiding waste from mines, concentrators, leach, and smelters, and ensuring copper availability for future generations. Treatment depends on scrap purity, with lower-grade scrap smelted and refined, higher-grade scrap fire-refined, and highest-grade scrap melted and cast without refining. Alloy scrap is melted and cast as alloy, with some slagging to remove contaminants.

Alloys :

Product name	Composition	Proprieties	uses
Copper (ASTM B1, B2, B3, B152, B124, R133)	Cu 99.9	Annealed Cold-drawn Cold-rolled	Electrical equipment, roofing, screens
Gilding metal (ASTM B36)	Cu 95.0, Zn 5.0	Cold-rolled	Coins, bullet jackets
Cartridge brass (ASTM B14, B19, B36, B134, B135)	Cu 70.0, Zn 30.0	Cold-rolled	Good for cold-working; radiators, hardware, electrical, drawn cartridge cases.
Phosphor bronze (ASTM B103, B139, B159)	Cu 89.75, Sn 10.0, P 0.25	Spring temper	
Yellow or High brass (ASTM B36, B134, B135)	Cu 65.0, Zn 35.0	Good corrosion resistance	Jewels
Manganese bronze (ASTM 138)	Cu 58.5, Zn 39.2, Fe 1.0, Sn 1.0, Mn 0.3	Annealed Cold-drawn	Forgings
Naval brass (ASTM B21)	Cu 60.0, Zn 39.25, Sn 0.75	Annealed Cold-drawn	Resistance to salt corrosion
Muntz metal (ASTM B111)	Cu 92.0, Al 8.0	Annealed hard	
Beryllium copper (ASTM B194, B196, B197)	Cu 97.75, Be 2.0, Co or Ni 0.25	Annealed Cold-rolled	Electrical, valves, pumps, oilfield tools, aerospace landing gears, robotic welding mold making
Free-cutting brass	Cu 62.0, Zn 35.5, Pb 2.5	Cold-drawn	Screws, nuts, gears, keys
Nickel silver (ASTM B122)	Cu 65.0, Zn 17.0, Ni 18.0	Annealed Cold-rolled	Hardware
Nickel silver (ASTM	Cu 76.5, Ni 12.5, Pb 9.0,	Cast	Easy to machine;

B149)	Sn 2.0		ornaments, plumbing
Cupronickel (ASTM B111, B171)	Cu 88.35, Ni 10.0, Fe 1.25, Mn 0.4	Annealed Cold-rolled	Condensor, salt-water pipes
Cupronickel	Cu 70.0, Ni 30.0	Wrought	Heat-exchange equipment, valves

IV.4.4. MAGNESIUM (Mg):

Magnesium ion is the most abundant structural metal ion in the ocean and hydrosphere, with the eighth most abundant element in the earth's crust. It is the third most abundant structural metallic element in the topmost 3.8 km of the ocean, making it a unique structural element that can be extracted from either the hydrosphere or lithosphere. Aluminum is sparse in the ocean and only extracted from the lithosphere.

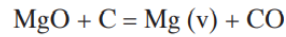
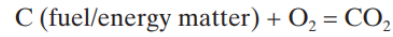
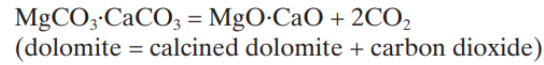
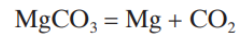
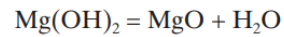
The lithospheric compounds from which magnesium is extracted are: dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), magnesite (MgCO_3), periclase (magnesium oxide) (MgO), hydro-magnesite ($3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), brucite ($\text{MgO} \cdot \text{H}_2\text{O}$), and silicates of magnesium (olivine(Mg, Fe) 2SiO_4 , serpentine $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ with partial iron substitution of magnesium, fosterite, biotite micas, etc.). The lithospheric minerals magnesium sulfate (epsomite- $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), langbeinite ($\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$), and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$), carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) are of hydrospheric origin found in evaporites. The hydrosphere – oceans, and terminal lakes – has magnesium as the second most abundant metallic cation in the salinity. Sodium, present in a larger quantity, usually provides the ionic balance for the chloride ion in saline waters; sulfate is needed to provide ionic balance of magnesium along with chloride ions. Magnesium minerals found from the evaporites in the chloride form include carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Two main chemical aspects involve mixing minerals with other compounds and removing elements and new compounds. Commercial processes consume 3 to 4 times the thermodynamic energy required for splitting raw material into finished metal, making it crucial to consider these factors when determining the extraction process.

IV.4.4.1. MAGNESIUM OXIDE AS RAW MATERIAL

Magnesium oxide can be produced from magnesium hydroxide, magnesium carbonate, or dolomite. Precipitated magnesium hydroxide can be made from sea water using calcined limestone or dolomite. Calcination, an endothermic process, consumes energy and releases

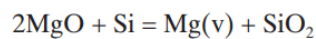
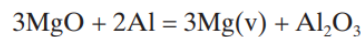
additional carbon dioxide in the form of fuel or energy matter, such as coal. Magnesium oxide carbo-thermic reduction takes place above 1900°C.



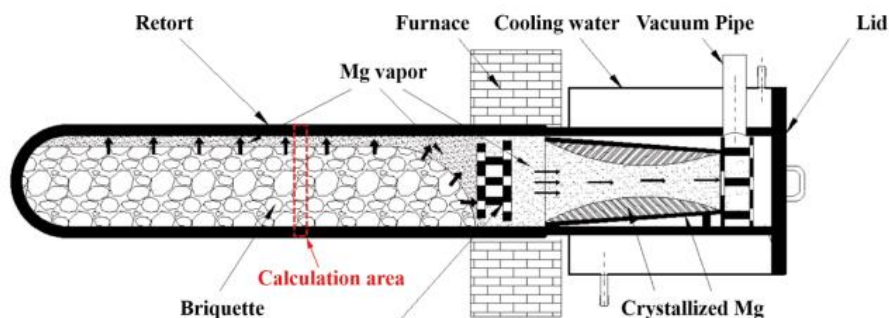
Magnesium and carbon monoxide are gaseous products that require special separation techniques. Hansgirg developed rapid quenching for gaseous mixtures. Calcium carbide as a reductant is useful for producing quality magnesium, as oxygen is taken up by calcium without reverse reactions.



The reaction involves vacuum retorts and can be reduced at high temperatures using metals like silicon or aluminium, as suggested by Bleecker and Morrison.



The Pidgeon process, a vacuum-assisted reaction at 1200°C, is a complex atmospheric pressure reaction that involves the formation of intermediate magnesium ortho-silicate or magnesium aluminates. This process is useful for lower-cost dolomite, which yields CaO·MgO when calcined, and lower-cost ferro-silicon in place of silicon metal. The reaction is conducted in evacuated retorts.

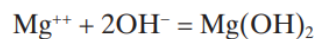


The Pidgeon process, a batch silico-thermic process, was upgraded to a semi-continuous process in the early 1960s by the Magnetherm process. This process converts the solid

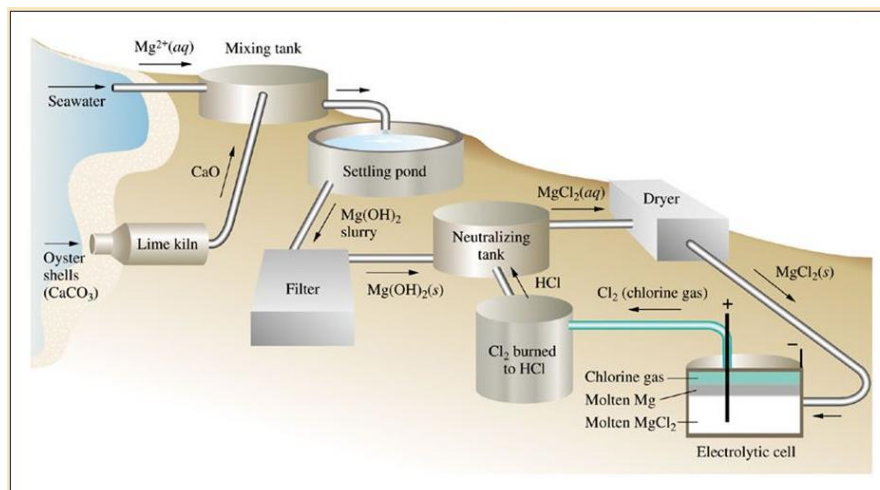
product silicate into molten slag, allowing electro-slag melting using a water-cooled electrode. This process allows for continuous feeding of calcined dolomite and ferro-silicon into the molten pool and continuous removal of magnesium vapor into large condensers.

IV.4.4.2. MAGNESIUM CHLORIDE AS RAW MATERIAL

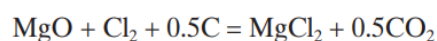
Magnesium, found in brines, can be precipitated as hydroxide or upgraded to concentrated magnesium chloride. Processes like the Dow process and Norsk Hydro – Norway used alkali like milk of lime or sodium hydroxide. Hydroxide is converted to magnesium chloride using hydrochloric acid. Oxide minerals like magnetite or magnesium silicates can also be converted into magnesium chloride solutions.



Evaporative crystallization is a cost-effective method for concentrating hydrospheric magnesium ions in brine into magnesium chloride-rich liquor, removing sodium and potassium chloride salts from the initial crystallization.

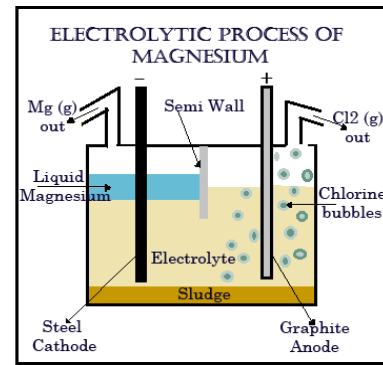


Hydrospheric magnesium ions can be extracted as a double chloride salt carnallite $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ from marine evaporites, underground potash minerals, or terminal lakes containing lower sulfate ions. However, Magnesium oxide from rocks – magnesite, silicates, or magnesium oxide from hydroxides converted by carbo-chlorination into magnesium chloride



The anhydrous magnesium chloride produced in two consecutive methods; either through dehydration of magnesium chloride brines or chlorination of magnesium oxide is sent to the

electrolytic cells. Electrolytic cells are vertical vessels with steel cathodes and graphite anodes submerged in a molten salt electrolyte containing alkaline chlorides. Magnesium chloride is added in concentrations of 6-18 percent, decomposing to magnesium metal and generating chlorine and other gases at the graphite anodes.



Uses of Mg as metal:

Magnesium is the third-most-commonly-used structural metal, following iron and aluminium.

- The main applications of magnesium are, in order: aluminium alloys, die-casting (alloyed with zinc), removing sulfur in the production of iron and steel, and the production of titanium in the Kroll process.
- When magnesium is burned in air, it emits a shining white light with strong ultraviolet wavelengths. In the early days of photography, magnesium powder (flash powder) was employed to illuminate the subject. Later, magnesium filament was utilized in single-use electrically lit photographic flashbulbs. Magnesium powder is used in pyrotechnics and maritime flares to produce a radiant white light. It was also utilized in a variety of theatrical effects, including lightning, gun flashes, and otherworldly apparition.
- Magnesium alloys are mixtures of magnesium and other metals, such as aluminium, zinc, manganese, silicon, copper, rare earths, and zirconium. They have a hexagonal lattice structure, making plastic deformation more complex than in cubic latticed metals. Cast magnesium alloys are used in modern automobiles, high-performance vehicles, camera bodies, and lens components. Most commercial magnesium alloys in the US contain aluminium (3 to 13%), manganese (0.1 to 0.4%), zinc (0.5 to 3%), and some are hardenable by heat treatment. Alloys AZ63 and AZ92 are most used for sand castings, AZ91 for die castings, and AZ92 for permanent mold castings. Forgings use AZ61, with alloy M1 used for low strength and AZ80 for highest strength. Extrusions use alloys AZ31, AZ61, and AZ80 for extrusions where increased strength justifies higher relative costs. Magnox (alloy), 99% magnesium and 1% aluminium, is used in cladding fuel rods in nuclear power reactors.