

EXTRACTION OF THE METALS FROM THEIR ORES

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Most of the elements in the periodic table are metals.

Periodic Table of the Elements																		
	I											III	IV	V	VI	VII	VIII	
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuh	112 Uub		114 Uuq		116 Uuh		


 metal
 semi-metal
 non-metal

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

The relative abundance of metals in the earth's crust ranges

from very low:

- (e. g. 0.001 – 0.01 ppm for Au, Os, Pt)

to very high:

- Si 27.7 % by weight,
- Al 8.1 % by weight,
- Fe 5.0 % by weight.

Element	Abundance (%)	Element	Abundance (%)
Oxygen	46.6	Vanadium	0.014
Silicon	27.7	Chromium	0.010
Aluminium	8.1	Nickel	0.0075
Iron	5.0	Copper	0.0055
Calcium	3.6	Zinc	0.0070
Sodium	2.8	Cobalt	0.0025
Magnesium	2.1	Lead	0.0013
Potassium	2.6	Uranium	0.00027
Titanium	0.44	Tin	0.0002
Manganese	0.095	Tungsten	0.00015
Barium	0.043	Mercury	8×10^{-6}
Strontium	0.038	Silver	7×10^{-6}
Rare earths	0.023	Gold	$< 5 \times 10^{-6}$
Zirconium	0.017	Platinum Metals	$< 5 \times 10^{-6}$

- Metals **seldom** occur in their native state in nature, except for some precious metals, such as Au, Ag and Pt (but only in limited amounts).
- **Most common metals are found in a wide variety of stable minerals, including oxides, sulphides, carbonates, fluorides and halides.**
- Parts of these occur as ores, containing mineral concentrations near the surface of the earth that can be mined economically.
- Ores are constituted by the metallic minerals and by the gangue.
- In mining, gangue is the commercially worthless material that surrounds, or is closely mixed with, a wanted mineral in an ore deposit.

Crystals of cassiterite, a commercially valuable mineral, in a matrix of quartz, that is the gangue.



Metal	Density Mg m ⁻³	Melting point °C	Principle ores	Average density Mg m ⁻³	Associated metals
Al	2.7	660	Bauxite Al ₂ O ₃ ·2H ₂ O	2.6	Ti, Fe, Ga
			Gibbsite Al ₂ O ₃ ·3H ₂ O	2.4	
Cr	7.1	1850	Chromite FeCr ₂ O ₄	4.6	Ag, Au, Ni, Pt, Pd, Re, As, Bi, Se
Cu	8.9	1083	Chalcopyrite (CuFe)S ₂	4.2	
			Chalcocite Cu ₂ S	5.6	
			Bornite Cu ₅ FeS ₄	5.1	
Fe	7.9	1537	Hematite Fe ₂ O ₃	5.3	
			Magnetite Fe ₃ O ₄	5.8	Zn, Ag, Cu, Fe, Sn, As, Bi, In, Sb
			Limonite Fe ₂ O ₃ ·nH ₂ O	4.0	
			Goethite Fe ₂ O ₃ ·H ₂ O	4.2	
			Siderite FeCO ₃	3.8	
Pb	11.3	327	Galena PbS	7.5	
			Anglesite PbSO ₄	6.3	
			Cerussite PbCO ₃	6.6	
Mg	1.7	650	Sea water		Co, Cu, Fe,
			Dolomite		
			MgCO ₃ ·CaCO ₃	2.8	
Ni	8.9	1454	Pentlandite (NiFe) ₉ S ₈	5.0	
			Pyrrhotite (NiFe) ₇ S ₈	5.2	
Sn	7.3	232	Cassiterite SnO ₂	6.9	
			Stannite Cu ₂ SnFeS ₄	4.4	
Ti	4.5	1660	Rutile TiO ₂	4.2	Fe
			Ilmenite FeTiO ₃	4.8	
Zn	7.1	420	Zinc blende ZnS	4.1	Pb, Ag, Cu
			Calamine ZnCO ₃	4.4	As, Cd, Ga

- Metal ores include mainly oxides, sulphides, carbonates and halides.
- **Metal extraction is mainly from oxides by chemical or electrolytic reduction.**
- Sulphides and carbonates are easily converted into oxides by roasting or calcination.

Why are most of the metallic elements present in nature in the form of oxides, sulfides, etc, and NOT as metals?

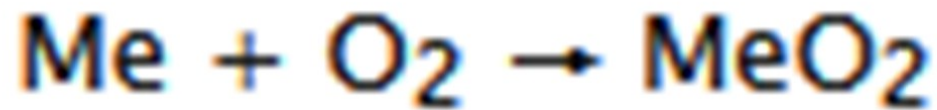
According to the principles of equilibrium thermodynamics, every material system tries to **minimize** its Gibbs free energy, **G**, to reach its equilibrium state.

The Gibbs free energy of oxides, sulfide, etc., is lower than the corresponding Gibbs free energies of pure metal.



The most metals in nature are not pure, but are bound to oxygen, sulphur, chlorine, etc.,

Example:
oxide formation



$$\Delta G < 0$$

Metal sulfides
are (usually but
not always)
characterized by
lower
thermodynamic
stabilities in
comparison with
those of
corresponding
oxides

Gibbs free energy of formation for several metal sulfides and oxides

Sulfide	ΔG_{1273K}^0 (kJ/mol S)	Oxide	ΔG_{1273K}^0 (kJ/mol O)
Al ₂ S ₃	- 191	Al ₂ O ₃	- 424
CoS	- 43.8	CoO	- 145
Cu ₂ S	- 95.7	Cu ₂ O	- 77.7
CuS	63.6	CuO	- 11.6
FeS	- 78.9	FeO	- 179
MnS	- 196.9	MnO	- 292
MoS ₂	- 78.3	MoO ₂	- 182
NiS	- 50.4	NiO	- 127
TiS	- 228	TiO	- 420

ORES with
Metal sulfides
and/or
Metal oxides
and/or
Metal hydroxides
and/or
Metal carbonates

+

Gangue

**EXTRACTION
PROCESS**



Pure metals



MINES



Bauxite

aluminium hydroxides

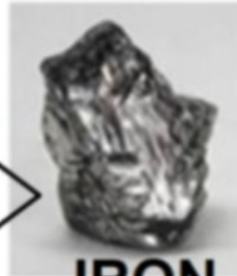


ALUMINUM

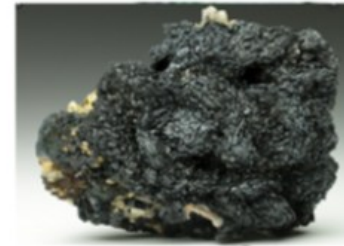


Haematite

iron oxide (Fe_2O_3)



IRON



Chalcocite

copper sulfide (Cu_2S)



COPPER

Metal ores are mined from the earth's crust, then metals are extracted from the ore.

Before the extraction process, the ore is treated in a **beneficiation plant** to separate the metallic minerals from the gangue and, consequently, **to improve the ore grade** of useful minerals as much as possible.

The process in a beneficiation plant exploits the different physical and chemical properties of minerals in the ore, to obtain the raw materials required for the following extraction processes.

The most common methods of beneficiation are

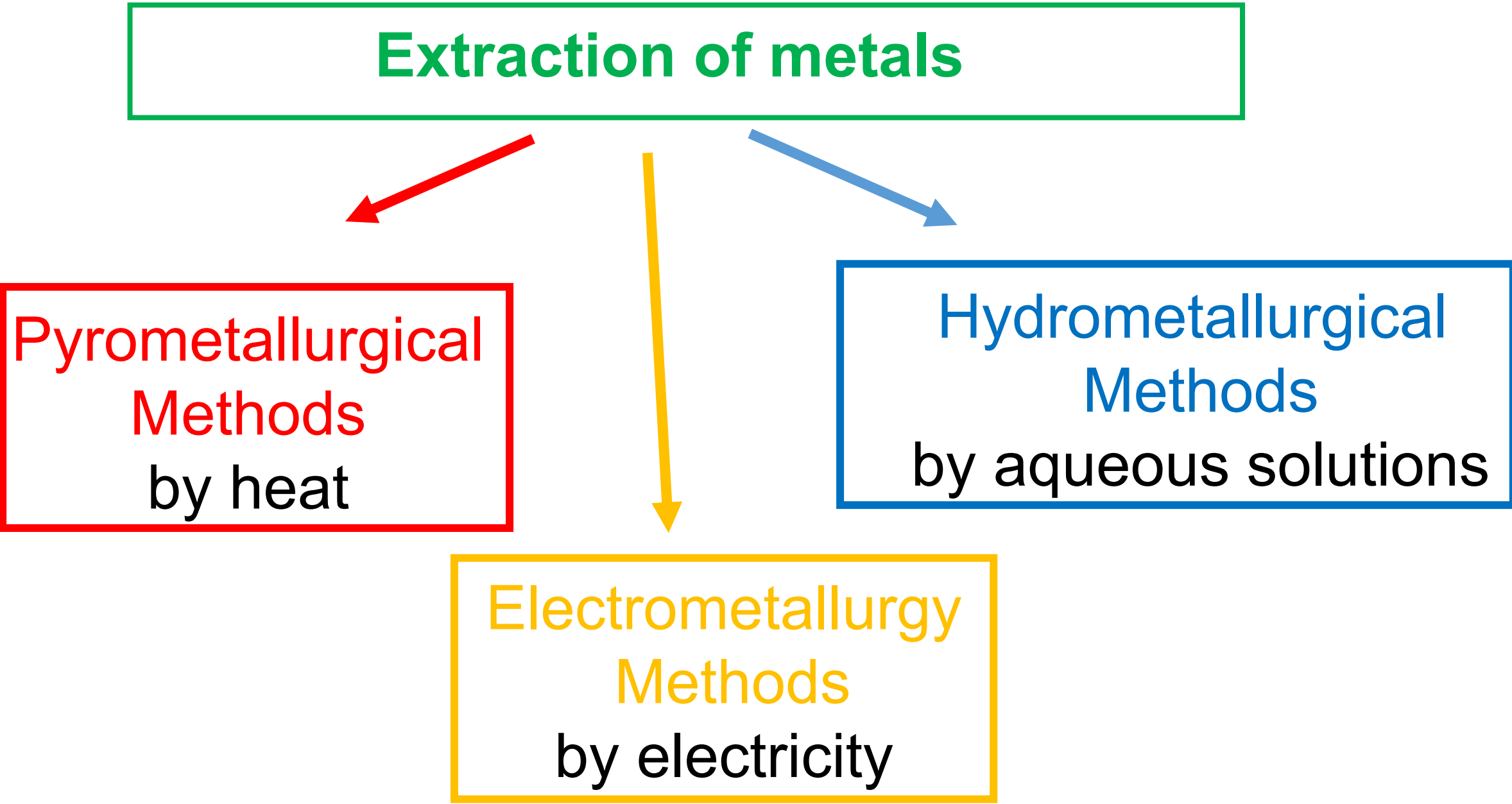
- magnetic separation process,
- flotation separation process,
- and gravity separation process.

After beneficiation the ore is ready for the final separation from the remaining gangue and for extraction of metals (reduction to the metallic form).

The types of processes used for the extraction of metals can be classified under three groups:

- Pyrometallurgy
- Hydrometallurgy
- Electrometallurgy

Extraction of metals



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graph TD; A[Extraction of metals] -- red --> B[Pyrometallurgical Methods by heat]; A -- yellow --> C[Electrometallurgy Methods by electricity]; A -- blue --> D[Hydrometallurgical Methods by aqueous solutions];
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Pyrometallurgical
Methods
by heat

Electrometallurgy
Methods
by electricity

Hydrometallurgical
Methods
by aqueous solutions

Pyrometallurgical extraction route

Pyrometallurgical extraction route is the most used:

- Pyrometallurgy involves high temperature processes where chemical reactions take place among gases, solids, and molten materials.

Principal steps:

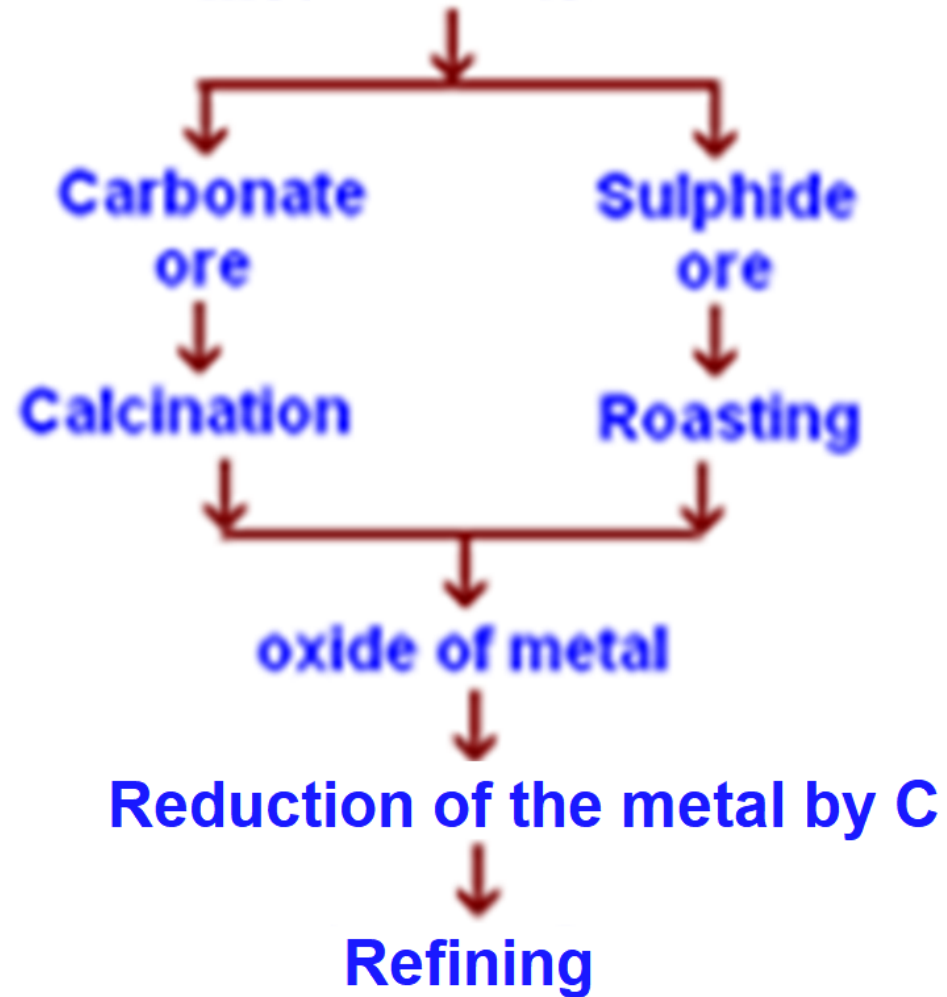
1. Roasting or calcination
2. Reduction of the metals by C.



3. Pyrometallurgical Refining

Pyrometallurgical extraction route

PYROMETALLURGY EXTRACTION



Pyrometallurgical extraction route

1. Roasting and calcination

Metallic minerals most commonly occur as:

- oxide
- sulfide,
- carbonate
- and hydroxide compounds.

It is easy to obtain metals from their oxides.

- Ores found in the form of sulphides and carbonates are first converted to their oxides by the process of roasting and calcination.
- Oxides of metals so obtained are converted into metals by the process of reduction.

Pyrometallurgical extraction route

1. Roasting and calcination

<i>Roasting</i>	<i>Calcination</i>
Ore is heated in excess of air.	Ore is heated in the absence or limited supply of air.
This is used for sulphide ores.	This is used for carbonate ores.
SO ₂ is produced along with metal oxide.	CO ₂ is produced along with metal oxide.
e.g. $2\text{ZnS} + 3\text{O}_2 \xrightarrow{\Delta} 2\text{ZnO} + 2\text{SO}_2$	e.g. $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2$

Pyrometallurgical extraction route

2. Reduction of the metal:

Most commonly, the ore (metal oxides) is heated and simultaneously reduced by solid carbon C



Solid carbon is NOT suitable for the reduction of metals that form very stable oxides (aluminum, magnesium, calcium, etc).

They are also not suitable for the reduction of metals such as Be, Cr, Ti, U and Zr, which readily form carbides or hydrides with consequent embrittlement of the metal.

For the metals that form very stable oxides (very reactive metals) and for metals that forms carbides, other techniques are used.

Pyrometallurgical extraction route

2. 1. Separation from the gangue and formation of the slag:

Commonly, the ore is heated to above the fusion temperatures of both the metal and the gangue in the reduction furnace.

The metallic oxides are usually miscible with the molten gangue, but are relatively immiscible when reduced to the metallic form.

Since the molten gangue has a lower density than the metal, it forms a separate layer called a *slag* and floats on top of the metal.

The slag is frequently required to act as a receiver for unwanted elements that are present in the ore.

Fluxes are added to lower the fusion temperature of the gangue and promote the formation of a larger volume of slag.

Pyrometallurgical extraction route

3. Pyrometallurgy Refining.

The metal obtained by pyro-extraction usually contains several other elements as precipitates and/or in solution.

The objective in refining is to remove the undesirable impurities.
Pyrometallurgical refining is conducted after separation of the metal from the smelter slag.

A wide variety of techniques is employed at this stage:

Some example are:

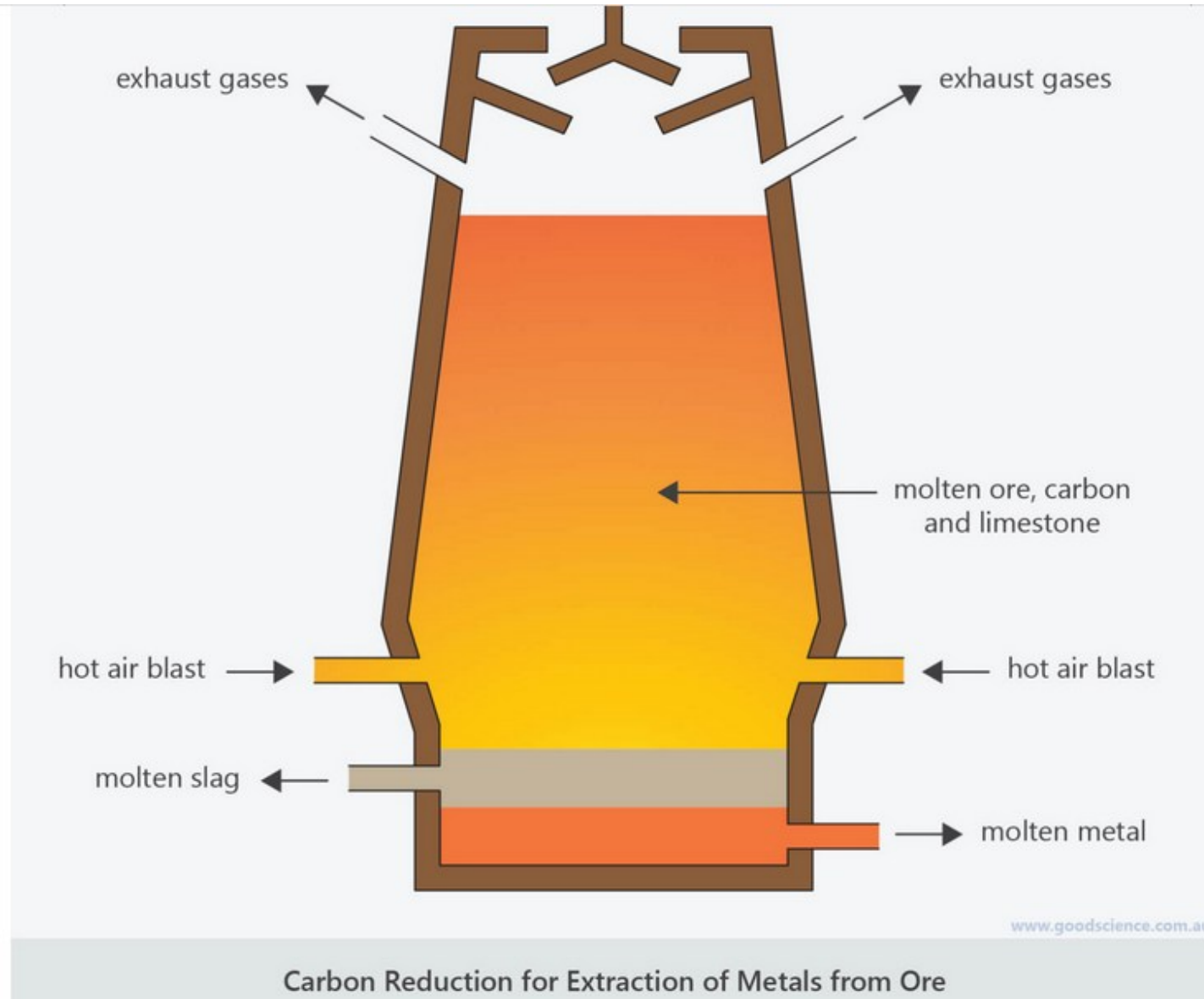
- Formation of a new slag, by addition of suitable compounds, that acts as a receiver for unwanted elements (they are removed selectively from the metal).
- Formation of a surface dross by adding selected elements that react with unwanted elements.

Pyrometallurgical extraction route

General considerations about pyrometallurgical process

- The capital cost of a pyrometallurgical furnace and the associated plant is very high.
- If coke is used as the fuel and/or the reductant, there is also a high cost for construction of the coke ovens and the gas handling equipment.
- Large evolution of the “greenhouse” gas, CO_2 , occurs when carbon fuels are combusted to provide the heat.

Pyrometallurgical extraction route



Why do we use C to reduce some metals?

Ellingham diagram can help us to understand why we use carbon to reduce some metals

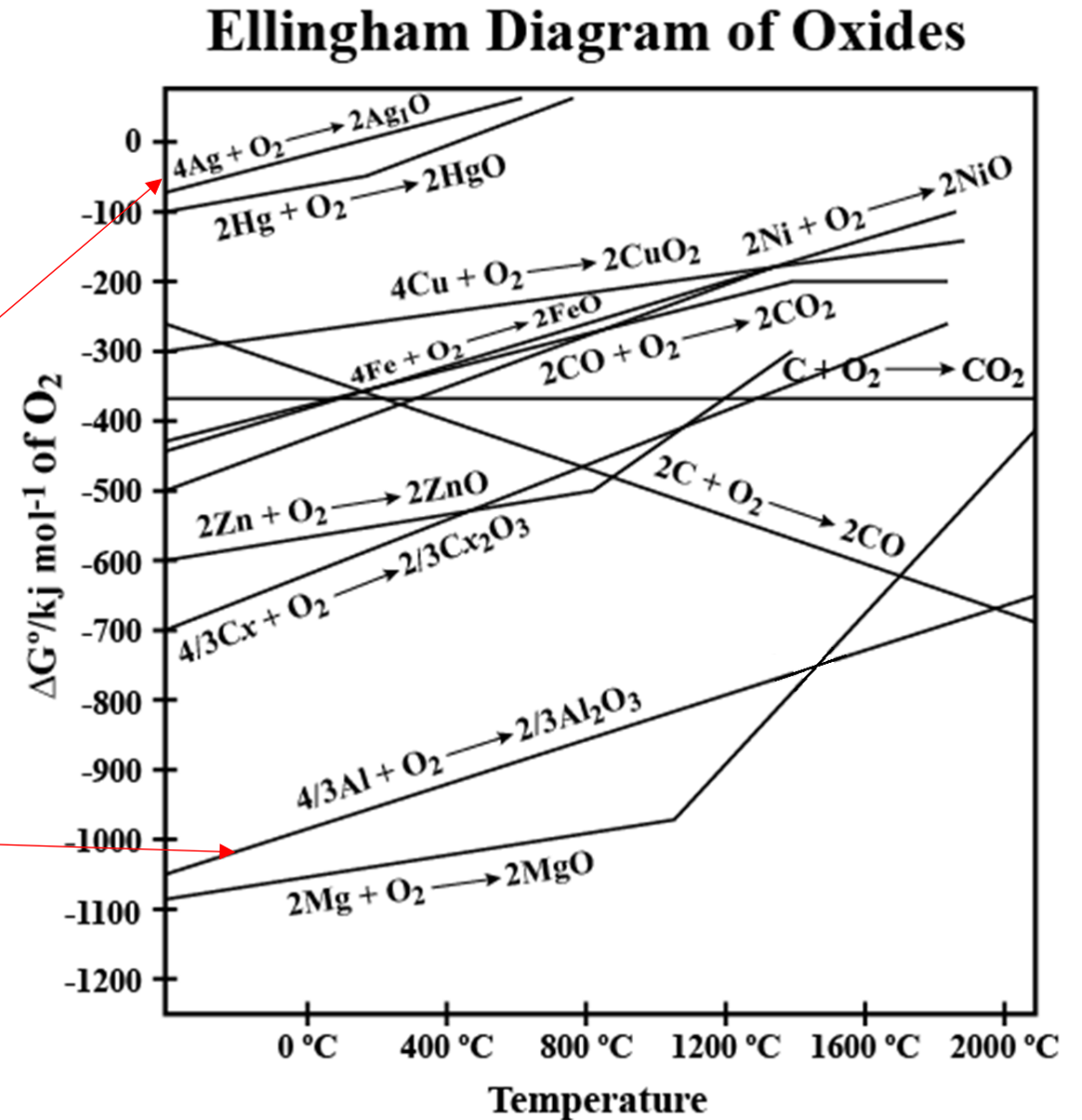
Ellingham diagram

An Ellingham diagram is a plot of ΔG versus temperature.

The position of the line for a given reaction on the Ellingham diagram shows the stability of the oxide as a function of temperature.

Reactions closer to the top of the diagram are the most “noble” metals, and their oxides are unstable and easily reduced.

As we move down toward the bottom of the diagram, the metals become progressively more reactive and their oxides become harder to reduce (Ca, Mg and Al).

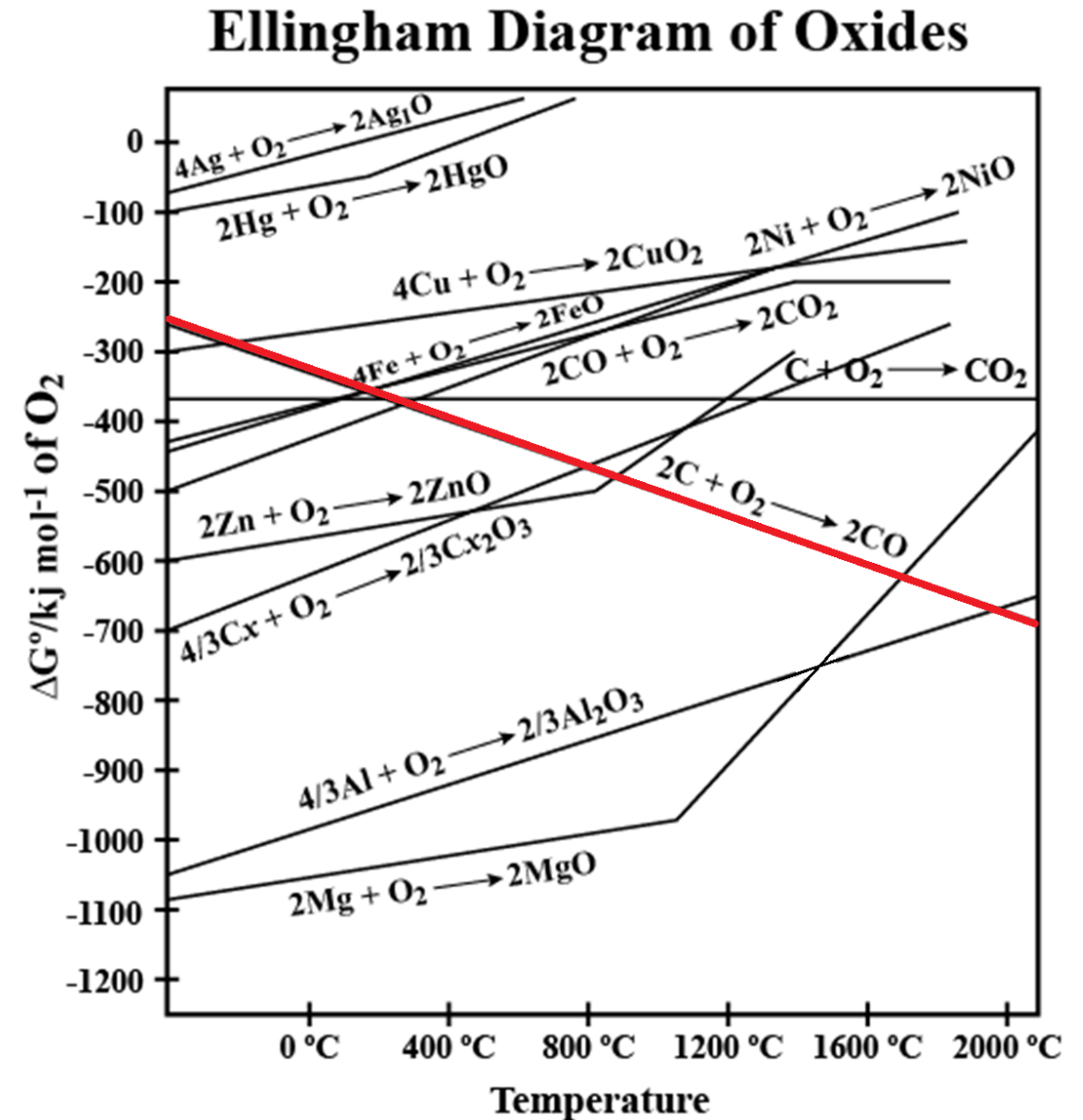


Ellingham diagram

The $2\text{C} + \text{O}_2 \rightleftharpoons 2\text{CO}$

line is downward-sloping, it cuts across the lines for many of the other metals.

This makes carbon unusually useful as a reducing agent, because as soon as the carbon oxidation line goes below a metal oxidation line, the carbon can then reduce the metal oxide to metal.



Hydrometallurgy extraction route

Hydrometallurgical extraction route:

- Hydrometallurgy is concerned with processes that use aqueous solutions to extract metals from ores.

This is an attractive way of recovering metals from low-grade deposits that are not sufficiently rich to justify pyrometallurgical treatment.

it is a very slow process and the concentration of the minerals in the effluent is also very low, making recovery difficult.

Hydrometallurgy involves two main steps:

- 1. Leaching
- 2. Metals recovery

Hydrometallurgy

1. Hydrometallurgical leaching

Two different ways:

- The metal is extracted from the ore as a soluble compound, leaving the gangue as a solid residue;
- The impurities (the gangue) is dissolve, leaving a pure metallic mineral.

Many metallic minerals can be leached (dissolved) in aqueous solutions.

Hydrometallurgy

1. Hydrometallurgical leaching

The rate of solution of the mineral increases with rising temperature and with the acid or alkaline strength of the liquid phase.

For leaching, usually acid solution are used.

The chemicals or lixiviants used for the dissolution of the minerals are mostly inexpensive

The chemicals that have to be used when the metal is recovered from the leach solution by techniques such as ion exchange or solvent extraction are more expensive.

Gold can only be leached completely in cyanide solutions:

- **problems of toxicity.**

Hydrometallurgy

2. Hydrometallurgy Metals recovery:

Further treatment is necessary to convert the soluble compound or the mineral to metallic form.

A wide variety of techniques are used for recovery.

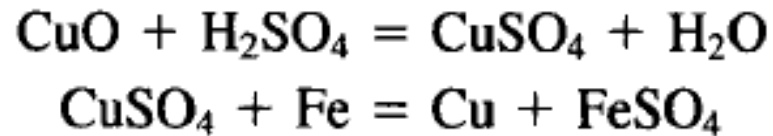
- cementation
- precipitation by changing the pH of the solution or by adding other chemicals,
- electrowinning
- *solvent extraction*
- *ion exchange*.

The last two methods can be highly selective, but are very expensive. Their use is limited mainly to the recovery of the more reactive metals that are produced in relatively small quantities and that command a high selling price.

Hydrometallurgy

Cementation:

The simplest and cheapest method is the conversion of the metal ion to the metal by a redox reaction. A typical application involves addition of scrap iron to a solution of copper ions. Iron dissolves and copper metal is deposited.



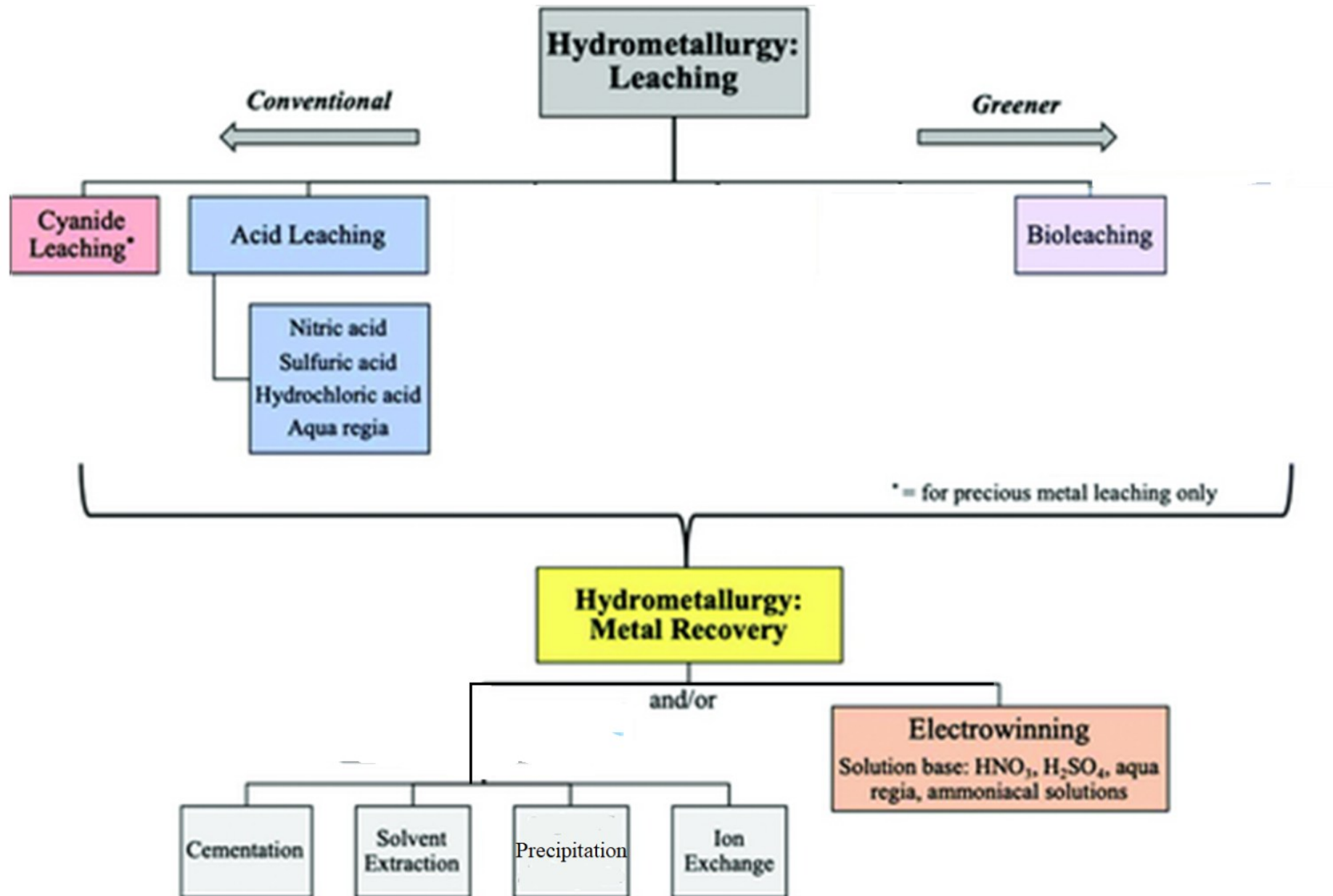
Precipitation by changing the pH of the solution or by adding other chemicals: a selective removal of a compound of the targeted metal or removal of a major impurity by precipitation of one of its compound.

Solvent extraction: is a mixture of an extractant in a diluent used to extract a metal from one phase to another.

Ion exchange: Chelating agents, natural zeolite, activated carbon, resins, and liquid organics impregnated with chelating agents are all used to exchange cations or anions with the solution.

Electrowinning: *see the previous slides*

Hydrometallurgy extraction route



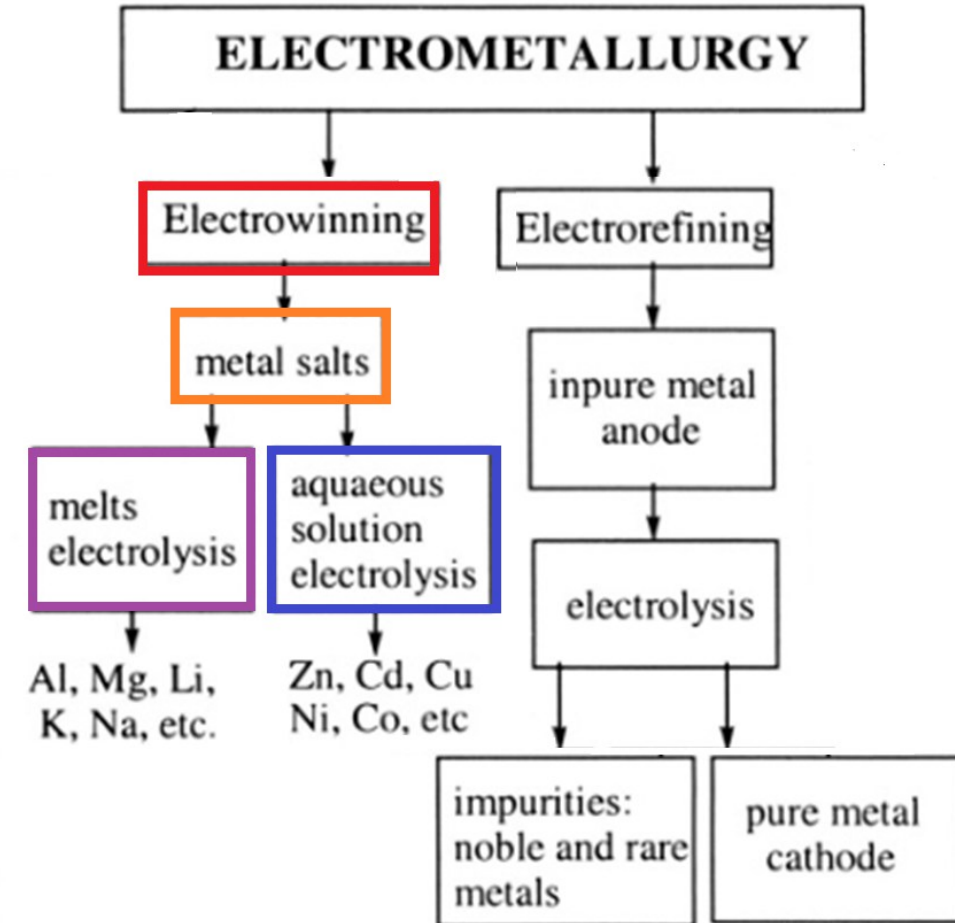
Electrometallurgy extraction route

Electrometallurgy involves metallurgical processes that take place in some form of electrolytic cell and uses electricity.

The most common types of electrometallurgical processes are:

- **Electrowinning (also called electroextraction)**
- Electro-refining (used to remove impurities)

Electrometallurgy use for the extraction and refining of metals by electrometallurgical techniques is **very expensive**.



Electrometallurgy extraction route

Electrowinning

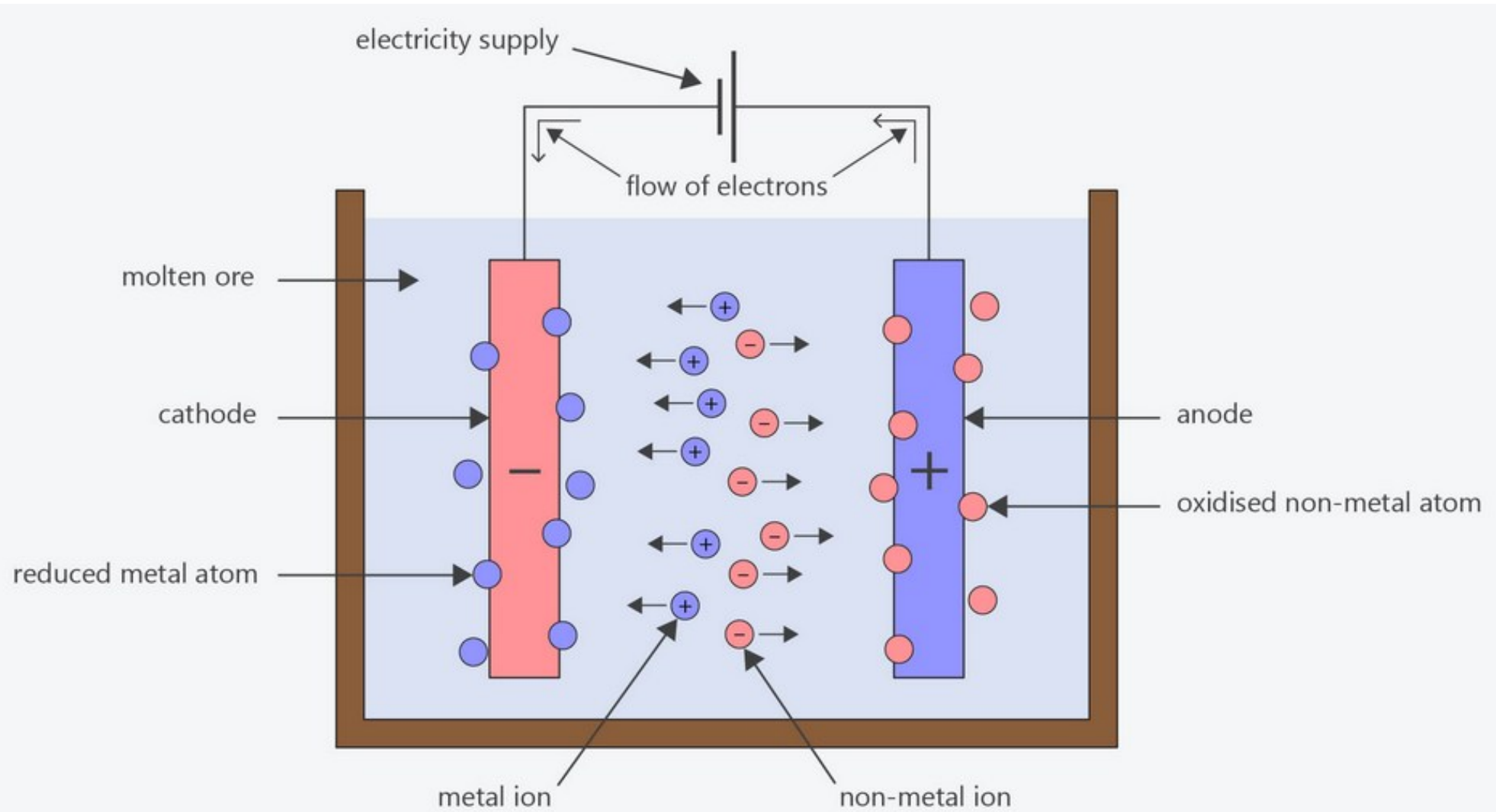
Electrowinning, also called electroextraction, is the electrodeposition of metals from their ores.

Passage of an electrical current between two electrodes immersed in a solution containing the metal salt causes the metal to be deposited on the negative electrode (cathode) in the cell.

The metal salt is usually contained in an aqueous solution, which may have been produced in a hydrometallurgical operation; but it may also be contained in a mixture of fused salt, as in aluminum and magnesium extraction.

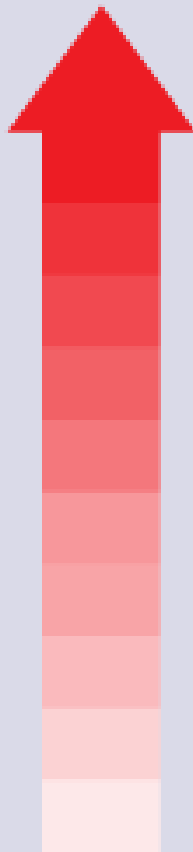
The high cost and consumption of electricity results in restriction of electrowinning to the extraction of the very reactive metals that are difficult to produce by other methods (e.g. Aluminum and Magnesium).

Electrometallurgy extraction route



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Electrolysis for Extraction of Metals from Ore

Metal	Method	Reactivity
Potassium	Electrolysis of molten compounds	Most reactive  Least reactive
Sodium		
Calcium		
Magnesium		
Aluminium		
(Carbon)		
Zinc	Heating with carbon	
Iron		
Copper		
Silver	Various chemical reactions	
Gold		

Summary – Metal Extraction Methods

Pyrometallurgy

-  Fast, suitable for large-scale production; works well for less reactive metals (e.g., Fe, Cu)
-  High energy consumption; releases CO₂ and SO₂ (pollution)

Hydrometallurgy

-  Lower energy use; good for low-grade ores; more environmentally friendly
-  Slower process; chemical waste (e.g., cyanide, acids) needs careful disposal

Electrometallurgy

-  High purity metal obtained; essential for very reactive metals (e.g., Al, Na)
-  Very high energy cost (electricity); expensive equipment