

VŠB - TECHNICAL UNIVERSITY OF OSTRAVA

**FACULTY OF METALLURGY AND MATERIALS
ENGINEERING**

**THEORY OF PRODUCTION
OF NON-FERROUS METALS AND
ALLOYS**

Study Support

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Obsah

1. Introduction

1.1 Technical categories of metals

1.2 Raw material sources of non-ferrous metals (NFMs)

1.3 Ore dressing

1.3.1 Comminution (crushing, milling, screening)

1.3.2 Ores separation

1.3.3 Processing of products of preparation

2. Pyrometallurgy

2.1 Drying and calcination

2.2 Roasting

2.2.1 Oxidizing roasting

2.2.2 Sulphate roasting

2.2.3 Reaction roasting

2.2.4 Reduction roasting

2.2.5 Roasting furnaces

2.3 Smelting

2.3.1 Concentration smelting

2.3.2 Coagulative smelting

2.3.3 Dissociative smelting

2.3.4 Thermal reduction processes – reduction smelting

2.3.5 Thermal processes of metal compounds reductions

2.3.6 Reaction smelting

2.3.7 Displacement smelting

2.4 Products of smelting

2.4.1 Slag

2.4.2 Matte

2.4.3 Speiss

2.4.4 Gasses and air pollutants

3. Hydrometallurgy

3.1 Leaching of metals, oxides and sulphides

3.1.1 Leaching of metals

3.1.2 Leaching of oxides

3.1.3 Leaching of sulphides

3.2 Leaching methods

3.2.1 Underground leaching (in-situ leaching)

3.2.2 Heap leaching

3.2.3 Percolation leaching – diffusion leaching

3.2.4 Agitation leaching

3.2.5 High-pressure leaching (autoclave leaching)

3.2.6 Biological leaching

3.3 Leaching agents

3.3.1 Summary

3.4 Separation of liquid and solid phases

3.5 Processing of aqueous solutions

3.5.1 Crystallization

3.5.2 Adsorption

3.5.3 Separation of metals from solutions using another metal – cementation

3.5.4 Separation of metals from solutions by gasses

3.5.5 Ion exchange

3.5.6 Solvent extraction

4. Electrometallurgy

4.1 Electrolysis

4.1.1 Standard electrode potentials – row of electrochemical potentials

4.1.2 Description of basic terms

4.1.3 Faraday's laws

4.2 Refining electrolysis

4.3 Electrolysis from aqueous solutions

4.4 Fused-salt electrolysis

5. Refining processes

5.1 Chemical refining processes

5.2 Physical refining processes

5.2.1 Refining processes based on different pressures of metal vapors and partial gas pressures

5.2.2 Refining processes controlled by different mutual dissolubilities in solid and liquid phases

6. Production of selected non-ferrous metals

6.1 Copper

6.2 Nickel

6.3 Lead

6.4 Zinc

6.5 Aluminium

6.6 Magnesium

6.7 Tungsten

6.8 Molybdenum

6.9 Titanium

6.10 Gold

6.11 Silver

1. Introduction



Study time: 2 hours



Objective

- Technical categories of metals
- Properties and applications of non-ferrous metals and their alloys in technical practice.
- Raw materials for non-ferrous metals production
- Mineral dressing



Lecture

1.1 Technical categories of metals

Technical distribution of metals includes groups of metals with significantly different physical and technological properties. From a technical point of view, metals can be distributed into two groups: 1. Iron and its alloys and 2. Non-ferrous metals. The numerous group of non-ferrous metals is further divided into several sub-groups.

I. Iron and its alloys

II. Non-ferrous metals and their alloys

1. General (heavy) non-ferrous metals

- a) with medium melting temperature: Cu, Ni, Co, Mn
- b) with low melting temperature: Zn, Cd, Hg, Pb, Bi, Sn, Sb, Ga, In, Tl

2. Light metals

- a) with medium melting temperature: Al, Mg, Be, Ca, Sr, Ba
- b) with low melting temperature (alkali metals): Li, Na, K, Rb, Cs

Note: some authors consider even Ti-4.5 g/cm³ **Noble (precious) metals**

- a) with medium melting temperature: Ag, Au
- b) with high melting temperature: Ru, Rh, Pd, Os, Ir, Pt

4. High melting temperature metals

- a) with BCC lattice: W, Ta, Nb, Mo, V, Cr
- b) with HCP lattice: Ti, Zr, Hf, Tc, Re

5. Rare earth metals

- a) trace metals: Sc, Y, La
- b) Lanthanides (at. no. 58-71): Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, etc.

6. Radioactive metals, transuranides and transactinides

- a) naturally occurring radioactive metals: Po, Fr, Ra, U, Th, Pa, Ac
- b) transuranides and actinides (at. no. 93-103): Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr
- c) transactinides and superactinides (at. no. 104-168): Rf, Db, Sg, Bh, Hs, Mt, Ds,?

Technical denotation of the purity of metals:

- Raw metal: 3-5% of impurities
- Technically pure metal: up to 1% of impurities (fluxing)
- Electrolytically refined metal: up to 0.5% of impurities – e.g. cathode Cu, Ni, Co, Zn
- For specific applications: Spectral, physical (minimum of derangements, dislocations and lattice defects), semiconductor, nuclear (for applications in nuclear technologies, with minimum admixtures contents, with higher effective absorption cross-sections of thermal neutrons) purities.

The Van Arkel denotation using the basic metal content in % is applied for a more precise definition of metals purities. This is the denotation of metals purities using nines (Table 1.1).

Example: 4N – 99.99 %; 4N8 – 99.998 % (0.002 % impurities content)

Table 1.1 Marking of purity using nines.

Purity marking	Content of metal v %	
	over	under
1 N	90	99
2 N	99	99.9
3 N	99.9	99.99
4 N	99.99	99.999
5 N	99.999	99.9999
6 N	99.9999	99.99999
7 N	99.99999	99.999999

For labelling of very low and trace amounts of admixtures and impurities, the following units have been introduced:

ppm = part per million (10^{-4} % of impurities \Rightarrow 0,0001 % \Rightarrow 6 N)

ppb = part per billion (10^{-7} % of impurities \Rightarrow 0,0000001 \Rightarrow 9N)

1.2 Raw material sources of non-ferrous metals (NFM)s

Raw materials for production of NFM)s are:

1. **Ores** – metal-bearing mineral mass, originated from local clustering of one or more elements. They are defined as utility minerals containing metals in amounts, which can be economically extracted using available technologies. Minerals of ores containing metals to be extracted are denoted ore minerals. The other (remaining) minerals in an ore are denoted waste. Ores, in which several metals are present, are denoted polymetallic.

Ores classification:

- pure metal form: Cu, Ag, Au, Bi, Pt
- oxygen compounds:
 - oxides (Cu_2O , SiO_2 , Fe_2O_3 , SnO_2 , TiO_2)
 - silicates ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)
 - carbonates (CaCO_3 , MgCO_3 , ZnCO_3)
 - sulphates ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, BaSO_4)
 - phosphates

- sulphur, arsenic and antimony compounds (FeS , Cu_2S , CuFeS_2 , PbS , ZnS , NiAsS , NiAs),
- halogen elements compounds NaCl , CaF_2 , AgCl , Na_3AlF_6 .

Ores with high metal contents (natural) can be processed directly. Minerals with poor qualities and low metals contents have to be converted using complex technological processes to concentrates (collective, selective) with metals contents high enough for further processing.

2. Wastes – energy savings up to 80%, rate of return of metals up to 50%.

Wastes classification:

- metallurgical semi-products and rests (slag, matte, speiss, light ash, solution, etc.),
- wastes of metals and alloys from metallurgical plants and factories of consumer industry,
- scrap of non-ferrous metals,
- rests from other industrial branches (ash, alumina solutions from Al_2O_3 production),
- solutions and liquids – Mg from sea water, Cu from mine waters and pickling baths.

Fig. 1.1 schematically depicts the individual technological steps of production of NFMs from mineral ores and wastes.

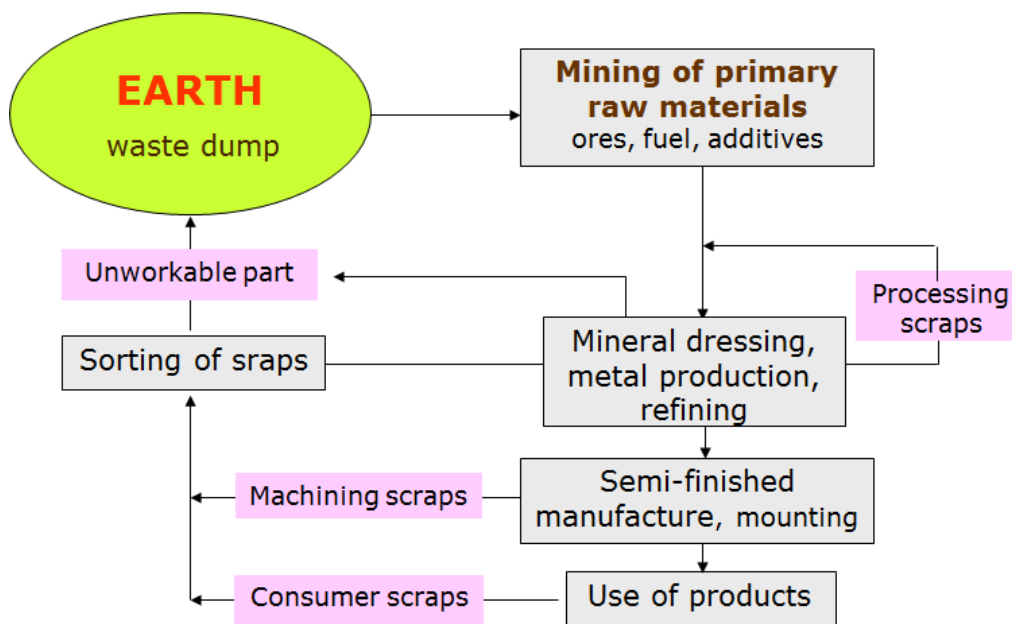


Fig. 1.1 Schematic depictions of processing of ores and production of wastes.

1.3 Ore dressing

Ores and other materials for production of NFMs usually contain various admixtures decreasing their value and aggravating, or even making impossible, their economic processing. Preparation technologies consist of a sequence of various processing steps, by which mechanical and physical properties, including the utility metal concentration, are changed. The aim of these processes is to separate utility components from trashy and harmful components and to obtain better technically and economically exploitable products.

Preparation of ores and other mineral resources includes the following basic steps:

1. Raw material preparation – mechanical ore disintegration by crushing and milling in order to

separate mineral and waste particles. Preparation processes include also particles assortment according to their size regardless their composition and quality.

2. **Separation** – processes leading to enrichment of the processed mineral and increase in metal content in the ore. Separation methods are based on differences in properties of the processed ore individual components, e.g. different densities of different minerals, magnetic properties, wettability and more.
3. **Processing** of the prepared products and preparation of metallurgical concentrates.

1.3.1 Comminution (crushing, milling, screening)

Crushing and milling are especially used to decrease ore lumpiness. The boundary between crushing and milling is exactly defined and is given by the applied disintegration technology or the final product granularity. Although the original lumpiness of a mined ore is typically around 1500 mm, it is usually around 500 mm. Every device for mechanical ores preparation operates effectively only in a certain granularity interval – see table 1.2. Therefore, the crushing and milling processes are always performed in several steps, between which the material is assorted.

Table 1.2 Final material granularities after mechanical processing.

Method	Granularity
1. coarse crushing	> 125 mm
2. intermediate crushing	> 25 mm
3. fine crushing	< 25 mm
4. grinding	< 1.25 mm
5. fine grinding	< 0.08 mm

The main types of devices used for material disintegration by crushing and milling are based on compression, shear, impact and bend:

- a) **Jaw crusher** – material is crushed between fixed and movable jaw. It is used for coarse and intermediate crushing of materials (Fig. 1.2).
- b) **Gyratory crusher** – material is crushed continually between two cocentric cones. It is used for coarse, intermediate and fine crushing of materials.
- c) **Hammer crusher** – material is crushed by rotating hammers with high rotation speed. It is used for intermediate and fine crushing of materials.
- d) **Edge mill** – material is milled by stones roll around on their edges, on a level circular bed.
- e) **Ball or rod mill** – most often used equipments for wet milling of various materials. As milling medium, the steel or ceramics balls (rods) are used, which rotate inside the cylinder around a horizontal axis, partially filled with the material.

Degree of crushing (milling): $S_d(m) = z_{orig.} / z_{fin.}$

$z_{orig.}$ - diameter of the largest lumps before disintegration; $z_{fin.}$ - diameter of the final product largest lumps.

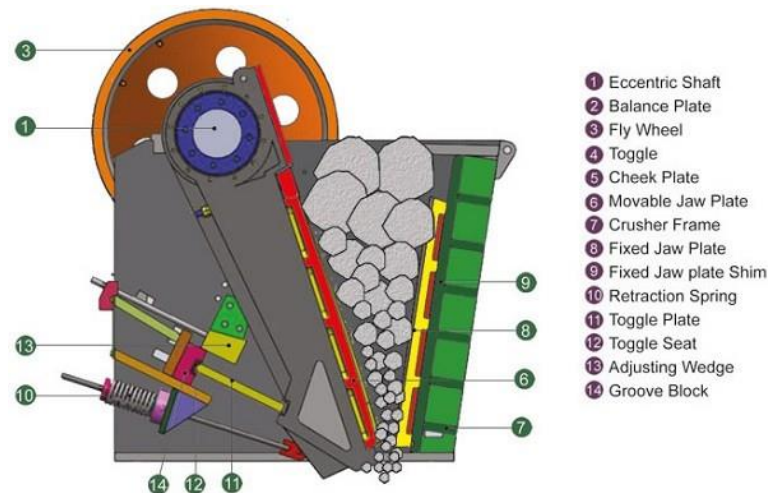


Fig. 1.2 Principle of jaw crusher [3].

1.3.2 Ores separation

Separation is the most important ores preparation step. During this preparation step the mineral chemical composition and its phase remain constant, while separation of a significant portion of waste, i.e. mineral enrichment, occurs. Its aim is therefore to convert utility components into a concentrate (final product with a higher metal content) and separate waste components.

Collective concentrate contains several metals of the same mineral group (e.g. collective sulphidic concentrate containing galena, zinc blende, chalcopyrite, pyrite, etc.). By further separation of a collective concentrate, several selective concentrates are produced, each one of which is enriched with a certain metal.

An appropriate separation method is selected according to the type of properties, which can be applied during the separation process. According to the properties, the separation methods can be denoted as:

1. *Physical* \Rightarrow picking, vanning, separation in heavy liquids, separation in electric or magnetic fields etc.
2. *Physical-chemical* \Rightarrow flotation
3. *Chemical* \Rightarrow processes combined with a thermal ore modification (e.g. calcination)

1. Physical separation methods

- a) **Gravity separation on jigs** – a necessary condition for an effective separation is a sufficiently large difference between the densities of mineral and waste components. The principle of this method lies in different falling speeds of individual minerals in an alternately descending and ascending water stream. A jig consists of two compartments – piston and separation ones. By a downwards movement of the piston, water in the separation compartment is driven upwards and contrariwise. This enables distribution of minerals on the mesh screen in the separation compartment in layers – grains with the highest density are located directly on the screen, lighter grains gradually above them.
- b) **Gravity separation on sluices** – uses different densities of individual ore components. A stream of water together with a mash flow in a thin layer across a longitudinally vibrating slightly tilted sluice plate (Fig. 1.3). Since gravity also applies during this separation process, the lightest grains are washed off the sluice in the shortest way, while heavy grains are transported to the end of the sluice via the vibrational movement.

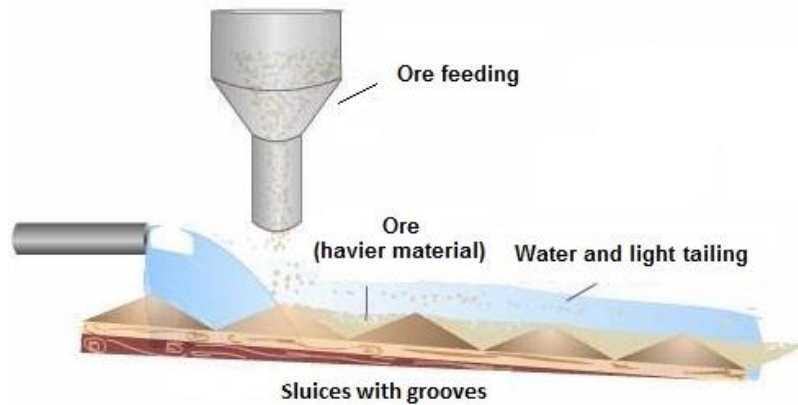


Fig. 1.3 Principle of gravity separation on sluices [4].

- c) **Separation in heavy liquids (suspensions)** – the ore is transported into a liquid separation environment, the density of which is lower than the density of one of the components (e.g. mineral), but higher than the density of the other components (e.g. waste). Lighter minerals float on the water level, while heavier minerals sink towards the bottom. As separation environments, aqueous solutions of salts (saturated CaCl_2), organic acids and aqueous suspensions are used.
- d) **Magnetic separation** – uses different magnetic properties of minerals contained in the ore, especially magnetic susceptibility and permeability. The basis of magnetic separation lies in a separation of the ore to magnetic and non-magnetic products. Grains which resist the effects of mechanic forces (gravity, friction, adhesion, viscosity of the environment and hydraulic resistance during wet magnetic separation) due to the application of a magnetic force are separated into the magnetic product. The main types of equipment for magnetic separation are drum and belt magnetic separators (Fig. 1.4).

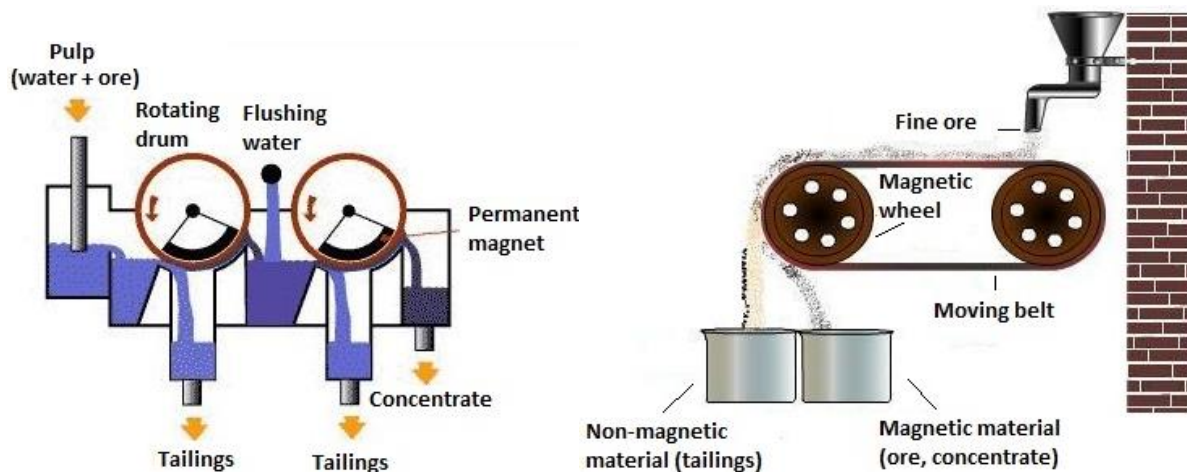


Fig. 1.4 Principle of magnetic separation of ore minerals: a) drum mag. separator; b) belt mag. separator [4, 5].

- e) **Separation in an electrical field** – is based on different electrical conductivities of minerals, on differences in their permittivities and on different forces acting on minerals particles during their passage through an electrical field. According to the electrical field character, electrostatic separators (Fig. 1.5) or separators with corona discharge are applied.

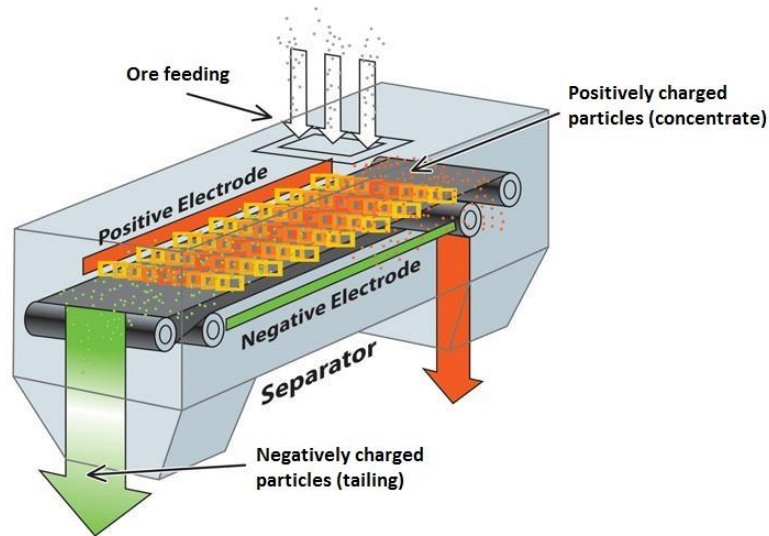


Fig. 1.5 Principle of electrostatic ore minerals separation [6].

2. Physical-chemical separation methods

To these methods belongs especially foam flotation, which is based on different physical-chemical properties of surfaces of utility minerals and waste, especially their different wettabilities. Flotation processes proceed on liquid-gas, solid-liquid and solid-gas phase boundaries (Fig. 1.6a). Hydrophobic (not-wetted – Fig. 1.6b) ore grains of a certain size are selectively adsorbed on surfaces of gas bubbles and subsequently separated to a foam, while hydrophilic (wetable – Fig. 1.6c) particles do not adhere to bubbles and fall to the bottom (Fig. 1.7).

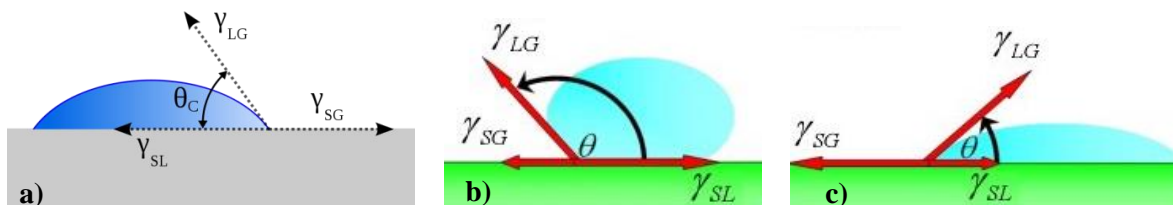


Fig. 1.6 Relation between θ contact angle and individual inter-phase energies [7].

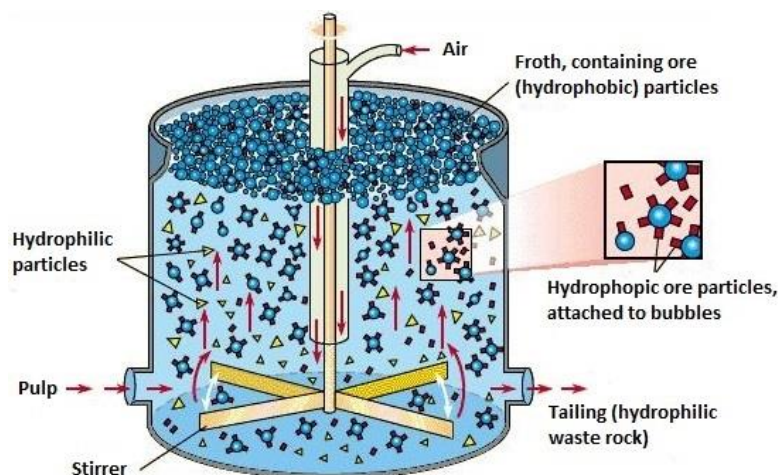


Fig. 1.7 Foam flotation principle [8].

Flotation process includes these steps:

1. Grinding to liberate the mineral particles.
2. Reagent conditioning to achieve hydrophobic surface charges on the desired particles.
3. Collection and upward transport by bubbles in an intimate contact with air or nitrogen.
4. Formation of a stable froth on the surface of the flotation cell.
5. Separation of the mineral laden froth from the bath (flotation cell).

Chemicals used for the flotation play an important role in this process, because they have an influence on the different flotation (surface) properties of minerals. They can be divided into these groups:

- 1) **Collectors** – are used to alter the surface properties of the particles and facilitate the attachment of air bubbles.
- 2) **Frothers** – the reagents that must modify the surface tension of the minerals to be floated, i.e. permit transportation of valuable mineral to the froth phase.
- 3) **Regulators** – control the interaction of collectors between individual minerals, i.e. they can increase or decrease the selective adsorption of collectors on specific minerals for achieving the separation of individual minerals. Modifying reagents can change the pH of the pulp.
 - a) *Modifier* - change the pH of the pulp.
 - b) *Depressant* – adsorption of modifying reagents on mineral surfaces create a hydrophilic mineral surface that cannot react with collectors.
 - c) *Activators* - remove collector coatings from the mineral surface, causing depression of the mineral.

1.3.3 Processing of products of preparation

Products of preparation steps are usually dry, fine-grained concentrates not suitable for further processing. Such concentrates need to be agglutinated in order to minimize the content of ash. For agglutination of fine-grained ores and ore concentrates, briquetting, pelletizing and agglomeration are typically used.

1. Briquetting

Fine-grained ores are agglutinated with or without binders by applications of high pressures up to 150 MPa (Fig. 1.8) Briquetting without binders is applied for ores already containing binding agents, such as limonitic and clayey components. However, strength of such briquettes is low. For briquetting with binders, components, which among their agglutination effect also reduce consumption of fuel or reducers, are added.



Fig. 1.8 Briquetting of fine-grained ores and concentrates.

2. Pelletizing

Pelletizing is typically applied for agglutination of very fine-grained ores (less than 0.5 – 0.2 mm). Moistened fine-grained ores and concentrates agglutinate in rotary pelletizing drums or plates into ball-shaped bodies called pellets (Fig. 1.9).



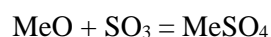
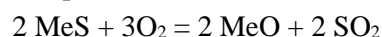
Fig. 1.9 Pellets from fine-grained ores and concentrates [9].

The initial moistening is important, since capillary forces are the main factor influencing effective agglutination. The optimum water content is approximately 10%. Final pellets are not used in the crude form, they are typically hardened by baking and sintering.

3. Agglomeration (sintering)

Agglomeration is the mostly applied agglutination method for fine-grained and dusty materials. It is a thermal-chemical process by which fine-grained ores and concentrates are turned into lump porous agglomerates. The principle of an agglomeration process lies in heating of a material on a temperature allowing the ore grains to smelt, agglutinate and sinter. The heat source is combustion of sulphur contained in the material. In order to prevent material melting as a consequence of a too high heat, it is sometimes necessary to reduce the sulphur content by pre-roasting. If the material contains no sulphur, it has to be mixed with fuel before agglomeration (coke, black oil etc.).

The principle of the agglomeration process is schematically depicted in Fig. 1.10. The air necessary for sulphur combustion or added fuel is sucked or pressed through a glowing layer of dusty ore or concentrate lying on a belt. The batch is then inflamed by e.g. a gas burner. By the influence of hot air, the glowing zone transfers continuously through the entire layer, grains soften and smelt on their surfaces, subsequently agglutinate and their boundaries disappear. During agglomeration, exothermal reactions between gas and solid phases occur:



Requirements on agglomerate:

- a) sufficient porosity enabling flow of reducing gases
- b) high strength, resistance against crushing and abrasion
- c) composition corresponding to a subsequent processing (required sulphur content, slag-forming agents ensuring melting and required slag basicity)
- d) usage of SO_2

Batch: Metal-containing raw material (ore, concentrate), recycling material (waste, semi-products – dust, ash, sludge), additives influencing the agglomeration process (limestone, sand, pyritic slops), possibly fuel.

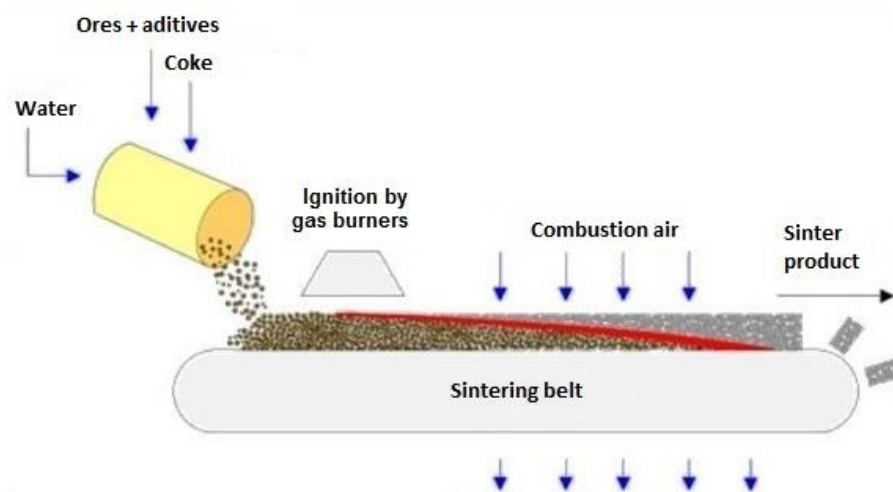


Fig. 1.10 Principle of ore raw materials agglomeration [10].



Summary of terms

Ores and concentrates

Technical classification and purity of metals

Crushing and milling

Gravity separation

Flotation

Magnetic separation

Briquetting

Pelletizing

Sintering



Questions to the topic

1. Which are the general (heavy) non-ferrous metals?
2. How can the purity of metals be expressed?
3. What is a raw metal?
4. What is a difference between the collective and selective concentrate?
5. How are the flotation chemicals classified?



Solved tasks

Example 1.1

Calculate a rational composition of Ni-Cu ore containing: 2,1 % Ni; 1 % Cu; 19 % Fe; 7 % S; 37 % SiO₂; 16 % MgO; 8 % Al₂O₃; 2 % CaO; 7,9 % other compounds + O₂. Calculations on 100 kg of charge. Ore consists of pentlandite (NiFeS₂), chalcopyrite (CuFeS₂), pyrrhotite (Fe₇S₈); hematite (Fe₂O₃) and a gangue.

♦ **Solution****1. NiFeS₂**

$$M(\text{NiFeS}_2) = 178,685 \text{ g/mol}$$

$$178,685 \text{ NiFeS}_2 \text{ g/mol} \dots\dots\dots 58,71 \text{ g/mol Ni}$$

$$x \dots\dots\dots 2,1 \text{ kg Ni}$$

$$x = \mathbf{6,39} \text{ kg NiFeS}_2$$

$$178,685 \text{ NiFeS}_2 \text{ g/mol} \dots\dots\dots 55,85 \text{ g/mol Fe}$$

$$6,39 \text{ kg NiFeS}_2 \dots\dots\dots x \text{ kg Fe}$$

$$x = \mathbf{2} \text{ kg Fe}$$

$$178,685 \text{ NiFeS}_2 \text{ g/mol} \dots\dots\dots 64,13 \text{ g/mol S}$$

$$6,39 \text{ kg NiFeS}_2 \dots\dots\dots x \text{ kg S}$$

$$x = \mathbf{2,29} \text{ kg S}$$

2. CuFeS₂:

$$M(\text{CuFeS}_2) = 183,515 \text{ g/mol}$$

$$183,515 \text{ CuFeS}_2 \text{ g/mol} \dots\dots\dots 63,54 \text{ g/mol Cu}$$

$$x \dots\dots\dots 1 \text{ kg Cu}$$

$$x = \mathbf{2,89} \text{ kg CuFeS}_2$$

$$183,515 \text{ CuFeS}_2 \text{ g/mol} \dots\dots\dots 55,85 \text{ g/mol Fe}$$

$$2,89 \text{ kg CuFeS}_2 \dots\dots\dots x \text{ kg Fe}$$

$$x = \mathbf{0,88} \text{ kg Fe}$$

$$183,515 \text{ CuFeS}_2 \text{ g/mol} \dots\dots\dots 64,13 \text{ g/mol S}$$

$$2,89 \text{ kg CuFeS}_2 \dots\dots\dots x \text{ kg S}$$

$$x = \mathbf{1,01} \text{ kg Fe}$$

3. Fe₇S₈:

$$M(\text{Fe}_7\text{S}_8) = 647,441 \text{ g/mol}$$

$$\Sigma \text{ kg S} = S(\text{NiFeS}_2) + S(\text{CuFeS}_2) = 2,29 + 1,01 = \mathbf{3,3} \text{ kg}$$

$$647,441 \text{ Fe}_7\text{S}_8 \text{ g/mol} \dots\dots\dots 8.32,064 \text{ g/mol S}$$

$$x \dots\dots\dots (7 \cdot 3,3) \text{ kg S}$$

$$x = \mathbf{9,34} \text{ kg Fe}_7\text{S}_8$$

$$647,441 \text{ Fe}_7\text{S}_8 \text{ g/mol} \dots\dots\dots 7.55,847 \text{ g/mol Fe}$$

$$2,89 \text{ kg Fe}_7\text{S}_8 \dots\dots\dots x \text{ kg Fe}$$

$$x = \mathbf{5,64} \text{ kg Fe}$$

4. Fe₂O₃:

$$M(\text{Fe}_2\text{O}_3) = 159,691 \text{ g/mol}$$

$$\Sigma \text{ kg Fe} = \text{Fe}(\text{NiFeS}_2) + \text{Fe}(\text{CuFeS}_2) + \text{Fe}(\text{Fe}_7\text{S}_8) = 5,64 + 2 + 0,88 = \mathbf{8,52 \text{ kg}}$$

$$\begin{array}{l} 159,691 \text{ Fe}_2\text{O}_3 \text{ g/mol} \dots\dots\dots 2.55,847 \text{ g/mol Fe} \\ \quad \quad \quad \times \dots\dots\dots (19-8,52) \text{ kg Fe} \end{array}$$

$$x = \mathbf{14,98 \text{ kg Fe}_2\text{O}_3}$$

$$\begin{array}{l} 159,691 \text{ Fe}_2\text{O}_3 \text{ g/mol} \dots\dots\dots 3.15,999 \text{ g/mol O} \\ 14,98 \text{ kg Fe}_2\text{O}_3 \dots\dots\dots x \text{ kg O} \end{array}$$

$$x = \mathbf{4,5 \text{ kg O}}$$

$$\mathbf{5. Gangue: m(\text{SiO}_2) + m(\text{CaO}) + m(\text{Al}_2\text{O}_3) + m(\text{MgO}) + m(\text{ost.}) = \mathbf{66,4 \%}}$$

Results:

Mineral / Component	Ni	Cu	Zn	Fe	S	O	MgO	CaO	SiO ₂	Al ₂ O ₃	Other	Total
NiFeS ₂	2,10			2,00	2,29							6,39
CuFeS ₂		1,00		0,88	1,01							2,89
Fe ₇ S ₈				5,64	3,70							9,34
Fe ₂ O ₃				10,48		4,50						14,98
MgO							16,00					16,00
CaO								2,00				2,00
SiO ₂									37,00			37,00
Al ₂ O ₃										8,00		8,00
Other											3,40	3,40
Total	2,10	1,00	0,00	19,00	7,00	4,50	16,00	2,00	37,00	8,00	3,40	100



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2. Pyrometallurgy



Study time: 3 hours



Objective

- Pyrometallurgical processes
- Drying
- Calcination
- Roasting
- Melting



Lecture

Pyrometallurgical processes include thermal processing of ores and concentrates at elevated or high temperatures, during which physical and physical-chemical reactions leading to generation of metals or other products occur. Their aim is to convert the processed material to mutually non-miscible phases, which can be separated by physical processes, such as smelting, crystallization, evaporation, separation based on different densities and other. The metal or semi-product concentrates in one phase as a result of chemical reactions, while admixtures concentrate in other phases or components. The individual metallurgical processes lead to controlled separation of admixtures and impurities and continuous concentration of the metal. After refining processes, the metal has the required purity and shape suitable for subsequent processing.

Basic pyrometallurgical processes:

1. Drying and calcination
2. Roasting
3. Smelting
4. Sublimation and distillation
5. Thermal disintegration
6. Refining via change in dissolubility during solidification

2.1 Drying and calcination

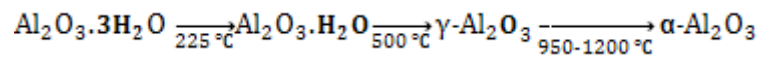
Drying means removal of free water – moisture – or other solvents from the processed materials (ores, concentrates) and their conversion into a gas phase. Sources of moisture can be e.g. mining and preparation processes, transportation, hydrometallurgical processes... The product of drying is a dry mass – material dried to a constant weight, usually at 150°C and at certain air humidity. Drying is performed in rotary drum furnaces, tunnel furnaces, or fluid furnaces, in which drying is performed by particles floating in a drying medium.

Calcination is a pyrometallurgical process, during which chemically bound water, e.g. hydrate and crystal water, is removed from the processed materials. Disintegration of some hydrates, carbonates, halides, sulphates and other compounds occurs as well.

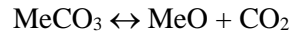
a) *calcination as a dehydration process* – e.g. fluid dehydration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (iron vitriol):



or calcination of aluminum hydroxide $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$:



b) **calcination as a dissociation of carbonates** – calcination can also denote other pyrometallurgical processes, which proceed with (or also without) access of air. An example can be dissociation of carbonates to oxides:



Some carbonates release CO_2 easily, others require quite high temperatures for the dissociation process. Each carbonate features certain dissociation temperature, at which pressure of the released gas reaches the value of atmospheric pressure $p_{\text{CO}_2} = 1$. Approximate dissociation temperatures of selected carbonates: $\text{ZnCO}_3 = 135^\circ\text{C}$; $\text{FeCO}_3 = 158^\circ\text{C}$; $\text{MnCO}_3 = 210^\circ\text{C}$; $\text{PbCO}_3 = 300^\circ\text{C}$; $\text{MgCO}_3 = 410^\circ\text{C}$; $\text{CaCO}_3 = 910^\circ\text{C}$.

2.2 Roasting

Roasting is a method of preparation of ores and concentrates before further pyrometallurgical or hydrometallurgical processing. The aim of roasting is to produce a calcine with suitable chemical and physical properties required for further processing. Roasting is performed at elevated and high temperatures, although still under melting temperatures to prevent a phase change of the processed material.

Chemical composition of a roasted material changes during roasting. Chemical bonds between individual elements are modified, new bonds occur, valences of elements change, some elements are removed in forms of various compounds and gasses.

Since heterogeneous reactions occur (gas-condensed phase), the main factor during roasting is the atmosphere in a roasting furnace. According to the character of the main roasting reaction (i.e. character of the gaseous atmosphere), possibly according to the composition of final roasting products, the following basic types of roasting can be distinguished:

1. Oxidizing roasting

2. Sulphate roasting

3. Reaction roasting

- a) chloride roasting
- b) segregation roasting
- c) chlorination and fluorination

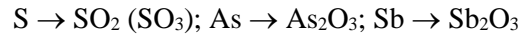
4. Reduction roasting

Important parameters during roasting are above all temperature, amount of air or gas, roasting furnace power output and raw materials input humidities. Calcine quality, i.e. degree of desulphurization, presence of sulphidic sulphur, development of ferrites and silicates, metallic compounds, physical properties etc., have to be regularly controlled.

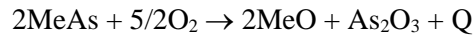
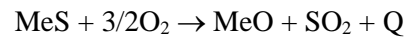
2.2.1. Oxidizing roasting

Raw materials for production of heavy and many other NFMs usually occur in the forms of sulphides, possibly arsenides or antimonites. Since most of the sulphides cannot be directly processed to obtain the basic metals due to their high sulphur content, they first have to be converted to oxides by oxidizing roasting. The oxides are subsequently reduced. Sulphur is removed during roasting and oxygen binds to the metals instead. Some components also volatilize.

All the roasting reactions are exothermal and run within heterogeneous systems. Since the affinity of metals to oxygen is higher than to sulphur, oxidation of metals as well as oxidation of sulphur from metal sulphides occurs to produce gaseous compounds. At the same time, the following volatile products are generated:

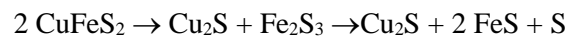
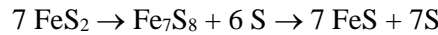


The higher is the affinity to oxygen, the easier roasting reactions occur. General equations of oxidizing roasting:

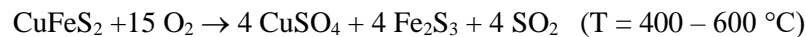
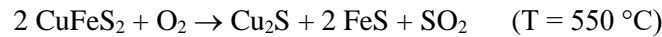


Secondary processes during oxidizing roasting:

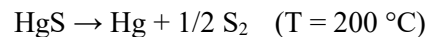
- a) Dissociative disintegration of complex sulphides and subsequent oxidation of the produced waste gasses:



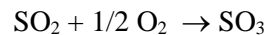
During oxidizing roasting, oxidation of the individual waste gasses components usually occurs during dissociation, or immediately after it. Oxidation of chalcopyrite:



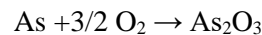
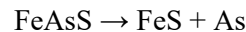
- b) Sulphides of some noble metals can dissociate to pure metals and release sulphur completely during heating – e.g. dissociation of cinnabar:



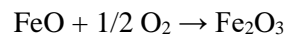
- c) Sulfation of oxides to compounds of MeO.SO₃ type:



- d) Volatilization of volatile oxides:



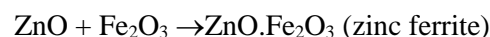
- e) Oxidation of oxides to higher oxidation states:



- f) Reactions of metal oxides with SiO₂ to generate silicates of MeO.SiO₂ type:

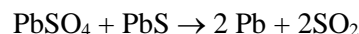
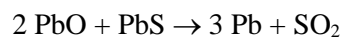


- g) Reactions of metal oxides with Fe₂O₃ to generate ferrites of MeO.Fe₂O₃ type:



Generation of ferrites is generally unfavorable since they lead to losses of metals due to their difficult dissociation.

- h) During oxidizing roasting, roasting-reaction processes occur sometimes as well. A portion of a non-oxidized sulphide reacts with oxides or sulphates to generate metals:



If this process develops during roasting on a roasting grid, encapsulation of the grid by a melted metal can occur, since lead has a very low melting temperature. Therefore, this process is unfavorable.

Equilibrium conditions for the condensed and gaseous phases can be depicted in diagrams showing regions of stability for the individual phases in relations to independently variable parameters – temperature, pressure, concentration etc. Using these Kellogg diagrams (Fig. 2.1), phases occurring

during metallurgical processes, such as roasting and smelting of sulphide concentrates, refining, metals reduction etc., can be denoted.

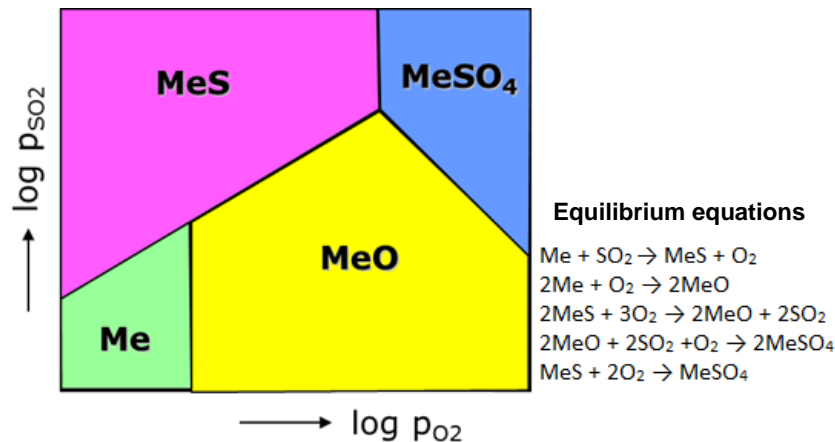


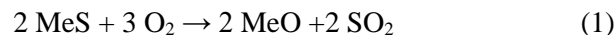
Fig. 2.1 General Kellogg's diagram and equations of phase equilibria.

Rate and development of the sulphide roasting process are influenced by these factors:

- physical and chemical properties of sulphides,
- grinding degree,
- process temperature,
- amount of air for mixing of a roasted material.

2.2.2. Sulphate roasting

Sulphate roasting is usually applied to convert sulphides or metals included in ores and concentrates to metal sulphates dissoluble in water or weak acids. It is a process, by which materials are prepared for hydrometallurgical methods of metals production. Sulphate roasting is a sub-type of oxidizing roasting, during which the following reactions occur:



(dissociation degree increases with increasing temperature)



By regulation of temperature and composition of the gaseous phase during roasting of sulphidic concentrates, the required amount of sulphates in the calcine can be produced. Auto-oxidizing reaction (2) is the reaction controlling sulphate roasting. This reaction is catalytically accelerated by iron oxides (Fe_2O_3) contained in the calcine. Lower temperatures support the reaction towards generation of SO_3 . The resulting SO_3 reacts according to equation (3) with metal oxides to produce sulphates. The situation reverses at higher temperatures, dissociation of SO_3 , as well as dissociation of sulphates, occur according to equation (3). During sulphate roasting it is necessary to carefully control process conditions, especially roasting temperature and composition of furnace gases, which should contain the maximum possible amount of SO_3 . An optimum selection of the roasting temperature enables dissociation of only selected sulphates – these with lower dissociation temperatures, which prevents their dissolution during subsequent technological operations (e.g. leaching).

2.2.3. Reaction roasting

The reactions during reaction roasting can be influenced by further additions of additional compounds into the batch (chlorides, coal) or by additions of active gases (Cl_2 , F_2) into the roasting

atmosphere. According to this, reaction roasting can be divided into two types:

- a) **reaction roasting with additions of active compounds into the batch**
 - 1. chloride roasting
 - 2. segregation roasting
- b) **reaction roasting in active gases**
 - 3. chlorination
 - 4. fluorination

1. Chloride roasting

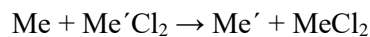
Chloride roasting is used as a preparation process for a hydrometallurgical production of metals, the aim of which is conversion of metal oxides or sulphides to volatile or water dissoluble chlorides. Before roasting, up to 10% of chlorides, such as NaCl, CaCl₂, MgCl₂ etc., are added to the roasted material. During the process, reactions between sulphur, chlorine and oxygen occur, the result of which is conversion of metals within the calcine to chlorides. A necessary condition for these reactions to occur is a presence of sulphur and iron in the ore. Although chlorination reactions occur already at 300°C, chloride roasting is usually performed at temperatures from 600 to 800°C.

2. Segregation roasting (TORCO)

It is a modification method for some low-concentrated ores of copper and nickel or for nickel and copper raw materials, which cannot be modified by other methods. The basis of the process lies in roasting of original nickel or copper ores with additions of coal (1 to 5% in batch) and chlorinating agents (0.5 to 10% in batch, usually NaCl or CaCl₂) at temperatures between 800 and 1000°C and in slightly reducing atmospheres. At such temperatures, nickel and copper bound in the original ores as oxides, sulphides or silicates are converted to chlorides, which are separated into a gaseous phase and reduce to metal nickel and copper on the surfaces of solid reducing agents (particles of coke and coal). The final calcine is subsequently processed by flotation processes.

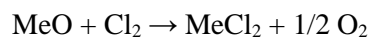
3. Chlorination

The raw material is roasted in an atmosphere or a reaction gas, or a reaction gas is released to the air by a roasting reaction (gaseous chlorine or gaseous chlorine compounds, e.g. HCl, CO+Cl etc.). The dependence of Gibbs free energy during metals chlorination:

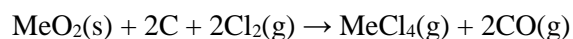


$$\Delta G_0(\text{Me}'\text{Cl}_2) > \Delta G_0(\text{MeCl}_2)$$

If the ΔG_0 curve of a MeCl₂ chloride lies deep below the ΔG_0 curve of a Me'Cl₂ chloride, then a reaction of displacement of Me' by Me metal occurs. It is basically a metal-thermal reduction. However, chlorides are also generated by chlorination of oxides during their heating in a stream of chlorine:



Chlorination of an oxide is however possible only if the change of Gibbs free energy is negative. This can be achieved by addition of a reducing agent (e.g. C).



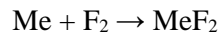
Similarly to oxides, sulphides can also be converted to chlorides by addition of chlorine or hydrogen chloride in a reducing or neutral atmosphere.

4. Fluorination

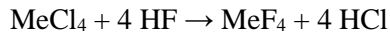
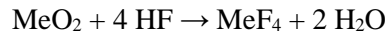
Fluorination is performed to convert metals, oxides, or other compounds to relevant fluorides, which are subsequently processed by metallothermic, electrolytical or hydrometallurgical methods. Among elemental fluorine, which is very reactive, gaseous fluorine can also be used for conversions of simple and binary fluorides of alkali metals, as well as halogens and carbohydrate fluorine-

derivatives. The generated fluorides are often volatile, which is advantageous for refining of some metals, or for separation of metals from alloys.

a) fluorination by elemental fluorine: elemental fluorine effects mainly on metal elements



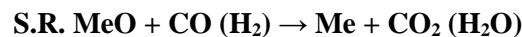
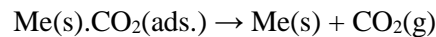
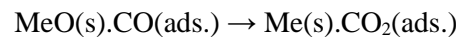
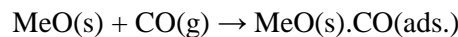
b) fluorination by gaseous hydrogen fluoride: dry hydrogen fluoride is used especially to convert metal oxides and chlorides to fluorides:



2.2.4. Reduction roasting

Additions of reducing gasses such as CO, H₂, CH₄ and others, results to the occurrence of reducing reactions in the roasted material, during which valences of the oxides are continuously decreased to their final reduction to metals. The mechanism of reduction of oxides using gaseous reducing agents is consistent with the adsorption theory – catalysis in three stages:

- 1) adsorption of a reducing gas on an oxide surface,
- 2) separation of oxygen from a metal oxide and its conversion to gaseous particles (CO, H₂), generation of CO₂ (H₂O) particles and of the Me metal crystal structure,
- 3) desorption of products of CO₂ (or H₂O) reduction from the surface of a new phase.



Reduction is reversible:



Reduction of oxides: ($\Delta G < 0$), $\Delta G_2 > \Delta G_1$

Oxidation of metals: ($\Delta G > 0$), $\Delta G_2 < \Delta G_1$

Since individual oxides do not have the same ability to be reduced (different dissociation pressures), reducing of only selected oxides or their portion – selective reduction – can be achieved by an optimum selection of a reducing atmosphere. Reduction roasting is applied to prepare ores for several hydrometallurgical processes or for subsequent magnetic separation.

2.2.5. Roasting furnaces

Roasting furnaces provide perfect contact of all particles of a roasted material with the air or a gaseous atmosphere. For roasting of ores and concentrates, the following types of aggregates are mostly used:

- a) Multi-rack furnaces
- b) Rotational drum furnaces
- c) Convection furnaces
- d) Fluidization furnace

2.3 Smelting

Smelting is a type of pyrometallurgical processing of raw materials, during which a metal-containing batch is heated above its melting temperature in order to separate metal content and waste within the smelt. During the process, two liquid phases are generated – metal concentrates in the heavier one and waste concentrates in the lighter one as slag. Sometimes, generation of three and more liquid phases is favorable, since metal concentrates in the heaviest one, its compounds in the lighter one, while slag is the lightest one. Raw materials for smelting, such as ores, ore concentrates, semi-products, wastes, rests, scrapings etc., contain among main metals also accompanying elements – admixtures and impurities. During smelting, reduction proceeds to produce a raw metal, which is subsequently refined to the required degree of purity. The metal can be subsequently concentrated to produce metal compounds, such as matte and speiss, or it can get separated into other smelting products – slag, air-borne dust, light ash, gasses and more. Smelting can be divided into two basic types:

A. *Smelting to produce compounds*

1. concentration smelting
2. coagulative smelting
3. dissociative smelting

B. *Smelting to produce metals*

1. thermal reduction processes
2. reaction smelting
3. reduction processes of smelting and reducing
4. displacement smelting
5. oxidizing smelting – convertor processing
6. refining smelting and remelting
7. electrolytical smelting etc.

Pyrometallurgical processing of ores and concentrates includes two main stages:

- a) metal reduction
- b) waste separation

During smelting, various batch components dissolve or react with each other to generate final smelting products – metal, matte and slag, having different properties (melting temperature, density, chemical affinity, viscosity etc.).

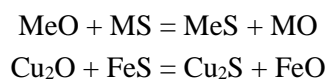
A. SMELTING TO PRODUCE COMPOUNDS

2.3.1 Concentration smelting

Concentration smelting consists in conversion of a metal compound into an individual semi-product, which can be separated from the waste due to their different physical properties, and from which the metal can easily be separated by further technological processing. It therefore consists in increasing in the content of an element in the semi-product – its concentration in the melt. Most of the heavy NFMs have a quite high affinity to sulphur. Therefore they concentrate to produce an individual sulphidic semi-product called matte – a compound of metal sulphides, in which the generated NMF is concentrated. A collective component for all the mattes is ferrous sulphide FeS. Among sulphides, mattes also contain a certain amount of oxygen, which is mostly bound to ferrous oxides.

NFMs with high affinities to antimonite and arsenic concentrate in an individual semi-product containing arsenides and antimonites called speiss. The density of a speiss is higher than the density of

a matte. Therefore, it is located between the matte and metal during smelting. The main components of speiss are arsenides and antimonites of nickel, cobalt, iron and copper (Ni_3As_2 , Ni_5As_2 , Ni_5Sb_2 etc.). The occurrence of speiss is usually unfavorable, since noble and precious metals divide between matte and speiss and do not concentrate in only one of these semi-products. Moreover, processing of a speiss is rather difficult. The basic reactions to produce a matte are:



MO oxides, generated by these reactions, concentrate in a slag, where they bound slag-producing oxides, such as SiO_2 , CaO , Al_2O_3 ...

Among copper, especially precious metals, tin, lead and non-volatile portions of antimonite, arsenic and bismuth and a bigger portion of nickel separate into a matte. Approximately half of the overall cobalt and zinc content and a significant part of iron separate into a slag.

2.3.2 Coagulative smelting

During this type of smelting, addition of a reagent results in separation of a certain component from the smelt on the basis of its different properties. For example, an addition of calcium into a liquid alloy of lead and bismuth leads to coagulation of Bi_3Ca insoluble compound, which then floats on the surface (Betterton-Kroll method). Similarly, silver and gold are separated from lead using zinc – Parkes process. This type of coagulation smelting is based on a formation of intermetallic compounds of silver and gold with zinc – Ag_2Zn_3 , Ag_2Zn_5 , AuZn , Au_3Zn_5 , which have higher melting temperatures than lead. During cooling of a lead bath, these compounds float towards the surface of a smelt and form foams (Parkes skimmings), which are collected at temperatures between 340 and 380°C. These skimmings, which represent wastes from lead refining and in which precious metals concentrate, are after separation of Zn used as raw materials for productions of precious metals by cupellation.

2.3.3 Dissociative smelting

It is a pyrometallurgical process, during which flux agents are added to ensure changes of phases and chemical compositions of the processed ores and concentrates. Ores for hydrometallurgical processes are usually prepared by dissociative smelting, since the change in chemical composition lies in conversion of insoluble metal minerals to soluble and extractable compounds.

According to the character of the flux agent and therefore the whole process, smelting can be either acidic, or alkalic. The important acid flux agents are normal and acid alkali metals sulphates (Na_2SO_4 , K_2SO_4 , NaHSO_4 , KHSO_4). The most important alkalic flux agents are NaOH, KOH, Na_2CO_3 , K_2CO_3 . The effect of alkalic dissociation can be increased by oxidation using oxidizing agents, such as NaNO_3 , KClO_3 , Na_2O_2 , or by reduction using NaCN, elemental sulphur, coke and other agents. Dissociation smelting is used usually to process ores of precious metals.

Example \Rightarrow smelting of tungsten with NaOH to generate soluble sodium tungstate:

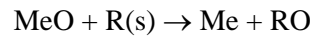
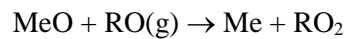


B. SMELTING TO PRODUCE METALS

2.3.4 Thermal reduction processes – reduction smelting

Reduction smelting is usually used to produce metals from raw oxide materials – e.g. production of Fe, Sn, W, Ta, Nb, Mn, Cr and other metals. To produce metals from raw sulphidic materials, e.g. production of Pb from galena, Zn from zinc blende, Mo from molybdenite, etc., the sulphidic raw material has to firstly be roasted by oxidizing to produce oxides, which are subsequently reduced to metals. Halides and many other metal compounds can be reduced as well.

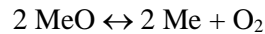
As reducing agents, H_2 , CO , CH_4 , products of natural gas or coal distillation dissociation, solid carbon, calcium carbide and various metals with higher electronegativities than of the reduced metals are usually used. The basic equations of oxides reductions can generally be expressed as:



where RO are reducing agents, i.e. all the agents able to dissociate oxygen from an oxide.

1. Dissociation of oxides as a reducing process

The easiest reducing reaction is dissociation of oxides:



The equilibrium constant of this reaction can be expressed by:

$$K_p = \frac{p_{O_2} \cdot a_{Me}^2}{a_{MeO}^2} = p_{O_2}$$

where p_{O_2} is the equilibrium pressure during thermal dissociation of a generated gas, which is in equilibrium with a thermally dissociated compound – dissociation pressure.

If only pure components are involved in the process, activities in solid states are constant values and $K_p = p_{O_2}$.

The temperature, at which the dissociation pressure p_{O_2} of a given compound is equal to the value of atmospheric pressure is the dissociation temperature (Fig. 2.2). Dissociation temperature is the lowest temperature needed for intensive dissociation and a complete conversion to simpler components.

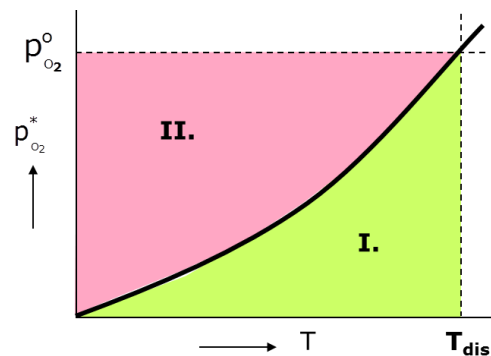


Fig. 2.2 Dependence of dissociation pressure p_{O_2} on temperature: I – dissociation to Me, II – stability of MeO.

2. Chemical reduction of metals

Reduction of metals is performed using reducing agents, which have higher affinities to oxygen than the reduced metals. Abilities of compounds to bind oxygen can be evaluated using values of Gibbs energies (ΔG) for generation of oxides at various temperatures. Temperature dependences of changes of the Gibbs free energies of reactions to produce oxides of individual elements are depicted in Ellingham–Richardson diagrams (Fig. 2.3). The more negative the value of Gibbs free energy change ΔG is, the more stable is the oxide (CaO , MgO , Al_2O_3). The lines for individual metals and their components change their directions at temperatures of melting T_M , boiling T_B and sublimation T_S . From the almost parallel character of changes of the Gibbs free energies with temperature for the individual metals during bonding ensues that metals can be reduced by different metals from their compounds of a same kind in a certain order. A metal with a lower (more negative) Gibbs free energy can reduce a metal with a higher Gibbs free energy. If a metal forms several oxides, the lowest oxides

are always the most stable, e.g. (Fe) \rightarrow FeO \rightarrow Fe₃O₄ \rightarrow Fe₂O₃. Therefore, higher metal oxides are reduced more easily than lower metal oxides.

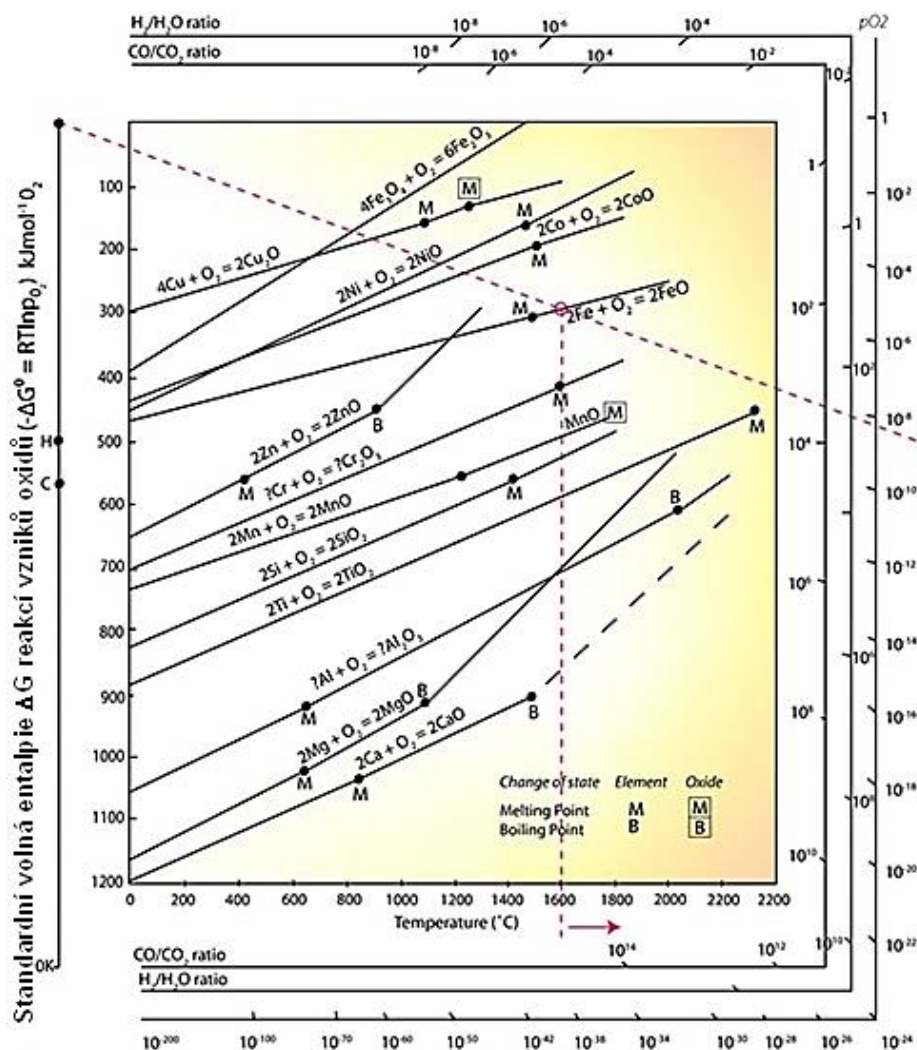
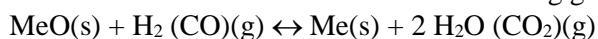


Fig. 2.3 Ellingham-Richardson diagram – temperature dependence of Gibbs free energies ΔG for reactions of metals oxides generation [3].

3. Reduction of oxides by gaseous reducing agents – H₂, CO, CH₄ etc.

General form of a reaction of reduction of oxides using gaseous reducing agents:

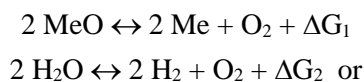


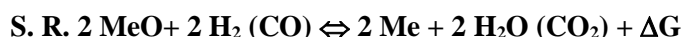
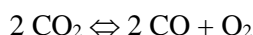
The equilibrium constant of this reaction can be expressed by:

$$K_p = \frac{p_{\text{H}_2\text{O(CO}_2)}}{p_{\text{H}_2\text{(CO)}}} = f(T)$$

The most effective reducing agents are carbon monoxide at lower temperatures and hydrogen at higher temperatures.

Reduction by a gas involves, from thermo-dynamic point of view, simultaneous processes of dissociation of a metal oxide and mutual action of a reducing gas with oxygen:





The possibilities of the final reducing reaction process can be evaluated using thermodynamic potentials of dissociation reactions (1) and (2):

$$\Delta G = 1/2 (\Delta G_1 - \Delta G_2)$$

Conditions for reduction of an oxide: $\Delta G < 0$; $\Delta G_2 > \Delta G_1$; $p_{\text{O}_2}(\text{g}) < p_{\text{O}_2}(\text{MeO})$

Conditions for oxidation within the system: $\Delta G > 0$; $\Delta G_1 > \Delta G_2$; $p_{\text{O}_2}(\text{g}) < p_{\text{O}_2}(\text{MeO})$

Equilibrium conditions within the system: $\Delta G = 0$; $\Delta G_2 = \Delta G_1$; $p_{\text{O}_2}(\text{g}) = p_{\text{O}_2}(\text{MeO})$

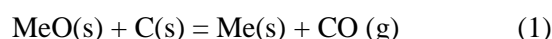
Speed of a metal oxide reduction depends on many factors:

1. character of the batch materials containing metal oxides to be reduced, i.e. their mineralogical composition and physical properties, such as size of ore pieces – lumpiness, ore porosity, uniformity of distribution of the oxide in the prepared material etc.,
2. process temperature,
3. reducing gas composition (mixture of gases),
4. speed of penetration of a gaseous mixture flowing through the batch and drifting carbon dioxide produced by reduction, other gaseous products and unused reducing gas – carbon monoxide.

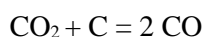
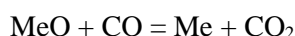
Pure carbon monoxide is used to reduce compounds of Ni, Cr and other metals within the carbonyl process. Hydrogen is used to reduce pure metal oxides – reduction of oxides of high-melting metals Mo, W, Re, production of pure metals Fe, Ni, Co, Bi and other. Hydrogen reduces metal oxides already at relatively low temperatures, which is favorable especially for reducing of oxides of high-melting metals. The products of the reaction are metal – usually as powder, and aqueous vapor.

4. Reduction of metal oxides by carbon

The reaction of a solid metal oxide MeO with carbon, denoted as direct reduction, can be summarized by equations:



Partial reaction of equation (1):



MeO is an oxide of Me metal (Cu_2O , PbO , NiO , FeO , ZnO). The MeO oxide, as well as the reduction product Me, can also be present as liquids during reduction smelting. Since an increase in volume occurs during reaction due to generation of gaseous products (CO, possibly CO_2), a decreased pressure supports the reaction in the direction from left to right. At high temperatures, the second reaction loses its importance, since with increasing temperature the portion of carbon monoxide in the gaseous mixture increases significantly by the Boudouard reaction ($\text{CO}_2 + \text{C} = 2 \text{CO}$) – see Fig. 2.4.

Direct reduction occurs only if particles of a reduced oxide are in a direct contact with a reducing agent. Reduction by carbon monoxide gaseous reducing agent – indirect reduction – is significantly faster than reduction by solid carbon, since a reducing gas surrounds the to be reduced particles and also penetrates to their pores. During this reduction, CO is consumed and CO_2 is generated. Subsequently, carbon monoxide regenerates from carbon dioxide by an addition of a solid reducing agent (carbon, coke, charcoal etc.) according to the Boudouard reaction. Kinetics of this reaction is given by speed of the chemical reaction at lower temperatures and by speed of diffusion at higher temperatures.

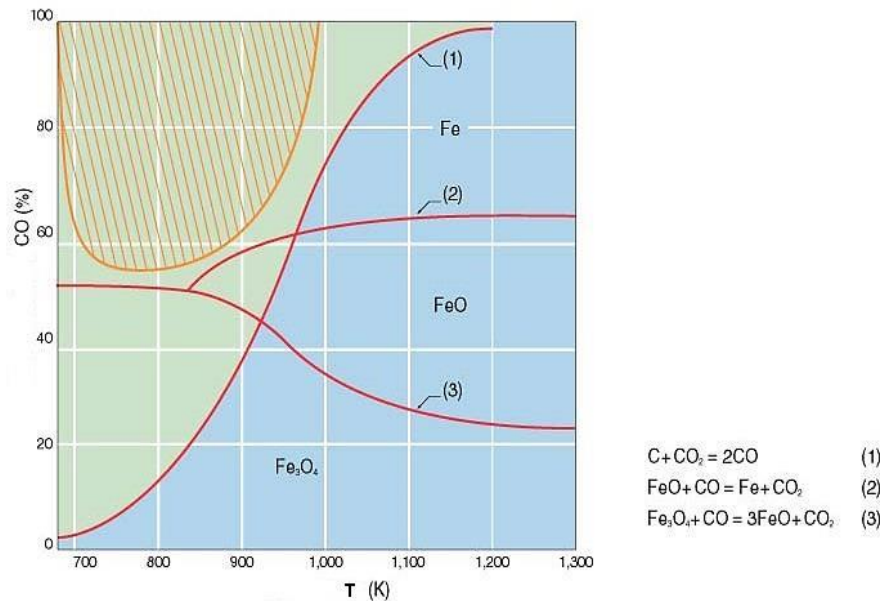


Fig. 2.4 Equilibrium curves of temperature dependences of reductions of metal oxides by carbon during the $CO_2 + C = 2 CO$ reaction – the Boudouard reaction [4].

2.3.5 Thermal processes of metal compounds reductions

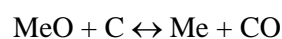
Among thermal processes belong also reduction processes of production of metals and their compounds, during which solid reducing agents and high temperatures are applied. From the heat intake and consumption point of view, the processes can be denoted as auto-thermal and electro-thermal. According to an applied reducing agent, the processes can be divided into:

- A. **Carbothermic processes** – the reducing agent is carbon in the form of coke, coal, graphite or pure soot.
- B. **Metallothermic processes** – the reducing agent to reduce metal compounds (oxides, halides, etc.) is a metal or another metallic element:
 - 1) Al \Rightarrow aluminothermic reduction process
 - 2) Mg \Rightarrow magnesiothermic reduction process
 - 3) Si \Rightarrow silicothermic reduction process
 - 4) Ca \Rightarrow calciothermic reduction process
 - 5) Na \Rightarrow sodium-thermic reduction process

During thermal processes, melting of metals and slags occur at high reaction temperatures in the reaction area.

A. Carbothermic reduction processes

These processes are used to reduce hardly reducible metal oxides by carbon reducing agents in pure forms at high temperatures, which are achieved via electric heating in the reaction area of an electric furnace. The necessary temperature and gas partial pressure for reduction of a selected hardly reducible oxide can be found in a relevant Ellingham-Richardson diagram – see chapter 2.3.4. A general carbo-thermal reaction can be described as:



Equilibrium state of the reaction can be influenced by:

- a) change of temperature, since ΔG is dependent on temperature

- b) change of equilibrium activity via
- reacting compounds
 - additive compounds (Cl, F etc.)

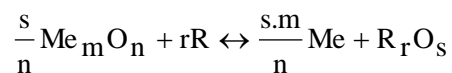
By a change of equilibrium reducing atmosphere (decrease in CO content), a required carbo-thermic reaction can proceed completely, since the CO partial pressure becomes lower than the equilibrium pressure. Equilibrium can also be broken by production of carbides of the prepared metals.

Carbo-thermic processes are used to produce metal Nb and possibly V and Mo, furthermore Ti and Zr compounds or master alloys with other transition metals, ferroalloys and more, using pure soot as a reducing agent.

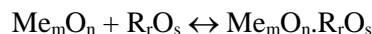
B. Reduction of metal compounds by metals – metallothermic processes

Metallothermic reduction of oxides

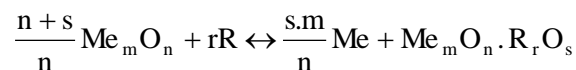
The basic reaction of reduction of metal oxides by metal reducing agents (Ca, Mg, Na, Al, Si) can generally be expressed as:



This equation summarizes a metal-thermal reaction, for which the oxide produced from a reducing agent is alkalic, e.g. CaO, MgO, Na₂O... If the reducing agent produces an amphoteric oxide, such as Al₂O₃, or acid SiO₂ oxide, then the basic oxide of the reduced metal reacts to produce complex compounds:



The summarizing reaction of metal-thermal reduction is then:

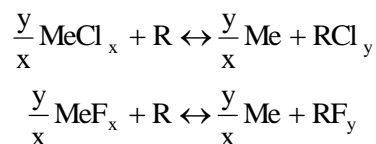


This reaction is not favorable since the reduced metal also separates into the slag, which lowers the effectivity of the reduction process.

Metallothermic reduction of metal halides

This process is used to produce metals, which cannot be reduced from their oxides, or can be reduced only hardly. The raw materials for reductions are usually metal chlorides or fluorides prepared e.g. by chlorination or fluorination.

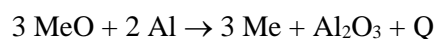
From such halides the metal can be reduced by another metal with a higher affinity to the applied halide element. These metallothermic reactions proceed according to general equations (R – reducing agents – Mg, Na, K, Ca etc.):



when displacement of a Me metal from its MeCl₂ chloride by a R metal, the affinity of which to chlorine is higher than the affinity of the produced Me metal, occurs.

1. Aluminothermic reduction process

The high reaction heat of aluminothermy reactions according to the following equation



is sufficient to reduce most oxides to the basic metals and enables operation without any additional

heat source. Aluminothermy is used to produce e.g. vanadium and niobium with 0.2% residual oxygen content and up to 15% of residual aluminum, which is subsequently removed by remelting in an electron furnace (final purity 99.9%). It can also be applied to prepare ferroalloys and to deoxidize steels as Si-Al, Fe-Si-Al, Fe-Al-Si-Mn, Fe-Al and more.

2. Magnesiothermic reduction process

Magnesiothermy is used primarily to reduce halides – fluorides and chlorides, less to reduce oxides. This method is applied to produce e.g. Be, Ti, Zr, Hf, U, Z, Th and others. Contrary to sodium and calcium, magnesium has a relatively low reaction heat, which is sometimes not sufficient and additional heat has to be supplied.

3. Calciothermic reduction process

Calcium is a strong reducing agent, which reduces all halides and many oxides to the basic metals (e.g. vanadium, uranium, chromium, titanium, thorium and plutonium oxides; uranium, thorium, plutonium and scandium halides etc.). In practice, calciothermy is mostly applied to reduce fluorides, which are contrary to chlorides usually solid and not sensitive to humidity at normal temperatures. Metal fluorides are often the final products after processing of ores or they can be prepared from oxides by application of hydrogen fluoride or ammonium fluoride.

4. Sodium-thermic reduction process

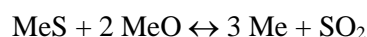
Sodiothermy is applied to reduce chlorides and fluorides of transition high-melting metals – titanium, tantalum, vanadium, zirconium, hafnium and thorium. Due to their low ΔG value, reduction of oxides by sodiothermy is very difficult.

5. Silicothermic reduction process

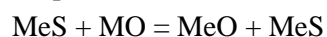
This type of reduction is performed using silicon or ferrosilicon. A disadvantage of silicon as a reducing agent is a formation of non-stable silicates, which cannot be evaporated by dissociation and evaporation of silicon due to their high boiling temperatures. In practice, silicothermy is applied to reduce chromium oxides, to prepare ferrochromium from ores and mixtures of ores with slag-forming additions and to prepare other ferroalloys and master alloys, such as Fe-Zr-Si, Si-Mn, Si-Cr, Fe-Nb, Fe-V etc. with silicon content from 4 to 20 (40)%.

2.3.6. Reaction smelting

Reactions between sulphides and oxides of a same metal or of different metals occurring within ores and concentrates are highly important during production of certain NFMs (Cu, Ni, Pb). During reaction smelting, two metal compounds react together at temperatures higher than melting to produce a metal. A reaction between a sulphide and an oxide of a same metal is the mostly occurring one:



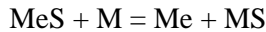
Metal oxides are generated either by oxidation of a portion of sulphides during smelting, or by exchange reactions between Me metal sulphides and M metal oxides.



The direction of a given reaction of conversion of a metal oxide to a metal sulphide can be entirely controlled if affinities of the individual metals to sulphur are known.

2.3.7. Displacement smelting

In some cases, displacements in sulphides (ZnS, PbS, HgS) by iron or other metals occur during their processing according to the reaction:



The basic presupposition for this reaction is a higher stability of MS sulphide than of Me. A disadvantage of this process is production of a matte, in which most of the reduced metal is melted.

2.4 Products of smelting

The following products are generated during smelting due to the occurrence of chemical, physical-chemical and physical reactions: metal, slag, matte, speiss, light ash, air-borne dust and gasses. It is necessary to separate all the products (Fig. 2.5). Separation of the present phases is influenced by the following factors:

- their mutual solubility and miscibility
- their different densities
- their different viscosities
- effective forces of surface tensions



Fig. 2.5 Product of smelting.

Separation of two mutually dissoluble phases is possible only if the difference between their densities is minimally 1 kg.dm^{-3} . The raw metals produced by reduction processes have to be subsequently refined.

2.4.1 Slag

Besides valuable minerals, ores and concentrates also contain admixtures, waste and deads, which have to be separated from the reduced metal into a slag. Selection of an optimum slag composition has the most significant influence on the smelting process. Main functions of a slag are:

- 1) to control heat transfer from a gaseous atmosphere into a melted metal,
- 2) to form a protective layer on a metal bath, making dissolution of gasses from a furnace atmosphere in the melted metal more difficult.

Slag is an alloy of oxides of metal and non-metal elements forming compounds and solutions. Among this it also contains a small amount of metals, metal sulphides and gasses. The main non-ferrous metallurgy slags components are SiO_2 , CaO , FeO . The rest consists of Al_2O_3 , Fe_3O_4 , MgO , BaO , PbO , ZnO ... The individual components affect each other, mutually react, form compounds (silicates, aluminates, ferrites etc.) and solutions, which can form eutectics with melting temperatures lower than of the original compounds.

Slags can be divided according to their characters to:

- a) alkalic (basic) – contain mostly CaO, MgO, FeO
- b) acid – contain mostly SiO₂, Al₂O₃ and Fe₂O₃
- c) neutral – equilibrium of basic and acid oxides

Slags can be characterized using basicity:

$$V = \frac{\Sigma \text{MeO} - \text{basic} (\%, \text{kg})}{\Sigma \text{MeO} - \text{acid} (\%, \text{kg})}$$

According to their chemical compositions, slags can be:

- a) silicate-based – featuring high SiO₂ content
- b) phosphate-based – containing mostly acid P₂O₅ component
- c) oxide-based – containing mixtures of various oxides

Contents of metals remaining in slags depend on chemical compositions of the slags and the smelting control process. Metals losses in slags can be:

- a) **chemical** – e.g. slags from copper production contain small amounts of Cu in the form of Cu₂O, which did not react with FeS to produce Cu₂S. These losses are usually low-negligible.
- b) **physical-chemical** – metals dissolved in slags in the forms of e.g. sulphides. These losses depend on the composition and temperature of a slag and the composition of a matte. They usually are 0.1 – 0.2% of the metal.
- c) **physical-mechanical** – mechanically stripped drops of the matte or metal in the slag due to a higher slag viscosity and small difference in densities. These losses are usually the highest, up to several % of the metal.

2.4.2 Matte

A matte is a product of concentration smelting and consists of a homogenous alloy of metal sulphides. In the matte concentrate metals with high affinities to sulphur, such as FeS, Cu₂S, Ni₃S₂, PbS, but also precious metals (Au, Ag) and rare and trace elements. The basic component for all the mattes is ferrous sulphide FeS. Among sulphides they also contain a certain amount of oxygen in the form of magnetite Fe₃O₄ or iron ferrite FeO.Fe₂O₃. The matte has lower density than a metal smelt, its melting temperature is between 950 and 1100°C.

The matte represents an inter-stage during production of some metals (Cu, Ni, Sn). The condition for its formation is sufficient sulphur content in the batch. Sulphur content in the matte is approximately 20 – 25%. Redundant amount of sulphur in the batch can be removed by roasting. Lack of sulphur can be compensated by an addition of pyrite, another sulphide concentrate etc.

Division of types of mattes according to:

1. produced metal:

- copper – basic components Cu₂S, FeS
- nickel – basic components Ni₃S₂, FeS
- lead – basic components: PbS, Cu₂S, FeS
- copper-nickel – basic components Cu₂S, Ni₃S₂, FeS
- tin – basic components: SnS, FeS

2. content of the basic produced metal:

- **raw mattes** (low Me content) – Me/Fe ratio < 1 concentrated mattes (rich in Me) – Me/Fe ratio > 1
- **white mattes** (almost pure Me metal sulphide) – Me/Fe ratio >> 1

2.4.3 Speise

The main speise components are arsenides and antimonites of nickel, iron and cobalt. This semi-product is produced especially during concentration smelting of nickel-cobalt ores with high contents of arsenic and antimony and during production of lead in shaft furnaces in the forms of Fe_3As_2 , Fe_2As , Fe_5As , Ni_5As , NiAs and others. Speiss melting temperatures are usually between 898 – 1160°C, depending on their chemical compositions. Their densities are usually approximately 5.8 – 8.3 $\text{kg}\cdot\text{dm}^{-3}$ and are higher than densities of mattes and lower than densities of metals.

Generation of a speiss is usually unfavorable, since 1. it contains arsenic, 2. precious and platinum metals are divided between the matte and speiss and do not concentrate only in one semi-product, and 3. processing of a speise is a difficult and expensive process.

2.4.4 Gasses and air pollutants

Gasses, metallurgical exhaust gasses, light ashes and air-borne dusts are also produced during metals productions. These gaseous products do not contain only gaseous components, but also liquid and solid particles. Exhaust gasses are systems consisting of a basic medium – gas, in which liquid and solid substances are dispersed:

- a) ***gaseous phase*** – among gaseous exhaust combustion gasses, this phase can also contain gasses produced by heating of fuel and batch and by reactions within the batch. Gasses from NFMs production usually contain especially these gaseous components:
 - combustible gasses generated by fuel combustion: CO_2 , H_2O , low contents of SO_2 and N_2 , SO_3
 - vapors of (volatile) metals and their gaseous compounds and exhaust gasses of gaseous halides
- b) ***liquid phase*** – drops of smelt (metal, matte, slag) stripped from a smelt bath by a stream of gas. Their content is usually small.
- c) ***solid phase in exhaust gasses*** – mechanically stripped particles of batch, such as shots and air-borne dusts, furthermore solid particles – light ash, originating from cooling of gasses or possibly from chemical reactions between individual components of an exhaust gas.



Summary of terms

Drying and calcination

Roasting

Matte smelting

Reduction smelting

Matte

Speise

Slag



Questions to the topic

1. How are the smelting products called?
2. What is the difference between the oxidizing and sulfatizing roasting?
3. Which are the requirements on slags?
4. What is metallothermic proces?



Solved tasks

Example 2.1

ZnS-ore contains: 76,34 % ZnS; 9,53 % MnCO₃; 2,4 % H₂O; 11,73 % SiO₂. Calculate a Zn-content (wt.%) and Mn-content (wt.%) before and after dead roasting (calculation on 100 kg of charge).

$$M(\text{Zn}) = 65,37 \text{ g/mol};$$

$$M(\text{ZnS}) = 97,44 \text{ g/mol}$$

$$M(\text{Mn}) = 54,938 \text{ g/mol}$$

$$M(\text{MnCO}_3) = 114,946 \text{ g/mol}$$

$$M(\text{ZnO}) = 81,379 \text{ g/mol}$$

$$M(\text{Mn}_3\text{O}_4) = 228,81 \text{ g/mol}$$

◆ Solution

1. Ore before roasting

$$97,43 \text{ ZnS} \dots\dots\dots 65,37 \text{ Zn}$$

$$76,34 \text{ kg ZnS} \dots\dots\dots x$$

$$x = \mathbf{51,2 \text{ kg}}$$

$$w_{\text{Zn}} = 51,2/100.100 = \mathbf{51,2 \%}$$

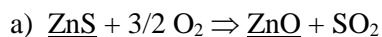
$$114,946 \text{ MnCO}_3 \dots\dots\dots 54,938 \text{ Mn}$$

$$9,53 \text{ kg MnCO}_3 \dots\dots\dots x$$

$$x = \mathbf{4,55 \text{ kg}}$$

$$w_{\text{Mn}} = 4,55/100.100 = \mathbf{4,55 \%}$$

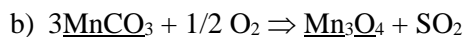
2. Ore after roasting:



$$97,43 \text{ ZnS} \dots\dots\dots 81,379 \text{ ZnO}$$

$$76,34 \text{ kg ZnS} \dots\dots\dots x$$

$$x = \mathbf{63,76 \text{ kg}}$$



$$3.114,946 \text{ MnCO}_3 \dots\dots\dots 228,81 \text{ Mn}_3\text{O}_4$$

$$9,53 \text{ kg MnCO}_3 \dots\dots\dots x$$

$$x = \mathbf{6,32 \text{ kg}}$$

$$\Sigma m_{\text{S}} = m(\text{ZnO}) + m(\text{Mn}_3\text{O}_4) + m(\text{SiO}_2) = 63,76 + 6,32 + 11,72 = \mathbf{81,8 \text{ kg}}$$

$$w_{\text{Zn}} = 51,2/81,8.100 = \mathbf{62,6} \%, \quad w_{\text{Mn}} = 4,55/81,8.100 = \mathbf{5,56} \%$$



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3. Hydrometallurgy



Study time: 3 hours



Objective

- Hydrometallurgical processes
- Leaching methods
- Liquid/solid separation
- Processing of aqueous solutions



Lecture

Hydrometallurgy includes processes of production of metals from ores, concentrates, semi-products and wastes by applications of aqueous solutions of chemical agents resulting in subsequent separation of metals or their chemical compounds from the solutions. It is used to produce various metals, including Zn, Au and platinum metals, Cu, Ni, Co, Al (Al_2O_3), U, W, Mo, Ta, V, rare earth metals and other precious metals. The basic steps of hydrometallurgical metals production are schematically depicted in Fig. 3.1.



Fig. 3.1 Basic steps of hydrometallurgical metals production.

Advantages of hydrometallurgical processes:

1. Highly efficient production of metals from low-concentrated and hard-to-be-concentrated raw materials
2. Complex processing of raw materials
3. Economic efficiency due to the usage of sorption and extraction technologies, concentration and separation methods
4. Efficient monitoring of environmental pollution and better operating conditions (lower dustiness and temperatures)

Basic terms:

Leaching agent = leaching solution

Leachate = solution produced by leaching

Leaching by-products = insoluble rest after leaching.

3.1 Leaching of metals, oxides and sulphides

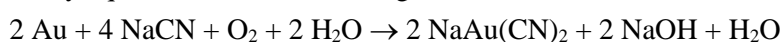
3.1.1 Leaching of metals

Leaching of metals can be the following:

1. Leaching of native metals (Au, Ag, Pt, Cu)
2. Leaching of metals produced as semi-products in metallurgical processes (Au, Ag, Pt, Se)
3. Leaching of metals produced during reducing of oxide ores (Cu, Ni, Co)

A typical leaching agent in these cases is cyanide – NaCN, which can also be substituted by non-toxic thiourea ($\text{NH}_2\text{CS.NH}_2$) with the access of air. The mostly used leaching agents for other cases (Ni, Co, Cu) are $\text{NH}_3 + \text{CO}_2$, $(\text{NH}_4)_2\text{SO}_4$ or H_2SO_4 with the access of air or another oxidizing agent.

Example: The summary equation of dissolution of gold:



The reaction is influenced by cyanide and hydrogen ions concentrations, temperature, oxygen concentration and presence of admixed ions.

3.1.2 Leaching of oxides

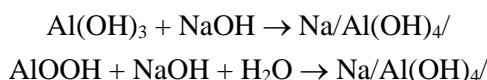
Oxide ores can be divided into two groups:

1. Ores containing simple oxides - $\text{Al}(\text{OH})_3$, Cu_2O , CuCO_3 , $\text{Cu}(\text{OH})_2$, SnO_2 .
2. Ores containing complex oxides - WO_3 , CaO , Cr_2O_3 , FeO , TiO_2 , FeO .

Leaching of oxides can be performed:

- a) with no presence of oxidizing agents (leaching of $\text{Al}(\text{OH})_3$, CuO , SnO_2),
- b) with a presence of oxidizing agents (U_3O_8 , UO_2),
- c) with a presence of reducing agents (MnO_2).

For leaching of bauxite $\text{Al}(\text{OH})_3$, NaOH solution is used:



Three groups of leaching agents are available for leaching of complex oxides:

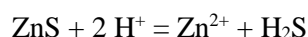
1. leaching of an alkalic oxide by an acid, while an acidic oxide is not dissolved,
2. leaching of an acidic oxide, while an alkalic oxide is not dissolved,
3. dissolving of the whole mineral.

3.1.3 Leaching of sulphides

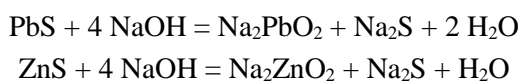
Leaching of sulphides can be performed by two methods:

1. with no presence of an oxidizing agent,
2. with a presence of an oxidizing agent.

Example: Dissolution of ZnS in a diluted acid:



Example: Dissolution of ZnS, PbS in a NaOH solution:



3.2 Leaching methods

The basic factor determining selection of a leaching method is character of the ore and the ability of the to-be-produced component to dissolve in the selected solution Basic types of leaching:

1. Underground leaching (in-situ leaching)
2. Heap leaching
3. Percolation leaching
4. Agitation leaching
5. High-pressure leaching (autoclave leaching)
6. Biological leaching.

3.2.1 Underground leaching (in-situ leaching)

Underground leaching was originally used for mining of water dissolvable salts and sulphur. Nowadays, it is used especially to leach low-concentrated deposits of copper, uranium and gold. During this method, solutions of suitable agents are pumped into drill holes in the vicinities of ores deposits, in some cases to the depth of 1,500 m (Fig. 3.2). The solutions penetrate the rock along its cleavage and fracture planes and dissolve the mineral contained in the ore. The leachate is pumped to the surface at a suitable place and subsequently processed. Regenerated leaching agent is returned to the leaching process.

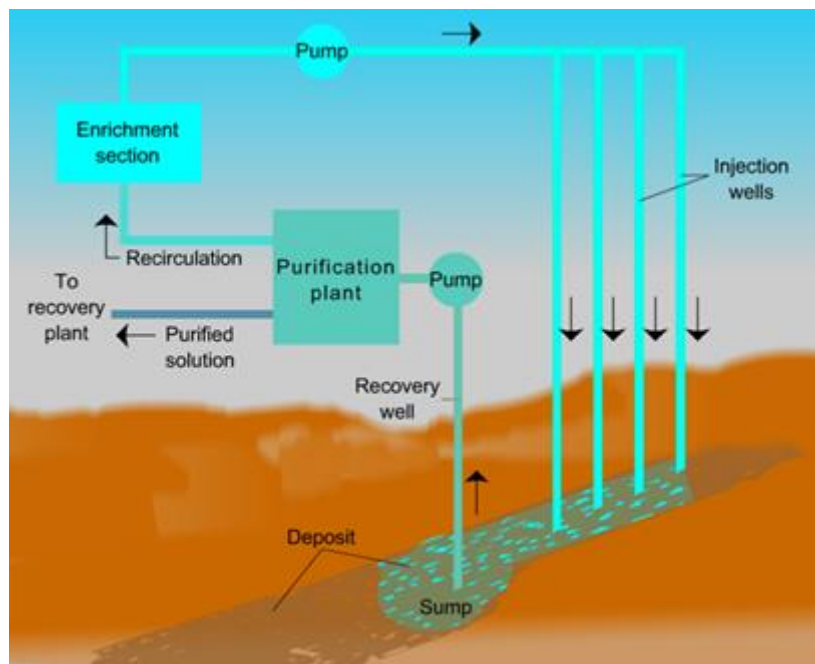


Fig. 3.2 Principle of underground leaching [2].

3.2.2 Heap leaching

A layer of ore in the height of 6 – 9 m is poured on a flat surface covered with asphalt or rubber. Then the ore is sprayed from the top with water or a diluted solution of H_2SO_4 , or a leaching solution is supplied into the layer using perforated pipes. Diameters of ore particles are approximately 25 mm.

Leachates are collected and further processed. The method is applied to leach low-concentrated uranium ores.

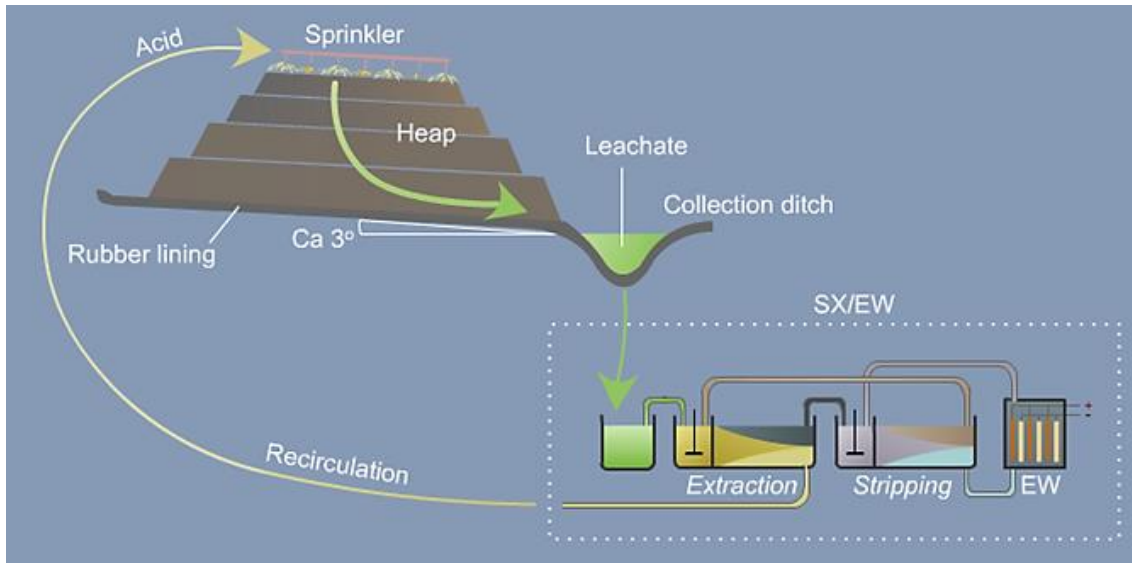


Fig. 3.3 Principle of heap leaching [3].

3.2.3 Percolation leaching – diffusion leaching

Percolation leaching is usually used for ores with bigger lumpiness, pellets or agglomerates, which can easily be leached. This method is used to leach e.g. old dumps and ores stored on platforms or in percolation tanks. It is often used to process copper, uranium and gold ores (Fig. 3.4). The critical factor for application of percolation is the penetration speed, which depends on porosity of the material, content of clay components and height of the layer. Its value should be higher than 2 cm h^{-1} . A leaching agent is either pumped from the bottom, or is poured freely onto the ore. Pumping of a leaching solution from the bottom has many advantages, such as its lower dilution, uniform penetration through the batch and a good penetration also while using non-sorted material containing finer particles.

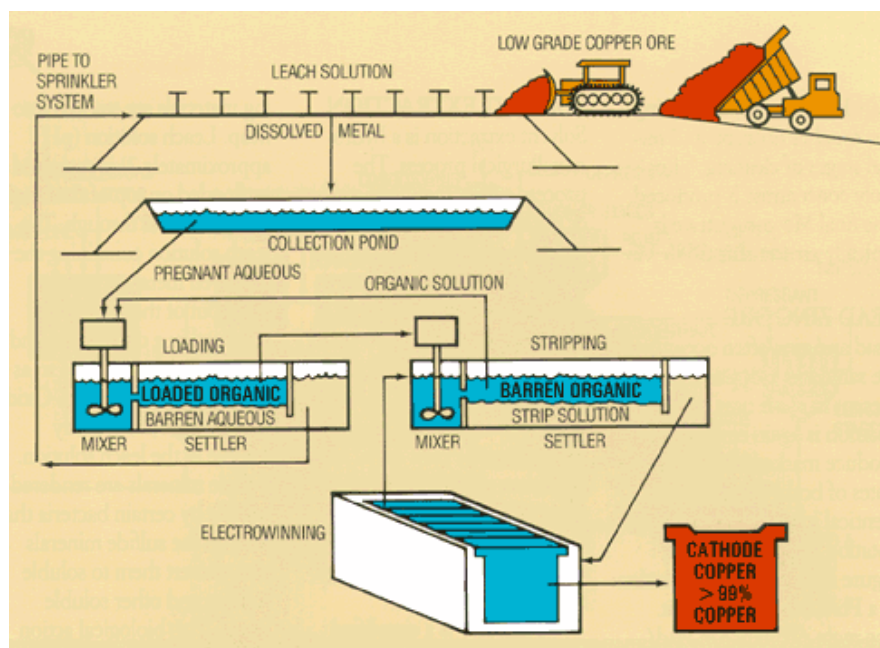


Fig. 3.4 Leaching of low-concentrated Cu-ores by percolation [4].

3.2.4 Agitation leaching

Leaching is significantly influenced by the proportion of liquid and solid phases. To ensure maximum leaching efficiency, this ratio has to be the lowest possible. Other factors influencing the leaching process are material lumpiness, temperature, pressure and intensity of contact of ore particles with the leaching solution. Agitation leaching can be performed either continuously, or discontinuously (Fig. 3.5).

During continuous leaching, a mash flows through a line of agitation units connected one by one. This method is usually supplemented with continuous vanning, thickening and filtering. During discontinuous leaching, a mash is pumped into simultaneously operating agitation units and then pumped out into a catch basin after leaching. This process is constantly repeated. Leaching tanks with agitators are divided into these groups:

1. mechanical:
 - a) mash collecting tanks (reservoirs of mash kept in a suspended state),
 - b) tanks with propeller agitators,
 - c) tanks with suction agitators,
2. pneumatic
3. combined.



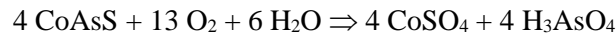
Fig. 3.5 Leaching tanks with agitators [5].

3.2.5 High-pressure leaching (autoclave leaching)

Application of increased pressure and temperature leads to acceleration of chemical reactions. Some reactions also begin to occur at these conditions. For example, ferrites of Zn or Cu are only hardly dissoluble in sulphuric acid under normal conditions. Nevertheless, if the leaching temperature increases to 160°C, they dissolve very easily. Leaching under high pressures is performed in specialized pressure vessels – autoclaves (Fig. 3.6) – which have to be resistant to high pressures (up to 10 MPa), to effects of various agents and to abrasion of transferred mashes. Dissolubilities of gasses multiply at increased pressures, which results in an occurrence of reactions between gasses and minerals, which would not occur (or only rarely) under normal pressure conditions.

Autoclave processes, running with a participation of oxygen, are processes during which:

1. Oxidation of metals or lower oxides to dissoluble forms occurs; for acidic leaching under pressure, the necessary sulphuric acid can be replaced by an addition of finely ground pyrite.
2. Oxidation of original elements, on which the produced metals are bound, occurs.



3. Oxidation of both the components occurs:

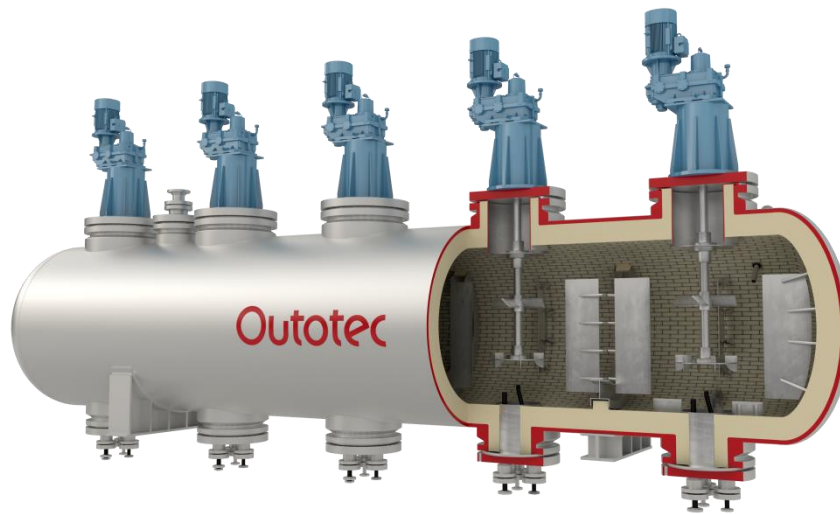
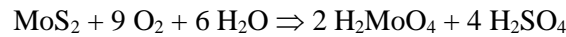


Fig. 3.6 Principle of Outotec's autoclave for gold leaching under high pressure [6].

3.2.6 Biological leaching

Biological (bacterial) leaching includes processes of ores leaching, during which microorganisms are used together with chemical agents to convert metals to solutions. Bacteria are generally wide-spread in soil, water and air. Depending on the materials necessary for their existence they can be denoted as:

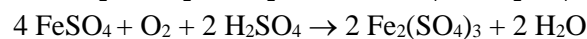
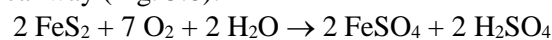
- a) *heterotrophic*
- b) *autotrophic*

Heterotrophic bacteria use final organic compounds (carbohydrates, proteins etc.), while autotrophy bacteria need only inorganic substances for their existence. Bacteria applied during leaching belong to autotrophic bacteria:

1. **Thio- bacteria**, e.g. *thiobacillus thiooxidans* – have the ability to oxidize sulphur and sulphides to sulphuric acid.
2. **Ferrobacillus** – the source of energy is an oxidation reaction of divalent iron.
3. **Thiobacillus ferrooxidans** – have the properties of both the above mentioned groups.

In hydrometallurgy of sulphides, the highest importance has the thiobacillus ferrooxidans (TF) and thiobacillus thiooxidans (TT) bacteria – Fig. 3.7.

Both types of these bacteria are suitable for hydrometallurgy, since they supplement each other. TF oxidizes pyrite to iron sulphate in a biochemical way and by this enables dissolution of other ores components in a chemical way (Fig. 3.8):



$\text{Fe}_2(\text{SO}_4)_3$ further chemically reacts:



The produced FeSO_4 is biochemically re-oxidized and therefore can again contribute to leaching



Elemental sulphur, generated as the final product during leaching of sulphides, accumulates on the ores surfaces and inhibits further diffusion. By this reason, the presence of TT bacteria oxidizing the generated sulphur to the sulphuric acid is necessary.



Biological leaching enables processing of old dumps, as well as underground leaching of deposits, which are non-mineable by other methods due to their low metals contents. Its significant advantage is a high yield degree, often up to 96%.

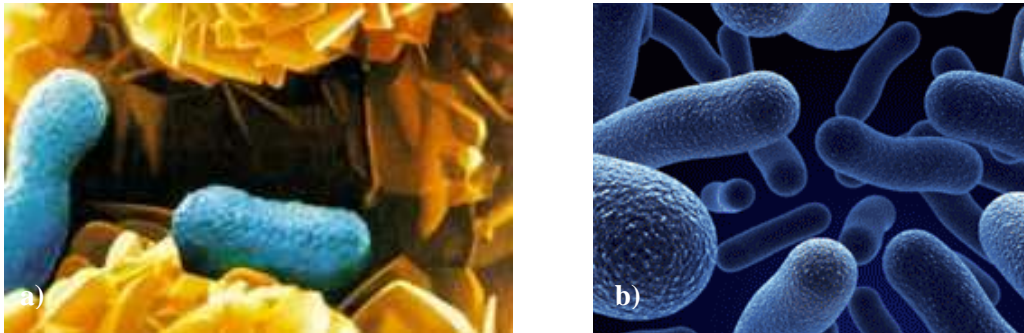


Fig. 3.7 Bacteria thiobacillus ferrooxidans (TF) (a) and thiobacillus thiooxidans (TT) (b) [7, 8].

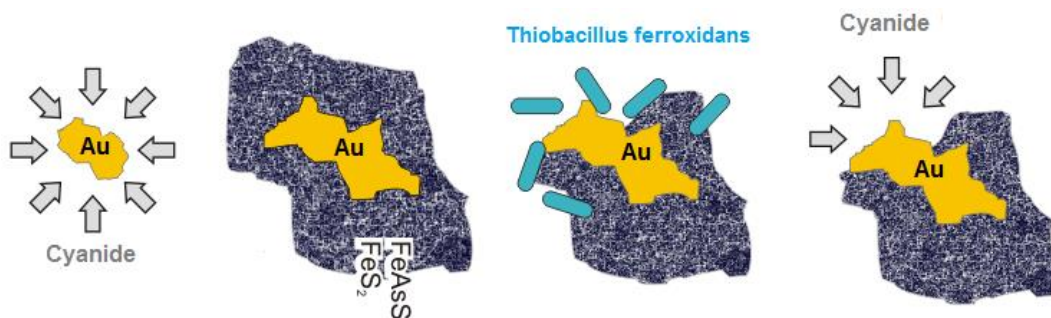


Fig. 3.8 Biological leaching of gold from pyrite and arsenic-pyrite ores [9].

3.3 Leaching agents

Selection of a leaching agent depends on many factors. Among the most important are:

1. Chemical and physical character of the leached material.
2. Cost of the dissolving agent.
3. Corrosion effects of the dissolving agent on the apparatus.
4. Selectivity of the dissolving agent regarding the leached material.
5. Possibility of regeneration of the leaching agent.

Selectivity of a leaching agent is influenced by:

- a) leaching agent concentration,
- b) temperature,
- c) contact time of the leaching agent with the leached material.

The mostly applied leaching agents are:

1. Water – for leaching of calcines after sulphate or chloride roasting, e.g. leaching of Re_2O_7 .
2. Aqueous solutions of salts:
 - $\text{Fe}_2(\text{SO}_4)_3$: leaching of CuS ,
 - NaCN : leaching of Au ,
 - Na_2S : leaching of Sb_2S_3 ,
 - $\text{Na}_2\text{S}_2\text{O}_3$: leaching of Ag .
3. Chlorinated water: leaching of ZnS .
4. Acids – mostly H_2SO_4 .
5. Alkalic agents:
 - Especially leaching of bauxites and Al ,
 - NH_4OH : leaching of Cu and Ni .

3.6.1. Summary

1. Leaching rate increases with decreasing lumpiness, since small particles have greater specific surface.
2. For a leaching process controlled by diffusion, the leaching rate depends on the intensity of agitation. Agitation should be sufficient to keep the solid particles floating.
3. Leaching rate increases with increasing temperature.
4. Leaching rate increases with increasing leaching agent concentration.
5. Leaching rate increases with decreasing content of solid particles in the mash.
6. If dissoluble by-products are generated during leaching, then the leaching rate depends on their character. Non-penetrable products decrease leaching rate.

3.4 Separation of liquid and solid phases

The basic methods of separation of liquid and solid phases are:

1. Sedimentation
2. Filtration (Fig. 3.9)
3. Centrifugation (Fig. 3.10)

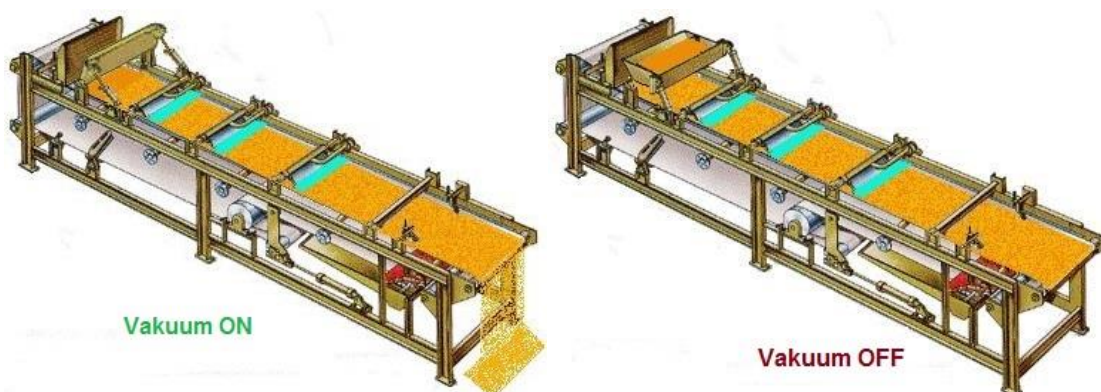


Fig. 3.9 Principle of vacuum filtration [10].

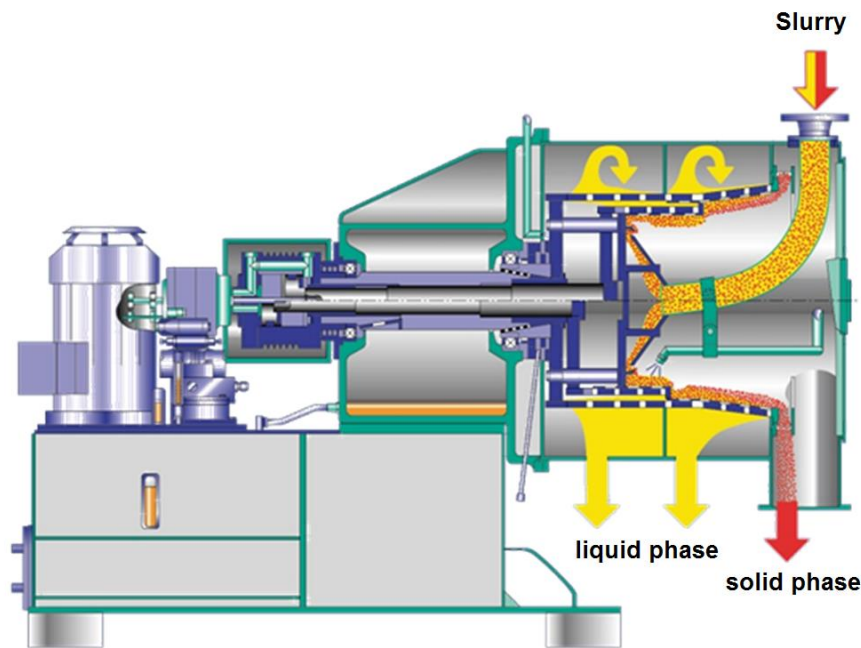


Fig. 3.10 Principal schema of separation of solid and liquid phases in centrifuges [11].

3.5 Processing of aqueous solutions

Among the basic methods of aqueous solutions processing are:

1. Crystallization
2. Adsorption
3. Separation of compounds with low dissolubilities
4. Separation of metals using another metal – cementation
5. Separation of metals from solutions by gasses

To an individual group belong:

6. Ion exchange
7. Fluid extraction

3.5.1 Crystallization

In hydrometallurgy of NFMs, this process is used to separate metals in the forms of pure salts, to separate elements with similar properties by the method of repeated crystallization of salts, for solutions cleaning etc. Crystallization occurs during cooling of a saturated solution or during evaporation of a dissolving agent. The process can be divided into several steps:

1. formation of an oversaturated solution
2. formation of crystallization nuclei – centers
3. crystals growth
4. re-crystallization

3.5.2 Adsorption

The adsorption process includes two stages:

- a) adsorption

b) separation of metals from adsorbents (desorption)

Some compounds have the ability to attach gases or liquids on their surfaces. This phenomenon is called sorption. Since sorption depends especially on the size of the sorbent's surface, it is greater for porous or finely dispersed substances. For example charcoal, fine-grained oxides and hydroxides and colloidal substances are used in practice.

At present, adsorption is used to produce platinum, palladium and osmium from diluted chloride solutions on activated carbon, rhenium and molybdenum selectively from acid solutions, gold and silver from cyanide solutions and more. Cleaning of leachates from arsenic and antimony or from colloidal sulphur before electrolysis is based on the sorption ability of a freshly agglutinated $\text{Al}(\text{OH})_3$.

3.5.3 Separation of metals from solutions using another metal – cementation

Coagulation of copper from mine waters using iron is one of the oldest hydrometallurgical processes. The basis of the process lies in displacement of a more noble metal from a solution of its salts by a less noble metal, which dissolves during the process. Dissolution of the less noble metal and coagulation of the nobler one occur due to different values of osmotic and dissolving pressures. During the process the dissolved metal charges negatively, while the surrounding solution charges positively.

The purity of a cemented metal is also influenced by contents of noble metals with which it coagulates. Therefore selective cementation is sometimes applied, during which the noblest metals are at first coagulated by a previously calculated addition of the cementing metal and subsequently, after their separation, the less noble metals are coagulated. This process is usual e.g. for cleaning of a zinc leachate from copper and cadmium. By application of a Zn powder, copper and subsequently cadmium coagulates are produced. To balance different concentrations of solutions, diffusion can be accelerated by increased temperature, flow of air bubbles or aqueous vapor.

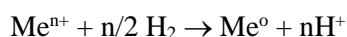
3.5.4 Separation of metals from solutions by gasses

Separation of metals from solutions by gasses processes at high temperatures and pressures, while:

1. With increasing temperature, dissolubility of most of the salts in water increases up to 120 – 150°C and then decreases with further temperature increase.
2. Dissolubility of salts in water usually depends on the presence of other salts. For example, dissolubility of CoSO_4 in water at ambient temperature decreases strongly with a presence of $(\text{NH}_4)_2\text{SO}_4$. At high temperatures, this dependence is opposite.
3. Dissolubility of gasses in water decreases with increasing temperature up to approximately 100°C, while with further increase in temperature it increases remarkably.
4. With a presence of salts, dissolubility of gasses usually decreases.
5. At high temperatures, hydrolysis occurs easily.

1. Reduction by hydrogen

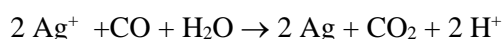
Reaction of metal cations:

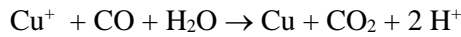


can occur as long as the hydrogen potential is lower than the electrode potential of metal: $\varphi_{\text{H}_2} < \varphi_{\text{Me}}$. Separation stops after establishment of equilibrium.

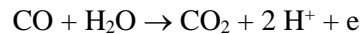
2. Reduction by carbon monoxide

Separation of silver and copper from sulphuric acid environment is possible via reduction by CO.

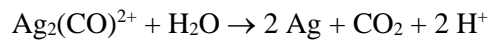
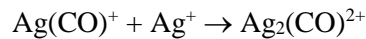
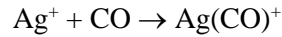




Reducing ability of CO depends on the change of Gibbs molar energy of the reaction:

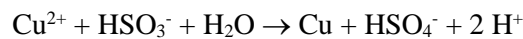
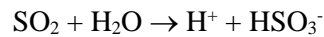


The probable mechanism of reduction by CO can be described by the following equations (analogically for copper):



3. Separation by sulphur dioxide

Separation of copper sulphite from H_2SO_4 environment at ambient temperature is possible via reduction by sulphur dioxide. Nevertheless, if the process proceeds at 100°C and the pressure of 0.34 MPa, metal copper is separated.



3.5.5 Ion exchange

The ion exchange process is based on the ability of some substances to adsorb ions from a solution and to release ions with the same charge back to the solution (Fig. 3.11). These substances are called ion exchangers. Ion exchangers (ionexes) are dissoluble high molecular solid compounds containing active groups able to exchange ions for ions of dissolved electrolytes. According to the type of the exchanged electrons, they are denoted as catexes (cations) and anexes (anions). In hydrometallurgy, ionexes are applied especially for sorption of metals from highly diluted solutions, such as mine waters, waste waters from productions and leachates with low metals contents, further for sorption from mashers, for separation of chemically similar metals etc.

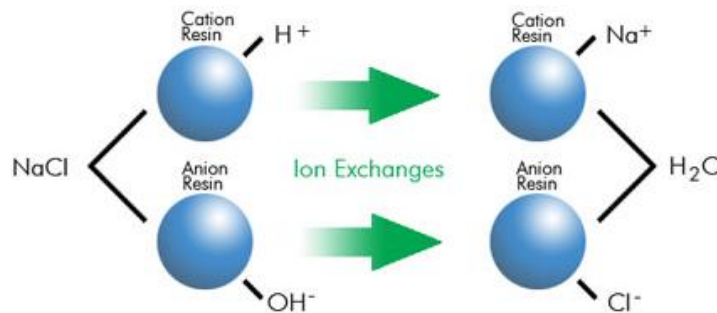
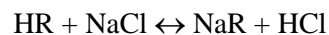


Fig. 3.11 Principle of ion exchange [12].

Catexes usually substitute their hydrogen cations for an equivalent amount of other cations present in the liquid phase. A typical reaction of cations exchange is:

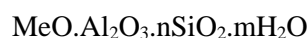


where R denotes the catex body, which is actually a macro-anion.

According to their origin and principle, ion exchangers can be divided into the following groups:

1. mineral ion exchangers – inorganic
2. organic ion exchangers

There are natural and fabricated ion exchangers in both the groups. Among natural inorganic catexes are aluminosilicates belonging to the mineralogical groups of hydrated micas, montmorillonites or zeolites. Comparing to synthetic catexes they have relatively low capacities. The general formula of zeolite is:



where Me can be Li, Na, K, Ca, Ba.

3.5.6 Solvent extraction

Extraction is a process of conversion of compounds from aqueous solutions to liquid organic phases non-miscible with water (Fig. 3.12). Subsequent re-extraction enables conversion of an extracted metal from the organic phase to an aqueous solution. The organic phase returns back to the process.

Extraction is, similarly to ion exchange, applied in hydrometallurgy to produce metals from diluted solutions and enables their separation from various admixtures. At present, extraction is applied to clean uranium, indium, thallium, germanium, tellurium, to produce copper and separate nickel, cobalt, hafnium, molybdenum and rhenium.

Extrahents are organic compounds forming complexes or salts with the extracted metals, which dissolve in the organic phase. They are organic acids, alcohols, ethers, ketones, amines and others. Dissolvents are organic liquids non-miscible with water dissolving the extrahents. The usually applied dissolvents are kerosene and its fractions.

Extraction processes can be divided into:

1. extraction based on cations exchange,
2. extraction based on anions exchange,
3. extraction by neutral extraction agents after prior solvation or hydrosolvation.

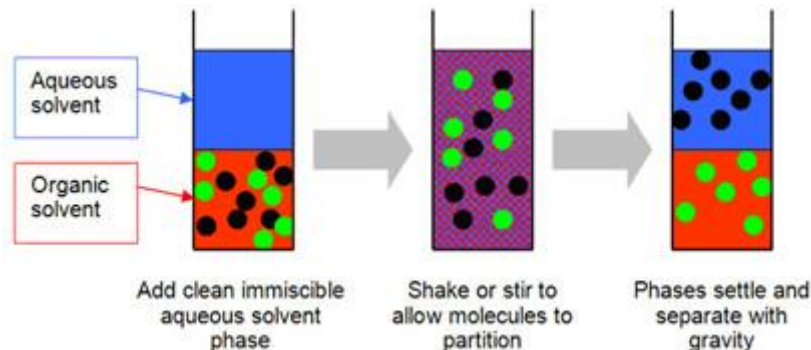


Fig. 3.12 Principle of solvent extraction [13].



Summary of terms

In-situ leaching

Heap leaching

Pressure leaching

Biobleaching

Leaching reagents

Filtration

Sedimentation

Ion exchange

Solvent extraction



Questions to the topic

1. What is the principle and application of in-situ leaching?
2. What are the methods used for solid-liquid separation?
3. Which factors do influence the selection of leaching reagents?
4. How can the ion exchangers be divided?



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4. Electrometallurgy



Study time: 2 hours



Objective

- Electro-chemical processes
- Standard electrode potentials
- Polarization
- Electrolysis from aqueous solutions
- Molten salt electrolysis
- Refining electrolysis



Lecture

The principle of electrometallurgical processes is a passage of electrical current through dissociated solutions (electrolytes) accompanied by oxidation and reduction processes on the electrodes. Electrometallurgy is used for production of metals from:

- leachates of ores
- smelts
- metallurgical semi-products
- metallurgical wastes

Electrochemical methods together with hydrometallurgy enable economical processing of low-concentrated complex ores and usage of all components of an original raw material.

4.1 Electrolysis

Electrolysis is a chemical process, during which chemical conversions in an electrolytic solution occur due to the effect of direct current supplied from an external source. A device, in which electrolysis proceeds, is called an electrolytic cell. A substantial part of an electrolytic cell consists of a vessel with a solution or smelt of an appropriate electrolyte. Direct current is supplied to the solution from a suitable source using electrodes. The electrode connected to the negative pole of a source, on which is always redundancy of electrons, is denoted cathode. The second electrode, connected to the positive pole, featuring lack of electrons, is denoted anode. Current conduction in an electrolyte is enabled by free movements of ions. When a cell is circuited, positively charged ions (cations) move to a cathode, while negatively charged ions (anions) move to an anode. Contacts of ions with electrodes result in an occurrence of oxidizing and reducing processes. The cathode transfers its redundant electrons to ions and reduces them, while the anode removes electrons from ions and oxidizes them. These phenomena are denoted as cathodic reduction and anodic oxidation (Fig. 4.1).

Electrolysis has a wide application in technological practice. It is applied especially to produce metals, which cannot be produced by chemical processes in an industrial scale. These include especially very non-noble metals, such as sodium, potassium, calcium, magnesium, aluminum, etc., which are produced by electrolyses of smelted salts. Electrolysis is also applied to refine metals produced by other processes.

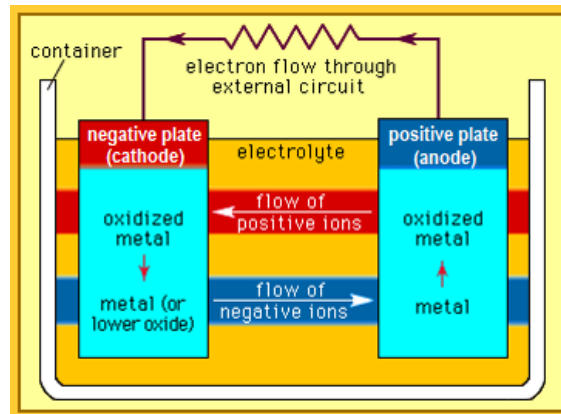


Fig. 4.1 General scheme of electrolysis [3].

4.1.1. Standard electrode potentials – row of electrochemical potentials

After an immersion of a metal into a solution of its salts, the metal starts to dissolve and generate ions, which generates a certain dissolving pressure. Against this pressure affects the pressure of surrounding ions in the solution, the osmotic pressure. After equalization of these pressures, equilibrium in a close vicinity of an electrode is established and a thin electric bi-layer generating a difference between the electrode and electrolyte potentials – electromotive force – is produced. The value of the force is different for different metals. A potential of such a half-cell cannot be measured, therefore two half-cells are usually connected and a difference between their potentials is then measured. A standard hydrogen electrode with the potential of ± 0.0 V was established to be the basic comparative half-cell. The charge of the standard potential is then obtained according to the relation of a given electrode to the hydrogen electrode.

Example: $\text{Cu}^{2+} / \text{Cu}$ is a positive pole in a cell if $a_{\text{H}^+} = a_{\text{Cu}^{2+}} = 1$ is $E_{\text{Cu}^{2+} / \text{Cu}} = +0,34$ V

$\text{Zn}^{2+} / \text{Zn}$ is a negative pole in a cell if $a_{\text{H}^+} = a_{\text{Zn}^{2+}} = 1$ is $E_{\text{Zn}^{2+} / \text{Zn}} = -0,76$ V

Standard potentials characterize reducing or oxidizing abilities of particles in aqueous solutions. The more negative is the standard potential, the stronger is the reducing agent (Fig. 4.2). Metals located at the bottom end of the row of electrochemical potentials (alkali and alkaline earth metals) represent very strong reducing agents and are easily oxidizable. Metals with negative standard potentials are denoted non-noble metals, metals with positive standard potentials are denoted noble metals.

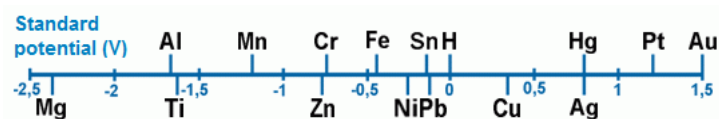


Fig. 4.2 Row of metals according to standard electrode potential values (according to the theoretical nobility).

4.1.2. Description of basic terms

1. Electrochemical potential

Substitution of charges, possibly electrons, between two materials is given by their electrochemical potentials. The tendency of a metal to convert to a solution of its salts is given by the Nernst equation:

$$E = E^0 - \frac{RT}{zF} \ln \frac{a_{\text{red}}}{a_{\text{ox}}}$$

The standard electrode potential of a hydrogen electrode, used as a primary standard for pH measurements, is equal to:

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2}}{(a_{H^+})^2} = 2,303 \frac{RT}{F} \log a_{H^+}$$

2. Dissociation pressure

To perform electrolysis of a given electrolyte, it is necessary to supply the electrodes with a sufficiently high voltage. The minimum voltage necessary to ensure passage of electric current through a solution is denoted electrolyte dissociation pressure. Its value is given by the relation:

$$U_r = U_p + I_z R$$

where U_p – polarization voltage; I_z – cut-off current; R – resistance of electrolyte.

The polarization voltage is equal to a difference between the polarization potentials of anode and cathode.

$$U_p = E_{pa} - E_{pk}$$

The potential of a polarized electrode is $E_p = E + \eta$, where η is overvoltage. Then the dissociation pressure is given as:

$$U_r = (E_a + \eta_a) - (E_k + \eta_k)$$

3. Polarization

Dissociation of a solution by an electric current results in a generation of a new cell by the occurring chemical reactions on the electrodes. The electromotive force of this cell affects against the electromotive force supplied from an external source. This is the polarization voltage.

- a) Concentration polarization – is a certain type of polarization which occurs during refining electrolysis due to the changes in concentrations of ions in the vicinities of electrodes. The concentration of ions increases around a dissoluble anode, while it decreases around a cathode. The generated concentration gradient, which is directly proportional to the intensity of electric current, can lead to a decrease in the rate of electrolysis. Therefore, its elimination by an intensive agitation of the electrolytic bath – enforced circulation using centrifugal pumps, mechanically or by flow of air bubbles – is necessary.
- b) Chemical polarization – is a result of generation of gasses and chemical compounds on the electrodes. It increases consumption of electrical energy. Therefore it is necessary to reduce its influence by an addition of a depolarizer into the electrolyte. Depolarizers are substances reacting with the produced chemical combustion gasses and therefore prevent chemical polarization.

4.1.3 Faraday's laws

1. Faraday's law

- The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity transferred at that electrode.
- Quantity of electricity refers to electrical charge, typically measured in coulombs, and not to electrical current.

$$m = q \cdot I \cdot t$$

m - the mass of the substance altered at an electrode (g); I – current (A); t - time (s).

2. Faraday's law

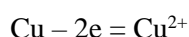
- For a given quantity of electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight.
- The equivalent weight of a substance is its molar mass divided by an integer that depends on the reaction undergone by the material.

$$m = \frac{M}{z \cdot F} \cdot I \cdot t$$

Q - the total electric charge passed through the substance; $F = 96\,485 \text{ C mol}^{-1}$ is the Faraday constant; M - the molar mass of the substance; z - the valence number of ions of the substance (electrons transferred per ion).

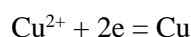
4.2 Refining electrolysis

A typical example of application of this type of electrolysis is refining of copper. The electrolyte is copper sulphate. The anode consists of a copper refined by fluxing, the cathode is a thin sheet of electrolytic copper. After connection of direct current, copper dissolves from the anode:

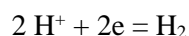


while the anode acquires the potential of approximately + 0.34 V and the cathode polarizes negatively.

Reduction of copper occurs on the cathode:



Neutral copper atoms produce crystals on the cathode. Discharge of hydrogen ions and generation of gaseous hydrogen.



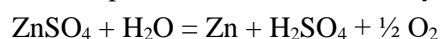
is not possible if the concentration of copper does not decrease to a negligible value, which does not occur in practice.

Depending on their electrochemical properties, admixtures in anode copper can be divided into four groups:

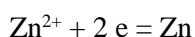
1. More electropositive – do not form ions, form sediments at the bottom of an electrolytic cell, e.g. Au, Ag, Pt.
2. More electronegative – convert to solutions, they get to the cathode by stripping of electrolyte, e.g. Zn, Ni, Fe etc.
3. Elements with a standard potential close to the standard potential of copper – content of these elements (especially As, Sb, Bi) has to be maximally decreased before electrolysis in order to prevent their separation on the cathode.
4. Electrochemically neutral admixtures – convert to anode sediments, e.g. Cu_2O , Cu_2S , Cu_2Se , Cu_2Te .

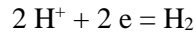
4.3 Electrolysis from aqueous solutions

Electrolysis from an aqueous solution is applied for example to separate Zn from a H_2SO_4 solution. The electrolyte has to be well refined from admixtures before the electrolysis, since Zn is more electronegative than other admixture elements. As electrodes, dissoluble lead anodes and aluminum cathodes are mostly used. The process can be described by the equation:

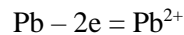
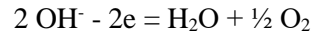


Zn is generated on the cathode and sulphuric acid is regenerated on the anode due to a generation of oxygen. Therefore, the following can separate on the cathode from a well refined solution:





Hydrogen should be generated primarily. The reactions occurring on the anode:



The first reaction is the main one, the second occurs only for new anodes and ceases quickly as a result of generation of PbO_2 on the surface of the anode. The quality of the anode increases with the addition of 1% Ag. If admixtures, such as Cu, Cd, Sb, Pb or Fe are present in the electrolyte, they generate on the cathode before zinc. Cobalt and nickel cause corrosion of the generated Zn and decrease current efficiency.

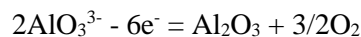
4.4 Molten-salt electrolysis

Production of some metals by electrolysis of aqueous solutions, such as aluminum (Fig. 4.3), is practically impossible due to their high electronegativities. Another reason is that these metals form stable oxides and it is impossible to keep them in the form of free ions in environments of aqueous electrolytes. In such cases, electrolysis of smelted salts is applied. Basic characteristics of the process:

1. losses of voltages on current supplies lead to higher effective voltage and electric energy consumptions
2. electrolytes are poly-component systems with high melting temperatures
3. if the melting temperature of a metal is lower than the melting temperature of the electrolyte, the metal separates in the form of crystals
4. if the melting temperature of a metal is higher than the melting temperature of the electrolyte, dissolution of the metal in the electrolyte in the form of smelt can occur, which leads to metal losses and a higher electric energy consumption
5. anode effect

Example: Production of Al, for which the electrolyte consists of $\text{Na}_3\text{AlF}_6 + \text{Al}_2\text{O}_3 + (\text{CaF}_2)$. The anode is formed from a graphite block, the cathode consists of a steel bath with graphite lining – the produced metal generates there.

Reaction on the anode:



Reaction on the cathode:

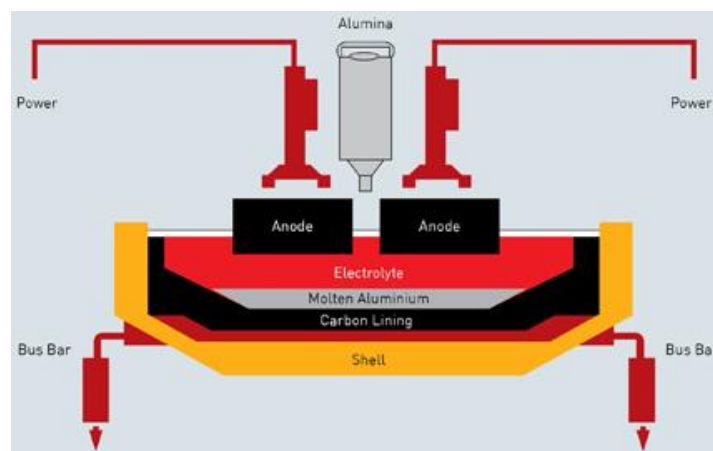
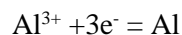


Fig. 4.3 Schematic depiction of electrolysis of aluminum [4].



Summary of terms

Electrolysis

Cathodic reduction

Anodic oxidation

Standard electrode potential

Polarization

Faradayovy zákony



Questions to the topic

1. What does 1. Faraday's law express?
2. Could you characterize the behaviour of more electropositive metals than Cu during electrolysis?
3. What are the basic characteristics of fused salt electrolysis?
4. What is the application of electrolysis from aqueous solutions?



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5. Refining processes



Study time: 2 hours



Objective

- Classification of refining methods
- Chemical refining processes
- Physical refining processes



Lecture

Raw metals, produced by pyrometallurgical or hydrometallurgical processes, contain many elements, which were separated together with a basic metal. Such admixtures and impurities usually negatively influence mechanical and physical properties of the basic metal (especially electrical conductivity decreases significantly), decrease its corrosion resistance and other. The process, by which the admixtures are separated from the basic metals, is called refining. During production of NFMs, such as Pb, Cu, Ni, Sb etc., precious metals (e.g. Ag, Au in Pb or Cu etc.) also separate with the basic metal. They can then effectively be separated during refining or from refining products. Pyrometallurgical metals refining is based on application of:

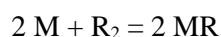
1. *chemical refining processes*
2. *physical refining processes*

Chemical refining processes enable to refine the basic metal from all impurities having higher affinities to oxygen, chlorine or sulphur (oxidation with a subsequent deoxidation, chlorination, sulphidation). Refinement therefore proceeds on the basis of different thermodynamic characteristics, e.g. Gibbs free energies of different admixtures, which are used to separation of various compounds from the basic metal via chemical reactions.

Physical refining processes are based either on usage of different pressures of vapors and partial pressures of gasses of admixtures and the basic metal (evaporation and condensation of the basic metal), or on their different mutual dissolubilities in liquid and solid states (segregation, coagulation smelting, directional crystallization, zonal melting etc.).

5.1 Chemical refining processes

During this refining, the metal is smelted with the presence of agents causing oxidation, sulphidation or chlorination (fluorination) of the basic metal with the aim to separate admixtures and impurities, which have higher affinities to oxygen, sulphur and chlorine (fluorine) than the basic metal. Air, air enriched with oxygen, pure oxygen or chlorine (fluorine) are used as the basic refining agents. These agents then react in the smelt with the basic metal Me, admixtures and impurities (M) according to the general reactions:



During refining, a small amount of the basic metal is separated as well. Therefore it is necessary to give refining slags rich in the basic metals back to the metallurgical technologies and to perform deoxidation (desulphidation) of the refined metal from the dissolved MeR products, since they cause e.g. brittleness of the metal. Refining by oxygen is applied e.g. during fluxing of Cu in hearth furnaces, when oxygen is blown by jets into the baths in oxidizing periods. Refining using

sulphur is applied e.g. to separate copper from lead. Refining by chlorine is applied to separate Zn from lead after the Parkess process, to separate As, Sb, Sn from lead by the Harris method and other.

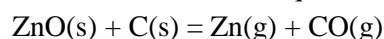
5.2 Physical refining processes

5.2.1. Refining processes based on different pressures of metal vapors and partial gas pressures

To these processes belong sublimation, distillation and possibly distillation using chemical transport reactions. Their principle lies in heating of a metal-containing raw material or a refined metal above the boiling temperature or above the temperature of evaporation of one or more components intended for separation. The components converted to a gaseous phase by heating are transferred into a separated area, in which they cool and condensate. The basic processes of the distillation and sublimation procedures are evaporation and condensation, which are applied e.g. to refine zinc, magnesium, calcium and other metals having high pressures of vapors.

1. Production of metals by distillation and sublimation

Distillation and sublimation are used to produce metals with low boiling or evaporation temperatures. These processes, occurring at high temperatures, can be effectively supplemented with other technological steps, such as roasting or smelting. In metallurgy, distillation is mostly used to produce Zn. By a reduction of zinc oxide by carbon and carbon monoxide in a retort, zinc in the form of vapors, which subsequently condense in condensers to liquid and powder zinc, is produced.



Sublimation as a method of metals production is mostly used to prepare molybdenum trioxide from a roasted molybdenum concentrate. It is based on a high volatility of MoO_3 , which sublimes at atmospheric pressure and temperatures of 400 – 450 °C.

2. Refining of metals by distillation

This refining method uses different boiling temperatures to mutual separation of metals. The pressure of metals vapors above the smelt (admixture and impurities in their raw forms form together a low-alloyed poly-component metal alloy) decreases proportionally with a decrease in their activities in the solution according to the equation:

$$p_{\text{Me}} = p_{\text{Meo}} \cdot a_{\text{Me}}$$

where p_{Me} – partial pressure of metal, p_{Meo} – partial pressure of compound, a_{Me} – activity of metal

Equilibrium in the system is given by temperature, pressure and composition. Therefore, components of the alloy can be separated either at a constant temperature by a change of pressure, or at a constant pressure by a change of temperature. This method is applied e.g. to refine zinc.

3. Vacuum metallurgy

The following types of vacuum are used in metallurgy:

- decreased pressure and rough vacuum, generated usually by vacuum pumps to $10 - 10^{-1}$ Pa
- high vacuum generated usually by diffusion pumps with silicone oil to $10^{-2} - 10^{-4}$ Pa
- ultra-high vacuum, generated by diffusion pumps to $10^{-5} - 10^{-11}$ Pa

The following types of metallurgical processes are performed in vacuum:

1. production of metals in vacuum
2. refining of metals in vacuum, including vacuum melting, alloying and casting of metals and alloys
3. degassing and dezoxidation of metals in vacuum.

Application of vacuum enables occurrence of such processes, which cannot be realized at

atmospheric pressure. It is also applied to produce or process metals, which need relatively high working temperatures. Application of vacuum decreases working temperature, which leads to a decrease in electric energy consumption.

Refinement of metals in vacuum is based on different boiling temperatures of the basic metal and its admixtures or impurities, from which it is to be separated. It is used not only to distill metals in their elemental states, but also using some easily evaporating decomposing compound. It comprises for example the following methods:

- a) **iodide method** – preparation of highly pure metals (e.g. Ti, Zr, Hf, V). The van Arkel process involves thermal fission of iodides on a glowing tungsten fiber in vacuum. An impure metal is converted to a volatile iodide, which decomposes at high temperatures. A highly pure metal is then generated directly from the gaseous phase, while iodine is returned back to the process to further iodides production.
- b) **sub-halides method** – production of highly pure aluminum (up to 99.999% Al) through its sub-chlorides. Aluminum and many of its trivalent compounds from monovalent or divalent compounds at higher temperatures. These compounds are stable in gaseous phase and with decreasing temperature decompose back to aluminum or its trivalent compound.
- c) **method of transport reactions** – in some cases, heating of the refined material in a stream of gas (e.g. H₂), with which the material can react, is used to separate admixtures by evaporation (preparation of highly pure metals). Hydrogen reduces many oxides, sulphides and halides. Reduced admixtures are evaporated and halides, sulphur and selenium are separated as HCl, H₂SO₄ etc.

4. Gases in metals, degasification and dezoxidation of metals in vacuum

The advantage of vacuum smelting lies in the possibility of elimination or significant reduction of the harmful influence of gases in metals and alloys. Hydrogen, nitrogen and oxygen form solid solutions with most metals. However, at higher concentrations they form hydrides, nitrides and oxides. These phases influence the physical-metallurgical properties of metals. Gasses can therefore be present in the smelt, possibly solid phase, dissolved or bound. Dissolving of gasses in metals is controlled by the *Sievert's law*, which says that the amount of gasses dissolved in a metal Q is proportional to their partial pressures in the gaseous phase p_g :

$$Q = C \cdot \sqrt[p_g]{p_g} \quad \% N_{\text{rozpušeno}} = C \cdot \sqrt[p_{N_2}]{p_{N_2}}$$

A decrease in the overall pressure of the gaseous phase leads to a decrease in the amount of gas dissolved in the metal.

5.2.2. Refining processes controlled by different mutual dissolubilities in solid and liquid phases

1. Refining by liquation

Refining by liquation can be performed by two methods:

- a) direct liquation
- b) indirect liquation

During direct liquation, the refined metal is smelted in a refining pot. The smelted alloy is continuously cooled down to a temperature slightly above the melting temperature of the component with the lowest melting temperature, while components with higher melting temperatures continuously crystallize according to an appropriate temperature dependence (liquidus-solidus) and convert to solid phases, which are continuously separated from the smelted metal. Due to the volume change during solidification and different densities of the generated solid phase crystals and the smelt, the crystals either float on the surface of the smelt as a lighter phase, or they can gravitationally liquate as a

heavier phase. During indirect liquation, the refined metal or alloy is in a solid phase (in a liquation furnace). During its continuous heating, components with lower melting temperatures than of the basic metal convert into the smelt, which continuously segregates and separates from the rest of the solid phase.

2. Refining using a third component – coagulative smelting

The basic metal can also contain perfectly dissoluble admixtures and impurities. These components can be separated by an addition of another metal into the smelt. This metal then forms with the admixtures either segregating crystalline skimmings, or coagulated chemical compounds with a significantly temperature limited dissolubility in the basic metal. This method is used e.g. during the Orford process of separation of copper and nickel mattes, which is based on melting of fine nickel matte containing Ni_3S_2 and Cu_2S with an addition of sodium sulphide (Na_2S) as the third component. This results in generation of two mutually non-miscible smelts, one of which is rich in nickel sulphides and the second in copper sulphides, which gravitationally segregate and separate on the basis of their different densities.

Refining methods using a third component also include refining, during which a certain third element (coagulant) is added to a smelted homogenous alloy of two metals. The coagulant and one component of the smelt then form a compound with a high melting temperature, which do not dissolve (or only limitedly) in the second smelt component. Examples of coagulation smelting are separation of noble metals Ag and Au using Zn (Parkes method) and segregation of Bi using Ca and Mg (Betterton-Kroll method) from lead smelts during refining processes.

The segregated compounds with the third components in the forms of refining skimmings are used as basic raw materials for production of metals, which were separated from the basic metal using the third compound.

3. Crystallization refining methods for production of high purity metals

The principle of these methods is based on different dissolubilities of admixtures in liquid and solid phases. The basic material parameter important for understanding of metals and alloys crystallization processes is the distribution coefficient. It depends on the conditions of crystallization and enables description of macro-distribution of admixtures and impurities on the phase boundary during zonal melting, directional crystallization and preparation of single crystals from melts. It is defined as an isothermal ($T_S = T_L = T$) ratio of concentration of an admixture element B in a solid phase x_{SB} (solidus) and in a liquid phase x_{LB} (liquidus):

$$k_o = \frac{x_{SB}}{x_{LB}}$$

Directional crystallization

The basis of this process lies in a slow movement of crystal-smelt phase boundary along a smelted ingot of a refined material of a length l_o and the original admixture concentration C_o (Fig. 5.1). On the solidifying boundary occurs redistribution of admixtures and impurities between the solid and liquid phases. Redistribution depends primarily on the k_{oB} admixture distribution coefficient, solidification rate on the crystallizing front and on the degree of agitation of the smelt, which together with an ideal diffusion equalizes concentration inhomogeneities within the smelt and transports the admixtures with $k_{oB} < 1$ from the crystallization boundary towards the smelt and admixtures with $k_{oB} > 1$ from the smelt towards the boundary.

The relation between the distribution coefficient, amount of solidified material and admixtures concentration for directional crystallization is stated by W.G. Pfann as:

$$C_1(x) = C_o k (1 - g)^{k-1}$$

where $C_1(x)$ – admixture concentration in the crystal, C_o – initial admixture concentration in the entire smelt volume, k – distribution coefficient of element B in the basic substance A, g – relative portion of the solidified ingot ($g = x/l_o$), x – distance from the beginning (end of the ingot).

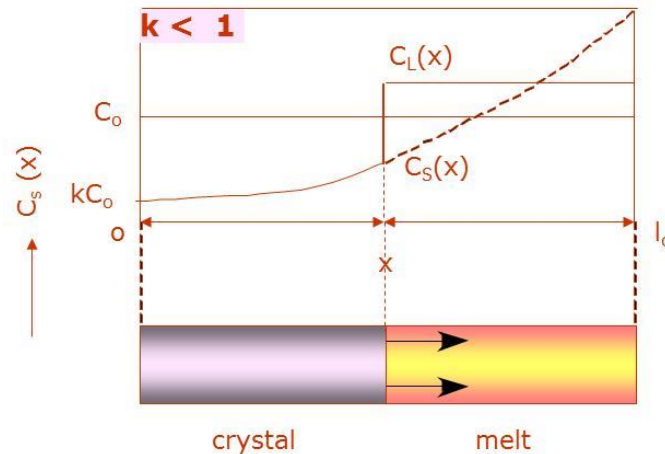


Fig. 5.1 Concentration relations during directional crystallization.

Zone refining

Zone refining/melting is a selective method of directional crystallization applied to refine materials to high purities. By periodical repeating of a refining crystallization process in a limited part of the smelted ingot – zone – controlled separation of admixtures and impurities within the refined material occurs (Fig. 5.2). The zone is generated using resistance, induction, laser, plasma, electron, arc or another heating method, while either a heating source moves along a static batch or a batch moves through a static heating zone.

During zonal melting, only a defined part of the ingot, a narrow zone of a thickness b , is melted within an ingot of a length l_0 . The melted zone with an admixture concentration in the melt C_L passing through the ingot has two boundaries between the melt and solid phases:

1. melting front – $(x+b)$, where the original solid phase with the concentration C_0 is smelted
2. solidifying front – the location (x) , in which the melted and by convection in melt homogenized material with the concentration C_L solidifies again, although with a new concentration $C_l(x)$.

Concentration profiles generated due to redistribution of admixtures on the solidifying boundary between the liquid – solid phases during passing of the melted zone through an ingot, can be described for the first passing of the zone using the Pfann equation.

$$C_1(x) = C_0 \left[1 - (1 - k) \exp\left(\frac{-kx}{b}\right) \right]$$

where C_0 – original concentration of a given admixture in the entire volume of the ingot, b – thickness of the zone, $C_1(x)$ – new admixture concentration in the solidified part of the ingot in the location x after one passing of the zone.

The refining effect of directional crystallization is higher than of one passing of a zone through a sample for an admixture with $k < 1$. Zonal melting is therefore an effective refining method only if performed as a repeated process. By such process, a so called final or limit distribution can be achieved, depending on the b , k and l_0 parameters.

After finishing of a n -multiple zonal melting process, the refined part of the ingot is sectioned and proceeded to subsequent processing. A higher effect can be achieved by a zonal refining with material removal, when the already refined material is removed continuously (e.g. after each passing of the zone) and the final small end part of the ingot (at $k < 1$) contains the highest amount of admixtures.

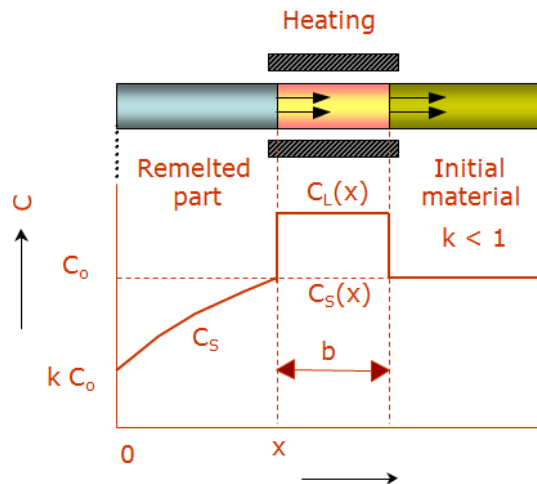


Fig. 5.2 Concentration relations during zonal melting.



Summary of terms

Destillation

Sublimation

Sievert's law

Liquation

Coagulative smelting

Distribution coefficient

Directional crystallization

Zone melting



Questions to the topic

1. What is the principle of coagulative smelting?
2. What does Sievert's law express?
3. How can metal be refined using chemical processes?
4. Which methods are used for the achievement of very high purity of metal? How can metal be refined using chemical processes?



References

- [1] Drápala, J. and Kuchař, L. *Metallurgy of Pure Metals*. Cambridge International Science Publishing Ltd., 2008.
- [2] ABEL, Lois A. *ASM handbook: nonferrous alloys and special-purpose materials*. Materials Park: ASM International, c1990, xv, 1328 s. ISBN 0-87170-378-5.

6. Production of selected non-ferrous metals



Study time: 3 hours



Objective

After careful study of this chapter you should be able to do the following:

- Define basic properties of selected metals: Copper, Lead, Zinc, Aluminium, Magnesium, Tungsten, Molybdenum, Silver, Gold;
- Describe basic preparing technologies of pure metals: Copper, Lead, Zinc, Aluminium, Magnesium, Tungsten, Molybdenum, Silver, Gold;
- Explain differences of metal preparing technologies;
- Describe basic classification of Cu, Ni, Al, and Mg alloys;
- Distinguish selected application of metals and their alloys considering their properties.



Lecture

6.1 Copper

Properties:

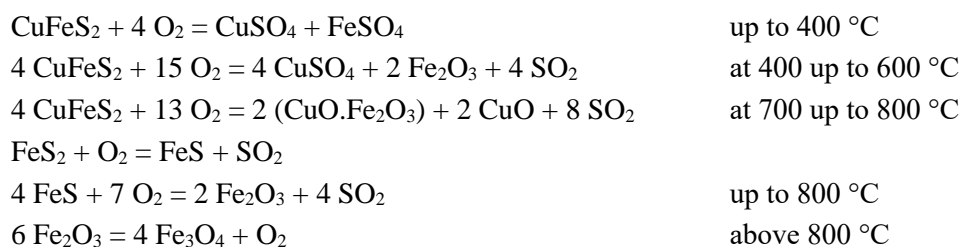
- $M = 63.57 \text{ g/mol}$; $\rho = 8.94 \text{ g/cm}^3$, $T_m = 1083 \text{ }^\circ\text{C}$; $T_v = 2300 \text{ }^\circ\text{C}$
- high electrical and thermal conductivity
- good corrosion resistance
- high formability ($A=50\%$)
- good weldability, soldering

Raw materials:

- sulphidic: Cu_2S – chalcocite
 CuFeS_2 – chalcopyrite
 CuS – kovelite
- oxidic: Cu_2O – cuprite
 $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ – malachite
- chlorides, arsenides, antimonides

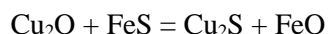
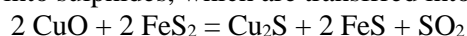
A. PYROMETALLURGICAL PROCESSES

1. Calcination

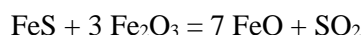
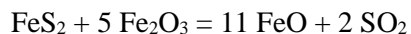


2. The melting of concentrates into matte

- a reaction between copper oxides and ferrite sulphides are transferred from copper oxides back into sulphides, which are transferred into matte, iron oxides are transferred into slag



- released FeO se váže na SiO_2 present in charges:



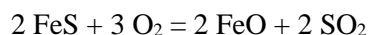
We distinguish them according to melting method into three types of melting in high furnaces:

- **pyrite** - it is used in processing coarse ores, containing at least 25 % pyrite and a certain amount of quartz, evenly laid-out in the iron ore. The heat source is the burning of pyrite into FeO and SO_2 . It achieves more than 80 % of desulphurization.
- **semi-pyrite** - it is used in processing coarse ores or briquette with an additive of 4 – 12 % of coke. It works up to one-hundred percent excess of air. It achieves 40 up to 80 % of desulphurization.
- **reduction** - it is used in the processing of agglomerates. The heat source is the burning of coke, why is added by 12 – 15 %. During its operation there is moderately low desulphurization (30 up to 40%).

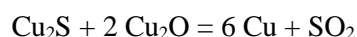
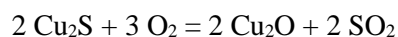
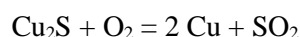
3. The Bessemer processing of copper matte

It is divided into two periods:

- I. At first, iron sulphide is oxidized into oxide, which is transferred into slag by adding silicon dioxide



- II. The oxidation of copper sulphate and there is a reaction between the oxide and left-over sulphide in the formation of metallic copper:



Converter copper is called raw or **blister copper**

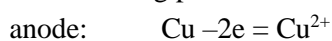
4. Refining copper

a) *softening refining*:

- removing elements with a higher affinity to oxygen than Cu – blowing air
- resultant deoxidation:
 - poling for density – removing SO_2
 - poling for malleability – the reduction of Cu oxides produced by dry distillation.

b) *electrorefining*: $U = 0,2-0,4 \text{ V}$, $A = 2,2 \text{ A.dm}^{-2}$, $\eta = 90 \%$.

- the production of Cu of a higher purity – hydroelectric Cu, for vacuum equipment
- removing precious metals and trace elements (Se, Te, ev.Bi)



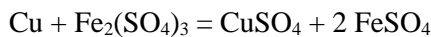
electrolyte: acidified solution CuSO_4 , $T = 50-60^\circ\text{C}$

mixture behaviour: E⁺ (Au, Ag, Pt, Se, Te, Bi) – they do not dissolve ⇒ sludge
 E⁻ (Zn, Fe, Ni, Co, Mn, As) – into electrolytes, or as indissolvable sulphates in sludges

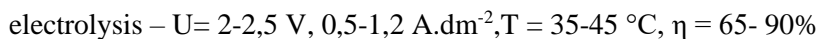
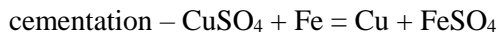
B. HYDROMETALLURGICAL PROCESSES

- processing in poor-grade iron ores (oxidic)
- the use of H₂SO₄, rozt. Fe salts, NH₄OH
- advantage, from most mixtures a few dissolvable sulphides are formed

Leaching:



Cu extraction:



Copper purities:

99,9-99,98 hm. % - impurities: Ag, As, Sb, Ni, Fe, Pb, Se, Te, O, S

- they are considerably reduced by electricity and thermal conductivity
- they increase hardness

deoxidation elements: Si, Zn, Sn, Al and P (however its additives can reduce in conductivity in left-over amounts) Li, Ca boride.

Pure copper

- metal with more than 99,3 % copper and it is not alloyed, copper is often casted with a controlled content of oxygen (for example. 0,04 %)

Use:

- electro-engineering industry- pressure gauge components, switches
- heat equipment – coolers, exchangers
- mechanical engineering – springs, bearing cases

Copper alloy classification:

- coppers and alloys with a high copper content
- brasses - Cu-Zn, Cu-Zn-Me alloys
- bronzes - Cu-Sn, Cu Pb, Cu-Al, Cu-Si, Cu-Sn-Pb alloys
- cupronickels, nickelins - Cu-Ni, Cu-Ni-Fe alloys

6.2 Nickel

Properties:

- M = 58.69 g/mol; ρ = 8.88 g/cm³; T_m = 1445 °C; T_v = 2730 °C
- mechanical strength at low and even at high temperatures

- good corrosion resistance
- stable in air, it oxidizes in heat
- alkalic solutions resistant, low acidic solutions resistance

Raw materials:

- $(\text{Ni, Fe})_9\text{S}_8$ – pentlandite
- NiS – capillary pyrite
- garnierite (Mg)
- NiAs – nickeline
- NiAs_2 – chloanthite

A. PYROMETALLURGICAL PROCESSES

block diagram: **oxidizing roasting** → **smelting** → **Ni processing** → **refining**

1. Oxidizing roasting

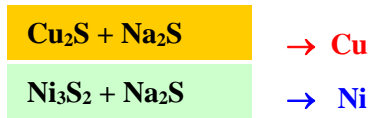
2. Concentrated melting into matte (Ni, Fe, Cu, S)

3. The preparation of light matte – the removal of Fe

- blowing air – $\text{Fe} \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ - slag
 $3\text{Fe}_3\text{O}_4 + \text{FeS} + 5\text{SiO}_2 = 5(2\text{FeO} \cdot \text{SiO}_2) + \text{SO}_2$

4. Ni-Cu separation

- Orford method – the formation of binary melting with Na_2SO_4 liquid mass

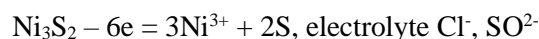


- flotation method – the use of separate crystallization Cu_2S , Ni_3S_2 and CuNi alloys with precious metals when slow cooling:

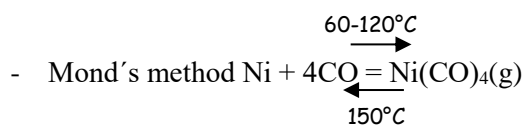
920°C Cu_2S
 700°C $\text{Ni}_3\text{S}_2 + \text{CuNi(S)}$ - a division of mag. separation
 575°C modification Ni_3S_2
 magnetic portion is floated at pH 11-13.

5. Processing Ni portions

- the casting of sulphide anodes – refining sulphides:



- roasting – $\text{NiO} \Rightarrow$ the reduction of H_2



- reduction in a liquid state by carbon with resultant refining.

6. Refining

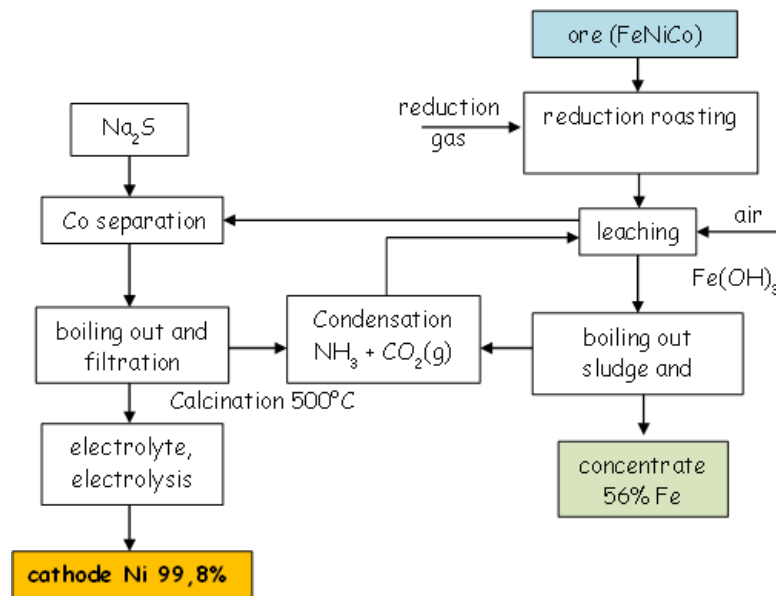
- electrolysis (NiSO_4 , Na_2SO_4 , HBO_2 , NaCl) \Rightarrow $A = 1,2-2,3 \text{ A.dm}^{-2}$; $U=2,3-2,5 \text{ V}$; $T= 60-70 \text{ }^\circ\text{C}$.

B. HYDROMETALLURGICAL PROCESSES

1. Pressure leaching

- equipment demands, high consumption of chemical agents, high production and quality, processing low-grade concentrates
- $v \text{ H}_2\text{SO}_4$: $T=230^\circ\text{C}$
- $v \text{ NH}_3$: $T= 80^\circ\text{C} + \text{oxidace O}_2$
- contraction using H_2S under pressure
- reduction of H_2

2. Ammonia-turbid leaching



Electrolysis: $A = 3-4 \text{ A.dm}^{-2}$; $U=4,5 \text{ V}$; $T= 90 \text{ }^\circ\text{C}$; Pb anodes; electrolyt: $\text{NiSO}_4 + \text{Na}_2\text{SO}_4$.

- reduction roasting – metallic Ni, Co, Fe_2O_3
- dissolving Ni, Co v rozt. $\text{NH}_3 + \text{CO}_2$ – dissolved salts

$$\text{Ni} + 1/2\text{O}_2 + (\text{NH}_4)_2\text{CO}_3 + 2\text{NH}_4\text{OH} = \text{Ni}(\text{NH}_3)_4\text{CO}_3 + 3\text{H}_2\text{O}$$

$$5\text{Ni}(\text{NH}_3)_4\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{NiCO}_3 \cdot 3\text{Ni}(\text{OH})_2 + 20\text{NH}_3 + 3\text{CO}_2$$

Use:

- parts of devices in alimentary industry
- the production of high-alloy alloys for the power industry and equipment working at high temperatures
- protective layers – galvanizing
- electro-equipment- resistances, thermal couples, accumulators, missile equipment

Alloys:

1. structural
 2. for special purposes
 3. high strength and creep resistant (superalloys)
- ad 1) *Monels* Ni(65) - Cu(30) + (Si, Mn, Fe, Al)
- corrosion resistant, good strength properties even at increased temperatures
 - pump components, turbine blades, the production of castings for heavy equipment and in an aggressive environments
- Ni - W, Ta, Th* - high corrosion resistance even at increased temperatures
- Fe-Ni* - heat resistant and corrosion resistant chromium-nickel steels (10-20%Ni)
- ad 2) *Alloys for thermocouples: Ni-Cr* - chromel (9-11%Cr), nickel chromium (20%Cr)
- Resistance alloys* :- Ni-20%Cr – chromium nickel, NiFeCr – nichrome, Ni-Cu – constantan, isotane, Ni-Fe – chromel,
- With magnetic properties:* Ni-Fe, Ni-Fe-(Co, Cu)- permalloy, magnetically soft; Ni alloyed steels; ALNICO – Fe +Al-Ni-Co – hard magnets
- With low thermal expansion:* Ni-Fe – invar, nilvar, kovar (Co)
- ad 3) *Superalloys* - precipitation strengthened by γ' -Ni₃(Ti,Al) and carbidic phases
- creep resistant
 - gas turbines, missiles, chemical industry, automobile industry.
- Hastelloy: Ni + 6%Fe, 16%Mo, 15%Cr, 4%W, 2%Co
- Udimet: Ni + 15%Cr, 17%Co, 5%Mo, (Ti, Al)
- RENÉ: Ni + 19%Cr, 11%Co, 10%Mo, (Ti, Al)
- NIMONIC: Ni + 15%Cr, 15%Co, 3,5%Mo, (Ti,Al)

6.3 Lead

Properties:

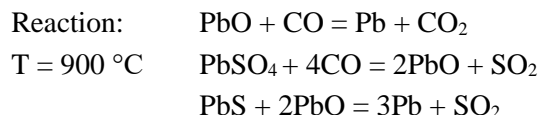
- M = 207.21g/mol; $\rho = 11.34 \text{ g/cm}^3$; T_m = 327 °C; T_v = 1740 °C
- alloys and compounds are toxic
- RTG radiation absorption
- low thermal and electric conductivity
- low hardness and strength, high ductility
- stable in an acidic environment (in non oxidant acids)

Raw materials:

- PbS – galenite
- PbCO₃ – cerussite
- PbSO₄ – anglesite
- they contain other metals (Cu, Zn, Sb, Fe, As, Bi, Sn, Au, Ag)
- floatation enriching
- processing secondary raw materials

Production:**1. Roasting and agglomeration****2. Melting in shaft furnaces – the reduction of Pb (90-96 %)**

- acquiring Pb + Ag, Au
- the production of low-grade sludges with a high Zn content
- separating Cu through matte formation

**3. Refining - pyrometallurgical procedures**▪ **decoppering:**

- a) rough – segregation, limited Cu dissolution in Pb used
- b) light – mixed with elementary sulphur or concentrates into melted Pb, and a high affinity of Cu to S used

T = 350 °C, Cu₂S floats out on the surface - Cu (0,002 %)

▪ **removing Sn, As, Sb** - affinity to oxygen used

- a) oxidation by air – the collection of litharge at various temperatures
- b) oxidation by sodium nitre NaNO₃ – Na₂O



- the formation of pure salts, separation on the basis of dissolvability in H₂O and NaOH

▪ **removal of precious metals**

Parkes process– the formation of intermediate compounds with Zn (↑T_m, ↓ρ) and limited dissolution of these alloys in Pb used

▪ **removal of Bi**

- a) up to 1% Bi Kroll's procedures - the formation of compounds Bi + KAZ (Ca, Mg) (↑T_m, ↓ρ)
- b) for ↑%Bi – electrolytically in diss. H₂SiF₆ + PbSiF₆

Use and alloys:

alloying element Pb – in different alloys ⇒ improvement of technological properties (brasses, automated steels, Pb- bronzes)

hard lead: Pb-6-7%Sb

- accumulator batteries, the chemical industry – resistance against H₂SO₄ – lead lined vans and equipment, underground cable coating

solders: Pb-Sn (Cd, Ag, Cu) - ↓T_m

Sn: 4 -90% according to purpose – radio equipment, the food industry

bearing metals: Pb-Sn-Sb (Cu, Ni)

- good strength in pressure, slide properties, good thermal conductivity, ↓T_m, uniformly placed components

Compounds:

- Pb₃O₄ – protective coated materials
- PbCO₃ – covering white

6.4 Zinc

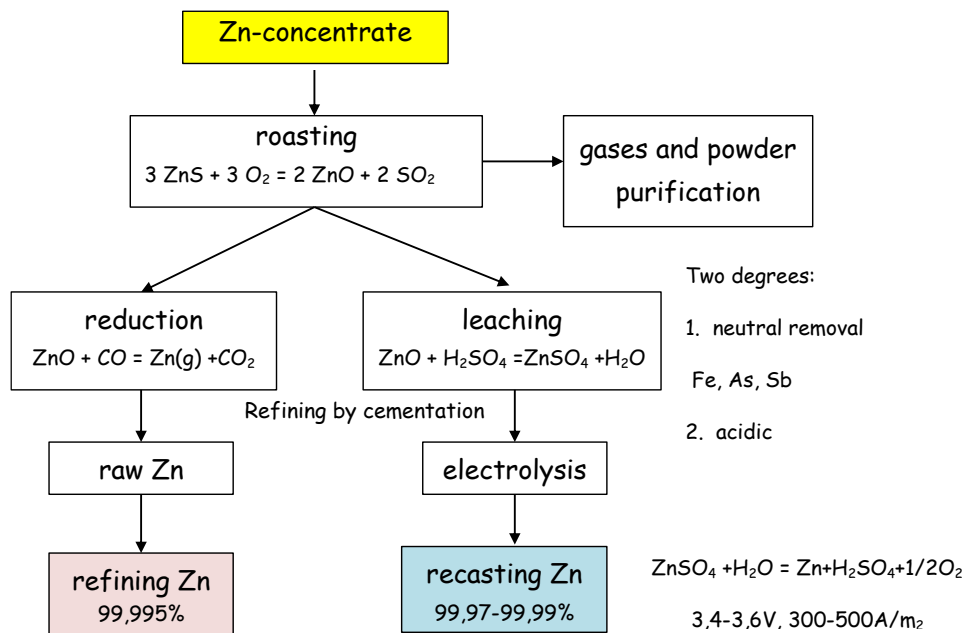
Properties:

- $M = 65.37 \text{ g/mol}$; $\rho = 7.13 \text{ g/cm}^3$; $T_m = 420 \text{ }^\circ\text{C}$; $T_v = 906 \text{ }^\circ\text{C}$
- good castability and hot formability
- occurrence of $\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ in air – protection against corrosion,
- moderately stable in water

Raw Materials:

- ZnS – sphalerite
- ZnCO_3 – smithsonite
- ZnO – zincite

Production:



„IPS“ Production

- hermetically closed high furnaces, preheated charge (agglomerate + cokes), preheated air,
- Zn vapours condense using Pb – the necessity of separation on the basis of falling dissolvability Zn in Pb with temperature
- distributing bath – draining of Zn layers – refining, Pb back into condensators

Refining:

- segregation of Pb and Fe – limited dissolvability used and various moderate masses
- distillation in fractional columns on the basis of T_v difference and vapour pressures in distillation temperatures
 - **Pb**: separation of Zn and Cd from Pb, Cu, Fe
 - **Cd**: separation of Cd from Zn

Use of alloys:

- galvanizing, sheets, strips
- production of brasses
- for foundry purposes – the production of thin-walled castings (Zn-Al(4%), Zn-Al(6%)-Cu(3%)

6.5 Aluminum**Physical properties:**

- $M = 26.98 \text{ g/mol}$; $\rho = 2.7 \text{ g/cm}^3$; $T_m = 660 \text{ }^\circ\text{C}$; $T_v = 2270 \text{ }^\circ\text{C}$.
- non-magnetic
- high thermal and electrical conductivity
- high corrosion resistance (increasing with purity of Al, formation of Al_2O_3 layer),
- low stability in strong alkalis
- low strength properties
- reduction properties

Raw materials:

- bauxites – $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (hydrargilit); $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (boehmit)
- non-bauxite – $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ nepheline

Production:

block diagram: **bauxite \rightarrow Al_2O_3 \rightarrow electrolysis \rightarrow refining \rightarrow Al**

Criterion for selecting the method of production

The quality of bauxite not only according to Al_2O_3 content, but also according to the silicon (bauxite) module:

$$\text{silicon module: } M = \frac{\text{wt.\% Al}_2\text{O}_3}{\text{wt.\% SiO}_2}$$

It is possible to classify bauxite according to its density into :

- a) **$M > 10$** \Rightarrow high-quality, suitable for Bayer's method, today the same as $M > 6-7$
- b) **$3 < M < 10$** \Rightarrow low-grade, which is used for the sintering method
- c) **$M < 3$** \Rightarrow unsuitable for the production of Al_2O_3

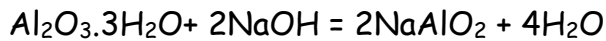
Production methods of Al_2O_3 : a) alkaline (alkaline leaching)

b) acidic (acidic leaching)

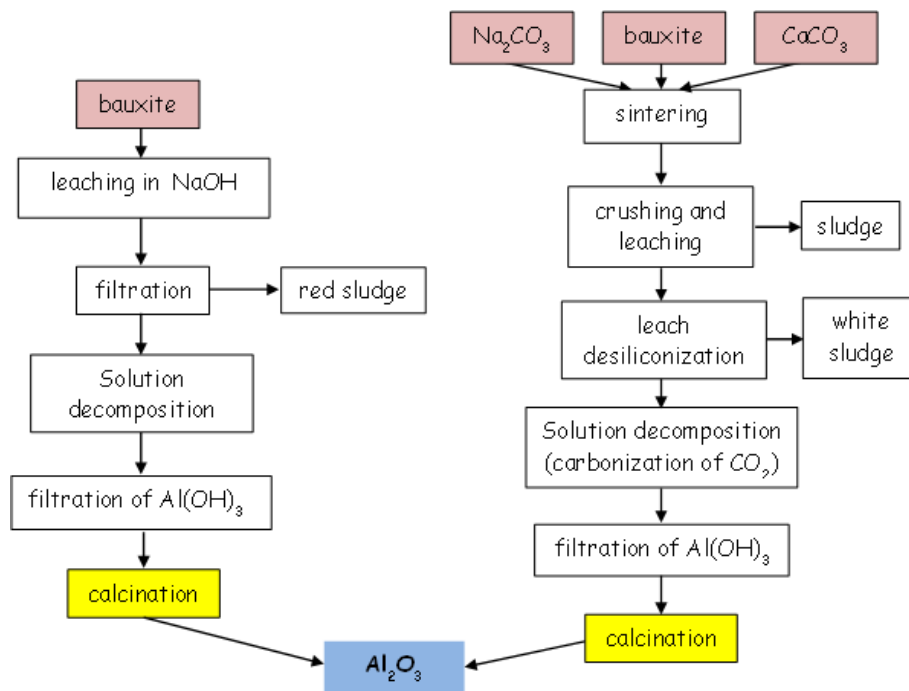
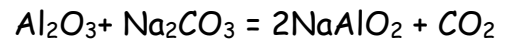
Alkaline production method \Rightarrow mostly used, possible to classify into 3 groups:

1. Bayer's method
2. Sintering method
3. Combined methods (Bayer's method + Sintering method)

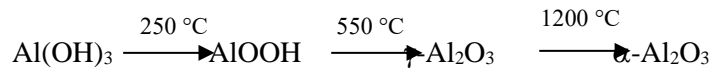
Bayer's method $M > 10$ (6-7)



Sintering method $3 < M < 10$



Calcination process:



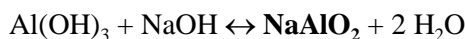
Bayer's method

➤ top-quality bauxite ⇒ 2-5% Al₂O₃.

Basis: pressure leaching by sodium hydroxide at 110-230 °C, pressure 0,1-3 MPa in autoclave, in the arisal of the aluminate solution of sodium and non-dissolvable remnants, which is consequentially filtered and hydrolyzed.



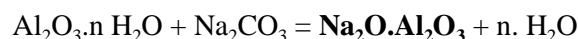
or also



Sintering method

➤ for processing bauxite with a higher content of SiO₂.

Basis: pulverized bauxite is sintered with sodium and calcium at 1150-1200 °C for sinter cake formation according to the equation:



- Al₂O₃ reacts well to sodium aluminate soluble in water
- it is further leached by water for formation of aluminate. solution and non-soluble remnants.

- iron oxide and silicon oxide are separated in sinter cake leaching by hot water in the form of non-soluble brown sludge.

Aluminate oxide electrolysis

Electrolytical production is usually carried out according to the chemical equation Fig. 6.1:

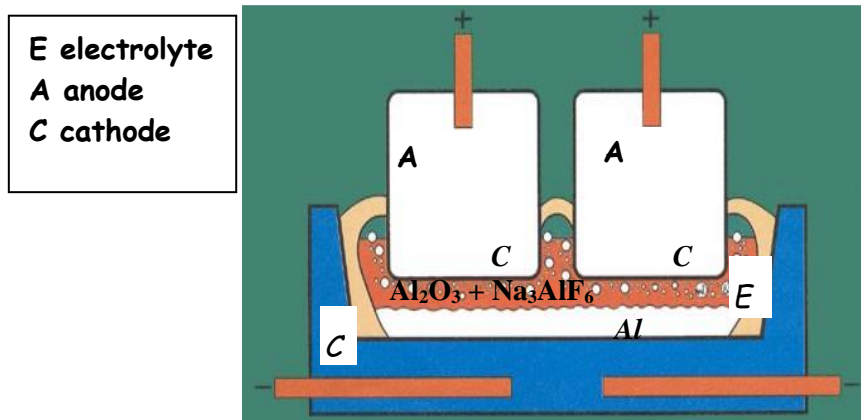
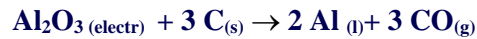
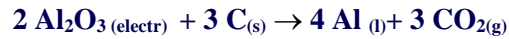


Fig. 6.1 Schema of aluminium production by electrolysis.

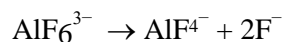
Electrolyte: cryolite Na_3AlF_6 , in which around 5% of Al_2O_3 is dissolved.

Additives:

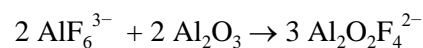
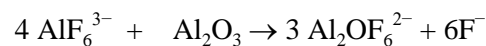
- they reduce the melting temperature of cryolite
- CaO , which reacts with cryolite into CaF_2 (content in Na_3AlF_6 -3-10%) Al_2O_3 , AlF_3 , (cryolite ratio NaF/AlF_3).

Molten cryolite dissociates: $\text{Na}_3\text{AlF}_6 \rightarrow 3\text{Na}^+ + \text{AlF}_6^{3-} \rightleftharpoons$ the degree of dissociation depends on the cryolite ratio.

Hexafluoroaluminate ions partially decompose in the melt:



Additive Al_2O_3 leads in the formation of oxyfluoride ions:



Properties of cryolite Na_3AlF_6

- does not chemically react carbon substance electrodes
- not very volatile
- with dissolvable Al_2O_3 sufficiently wettens the surface of the C anode
- does not contain more electropositive elements
- lower density than the Al melt
- sufficient electrical conductivity
- suitable viscosity

Anode:

non-dissolvable (C) – pre-baked or self-baked (Söderberg) anodes

**Cathode:**

a steel bath with C lining - it is leached with the metal of interest in it :

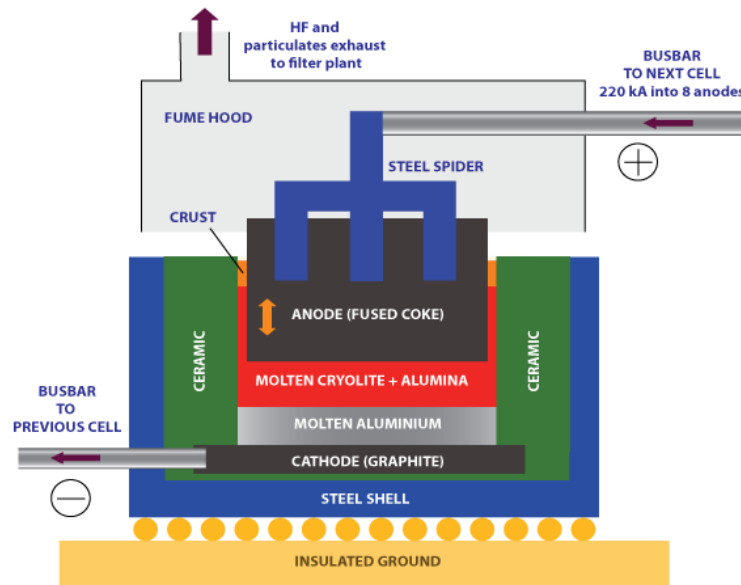


Fig. 6.2 Structural schema of a Hall-Héroult electrolyser with prebaked anodes [1].

Anode effect – a voltage drop between anode and electrolyte (a growth of voltage on the anode).

Negative effects:

- overheat resulting in energy loss
- melting of blast furnace wall lining
- low current efficiency
- harmful gas emission (CF_4 and C_2F_6)

Positive effects:

- a direct indication of a stage of low Al_2O_3 concentration
- purification of the anode surface, esp. from carbon foam in electrolyte

Refining aluminum:

- *Refining methods on an industrial scale:*
 - settling of Al melt
 - vacuum refining - H, Na
 - gas scrubbing – removal of H, metallic impurities (Ca, Na, Mg) or inclusions
 - by saline additives
 - filtration

- *Special refining methods:*
 - fractional crystalization (3N6-4N)
 - three layers electro-refining (4N - 4N8)
 - electrolysis in organic media (5N)
 - zone refining (5N - 6N)

Electrolytic refining: purity of 4N

- three layers electro-refining: anodic dissolution of Al from its alloy (Al-25%Cu) and reduction at the cathode
- T = 760-800°C

anode: Al25Cu (high $\rho = 3.2-3.5 \text{ g/cm}^3$ – on the bottom of the bath)

electrolyte: 60 % BaCl₂; 19-23 % AlF₃; 17 % NaF; 3-4 % NaCl, $\rho = 2.7 \text{ g/cm}^3$

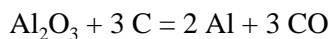
cathode: graphite- in Al melt; $\rho = 2.3 \text{ g/cm}^3$

E⁺: Fe, Si, Mn, Cu – they don't dissolve, they stay in the anode metal

E⁻: Mg, Ca, Na – they don't dissolve, they have higher leaching potential – in electrolysis.

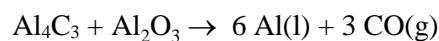
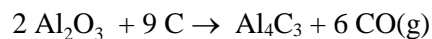
Carbothermic reduction

Carbothermic reduction process is based on the reaction:



Resulting in approximately 70 % Al and 30 % Al-Si alloy.

Carbothermic reduction produces at high temperatures of 2000°C – heat losses are high. Tendency of preferential formation of Al₄C₃ and gaseous product of CO is very high and if excess of Al₂O₃ is possible oxycarbides are formed:



Examples of Al production and use:

- sheets, profiles, bars, strips, pipes, wires, stampings
- dishes, drink cans, foils
- deoxidizers
- transformer coilings
- aluminum plating
- alloys (with elements of Si, Cu, Zn, Ti, Mg, Mn, Li,...)

Aluminum alloy classification:

- The main reason for alloying aluminum: strength increases, hardness and resistance against wear, creep, relaxation of tension and fatigue
- **aluminum alloys = multicomponent alloys → the difference and microstructural complexity of the alloys**
- it is possible to derive them from several basic binary or ternary alloys:
 - Al-Cu, Al-Mg, Al-Mn, Al-Si, Al-Zn;

Al-Cu-Mg, Al-Cu-Si, Al-Cu-Ni, Al-Cu-Zn, Al-Mg-Si, Al-Mg-Mn,
Al-Zn-Mg, ...

a) alloys determined for forming (wrought alloys):

- at a higher temperature - formed by a homogeneous solid solution (substitute solid solution α), which is more solid and harder than pure Al,
- at a lower temperature – lower solubility of alloying elements results in precipitation of another phase – a strengthening contribution

b) alloys determined for casting (cast alloys):

- higher content of alloying elements → eutectic microstructure
- with increasing amount of eutectics - increasing fluidity but decreasing formability;

c) alloys produced by powder metallurgy (SAP)

- the structure is created by Al or Al alloy and Al_2O_3 (6-22%), increased strength, high corrosion resistance, creep resistance (up to 500 °C)

d) composites

- the structure is formed of matrix (Al or Al alloy) and reinforcement (particles or fibres of Al_2O_3 , SiC etc)
- preparing method – powder metallurgy, die casting, ...
- properties - higher strength and creep resistance than Al and its alloys

6.6 Magnesium

Physical properties:

- $M = 24.31 \text{ g/mol}$; $\rho = 1.74 \text{ g/cm}^3$; $T_m = 650 \text{ °C}$; $T_v = 1090 \text{ °C}$
- reactive with oxygen - oxid layer on the surface,
- strong exothermic reaction with O_2 – flammable metal
- low mechanical properties
- good formability at higher temperatures
- damping properties - it absorbs elastic vibrations excellently

Raw materials:

- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ – bischofite
- MgCO_3 , CaCO_3 – dolomite
- MgCO_3 – magnesite
- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ – in sea water

Production:

block diagram: **magnesium ore → anhydrous MgCl_2 → electrolysis → refining → Mg**

preparing anhydrous MgCl_2 :

a) *from magnesite*



b) *from bischofite*

dehydration into $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

final dehydration in the HCl stream $T > T_m$ MgCl_2

Elektrolysis:

electrolyte: 10-12 % MgCl_2 , 75-78 % KCl, 6-8 % NaCl, 4.5% CaCl_2

cathode: steel

anode: graphite

Refining:

a) remelting with additives – protection from oxidation and the fluxing mixture (chlorides of alkaline metals and rare earths)

b) sublimation – based on vapour pressure differences of Mg and mixtures (in vacuum, at 600 °C)

purity: 99.92 –99.98 wt.% Mg , remain: Fe, Si, Ni, Na, Al, Cu

Silicothermic production:

▪ calcination: $\text{MgCO}_3 \cdot \text{CaCO}_3 = \text{MgO} \cdot \text{CaO} + \text{CO}_2$ – effect on yielding

▪ reduction: $2\text{MgO} \cdot \text{CaO} + \text{Si} = 2\text{CaO} \cdot \text{SiO}_2 + 2\text{Mg}(\text{g})$

using FeSi75 at 1150-1200°C in a vacuum, addition of CaF_2 , shaft resistance furnace

▪ condensation: 475-550°C

Alloys - alloy classification:

1. Cast alloys – high-pressure casting

Mg-Al (Elektron) - up to 10 % Al, up to 6 % Zn, up to 2,5 % Mn, up to 1 % Zr

Mg-Al-Zn-Mn (AZ)

Mg-Al-Mn (AM) application in sea water

Mg-Al-Si-Mn (AS) automobile and aviation industries

Properties: higher strength, low density, good corrosion resistance, high strength at higher temperatures, good castability, weldability, inconvenient with gas applications.

2. Wrought alloys

- difficult to cold forming – hcp structure with potential slip plane (0001)

- at higher temperatures - additional slip planes (1011), (1120)

- the lower the deformation rate the higher the level of plasticity

- forgings, bars, strips, tubes, sheets.

Mg-Mn \Rightarrow low strength, good plasticity and weldability

Mg-Al-Zn \Rightarrow high mechanical properties, resistant to stress corrosion cracking

Mg-Zn.Zr \Rightarrow high mechanical properties, resistant to stress corrosion cracking, higher cracking tendency during hot working, declined weldability

Mg-Al-Mn +Th – susceptible to stress corrosion cracking

The properties of magnesium alloys

▪ *Mechanical:* most Mg alloys has a specific tensile strength comparable to classic structural materials.

- *Hardness and wear resistance*: sufficient for all structural elements with the exception of big abrasion.
- *Fatigue strength*: higher for wrought than for cast alloys.

Use:

- aviation industry - transmission cases, gearboxes
- automobile industry – for example, the bracket panels of control columns, the consoles of brakes and clutch pedals, the frames of seat bottoms and arm rests, accumulator baths, etc.
- electrotechnics - anodes, dry batteries, stand-by batteries
- information and communication equipment – cases and chassis for audio-video equipment, PC, mobiles
- transporting and loading of goods- gravitation conveyors, bucket conveyors
- industrial machines (textile, printing) – functional at high speeds – light in order to reduce centrifugal forces
- working tools
- nuclear equipment – envelopes of nuclear fuel cell

6.7 Tungsten

Properties:

- $M = 183.85 \text{ g/mol}$; $\rho = 19.32 \text{ g/cm}^3$; $T_m = 3395 \text{ }^\circ\text{C}$; $T_v = 5930 \text{ }^\circ\text{C}$
- ductile in pure state
- chemical stability even in moist air
- unstable in the presence of oxidizing agents
- oxidation in air at $600 \text{ }^\circ\text{C} \rightarrow$ failure

Raw materials:

- $(\text{Fe, Mn})\text{WO}_4$ – wolframite
- CaWO_4 – scheelite

Production:

- concentrates - by floatation and magnetic concentration: from 2-3% W \rightarrow to 45-55% W
- roasting (removal of As, S),
- producing Na_2WO_4 – alkaline pressure digestion by leaching in NaOH
roasting with soda Na_2CO_3 (800-900 $^\circ\text{C}$):
$$(\text{Fe, Mn})\text{WO}_4 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{WO}_4 + (\text{Fe, Mn})\text{O}_2 + \text{CO}$$
- purification - leaching in H_2SO_4 (the removal of P)
- leaching in hot H_2O the removal of Fe, Mn
- the production of H_2WO_4 acid using boiling HCl:
$$\text{Na}_2\text{WO}_4 + \text{HCl} = \text{H}_2\text{WO}_4 + 2\text{NaCl}$$
 – yellow precipitates of H_2WO_4
- dissolution of H_2WO_4 in ammonia solution and refining by crystallization from ammonium paratungstate solution of high purity
- calcination \rightarrow formation of WO_3

- reduction of W powder \Rightarrow using C, H₂
 - 1st stage: $\text{WO}_3 + \text{H}_2 = \text{WO}_2 + \text{H}_2\text{O}$ (500-700 °C)
 - 2nd stage: $\text{WO}_2 + 2\text{H}_2 = \text{W} + 2\text{H}_2\text{O}$ (1000-1100 °C)
- following sintering in H₂ při 3200°C
- wolframite concentrates - can also be smelted directly with charcoal or coke in an electric arc furnace to produce ferrotungsten (FeW) - used as alloying material in steel production.
- pure scheelite concentrate- may also be added directly to molten steel.

Use:

- light bulb fibres, arc lamp electrodes, RTG lamps, electric contacts, electrodes of spark plugs, thermal couples for $T > 2000$ °C, heat resistance up to 2500 °C
- alloyed steels and other alloys
- alloyed carbides (tool plates) – widia, diadur

6.8 Molybdenum**Properties:**

- $M = 95.94$ g/mol; $\rho = 10.22$ g/cm³; $T_m = 2622$ °C; $T_v = 4800$ °C
- ductile, it can be rolled and soldered
- chemical stability in air, alkaline or acidic solutions at room temperature
- unstable in the presence of oxidizing agents
- oxidation in air at 600 °C \rightarrow failure

Raw materials:

- MoS₂ – molybdenite
- PbMoO₄ - wulfenite
- appearance together with Sn, W, As, Cu, Bi
- very low-grade raw ores

Production:

- concentrates - by floatation
- roasting 650-700 °C \rightarrow MoO₃:
 - $\text{MoS}_2 + 7 \text{O}_2 = 2 \text{MoO}_3 + 4 \text{SO}_2$
- refining MoO₃ \rightarrow sublimation at 1000 °C
- leaching in ammonia solution NH₄OH followed by hydrolysis and calcination
- reduction of H₂:
 - 1st stage: $2\text{MoO}_3 + \text{H}_2 = \text{Mo}_2\text{O}_5 + \text{H}_2\text{O}$
 - 2nd stage: $\text{Mo}_2\text{O}_5 + \text{H}_2 = 2\text{MoO}_2 + \text{H}_2\text{O}$ (400 - 450 °C)
 - 3^d stage: $\text{MoO}_2 + \text{H}_2 = \text{Mo} + 2\text{H}_2\text{O}$ (1100 °C)

Electrolysis:

electrolytes: tetraboritanes, chlorides, fluorides + MoO₃ \rightarrow Mo powder

Mo powder is pressed and sintered at 2200 – 2400 °C

Use:

- alloyed heat-resistant steels and alloys
- electrotechnics – hinges and winding core of light bulbs, components related with sealing into glasses and quartzes in vacuum technics, electron screens
- meshes and wires corrosion resistant grids in the chemical industry

6.9 Titanium

Properties:

- $M = 47.9 \text{ g/mol}$; $\rho = 4.51 \text{ g/cm}^3$; $T_m = 1670 \text{ }^\circ\text{C}$; $T_v = 3285 \text{ }^\circ\text{C}$
- chemical stability in air even at high temperatures (oxide layer - TiO_2)
- reactivity at high temperatures with O_2 , H_2 , N_2 , $\text{C} \rightarrow$ hydrides, nitrides, oxides, carbides \rightarrow brittleness
- with S and halogens – volatile compounds
- resistant against sea water and some acids, soluble in HCl, HF, aqua regia
- usually: good corrosion resistance, good strength, good high-temperature resistance, relatively low density (comparing steels)

Raw materials:

- FeTiO_3 – ilmenite
- TiO_2 – rutile
- CaTiO_3 – perovskite
- $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ – titanite

Production:

High reactivity of titanium with oxygen at high temperatures restrains its direct reduction from TiO_2 oxide. Titanium metal is produced using Kroll method - thermic reduction of TiCl_4 by means of Mg. Final form of titanium is porous material called “Ti sponge”. Method is described in Fig. 6.3 and in following flow chart:

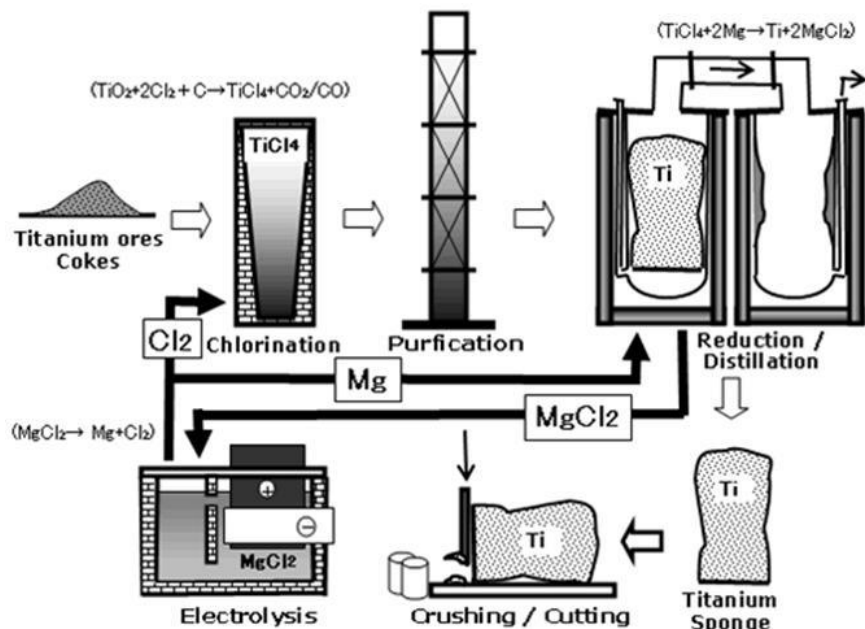
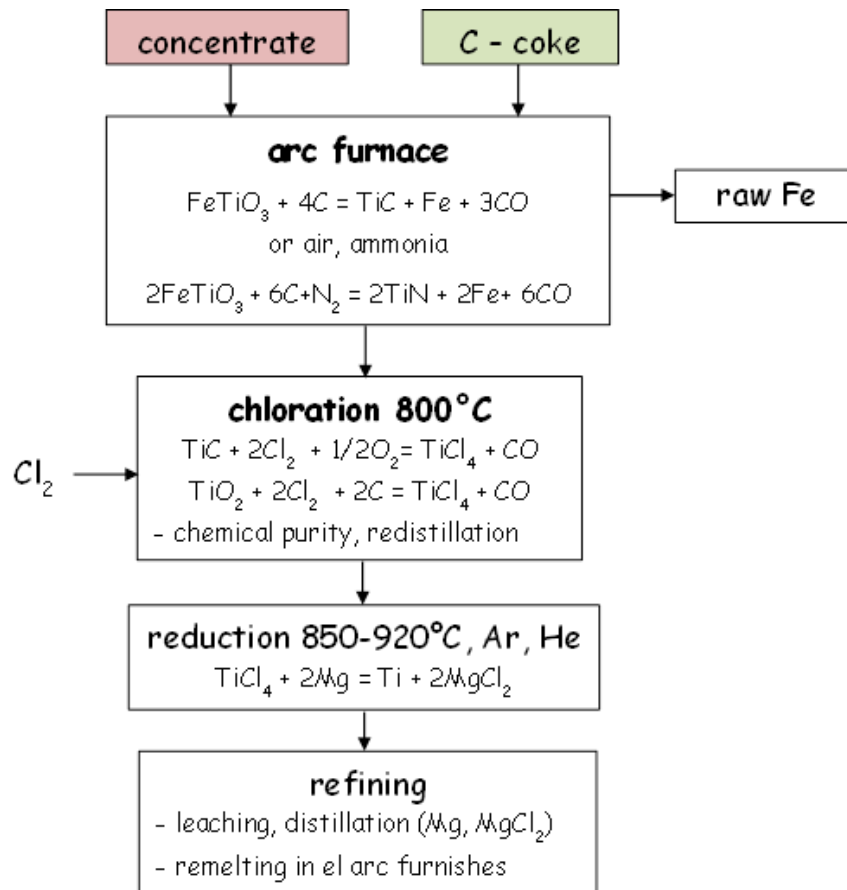


Fig. 6.3 Structural schema of Kroll process [2].



Titanium sponge is remelted and cast to titanium ingots or titanium alloys.

Use:

- alloying element in alloys based on Ni, Al, Fe and other metals
- alloys on the base of α , β and $(\alpha + \beta)$ phases with wide areas of applications:
 - a) structure of chemical equipment - pumps, fittings, tanks, exchangers;
 - b) aircraft industry – turbine blades, compressors : alloys of Ti-Al (Sn, Zr, Mo), Ti-V10(Fe, Al), TiAl6V4 (the most important alloys with $(\alpha + \beta)$ microstructure);
 - c) biocompatible materials - stents, joint replacements, micro-plates, arche wires, surgical tools: TiAl6V4, Ti, Ti-Al, TiNi, etc.;

shape-memory alloys - NiTi, TiNb - as biocompatible materials, thermostatic components, thermostatic batteries, actuators, vibration damping materials, fasteners, etc.
- compounds: TiO_2 – titanium white, TiC – hard metal

6.10 Gold

Properties:

- $M = 196.97\text{g/mol}$; $\rho = 19.28\text{g/cm}^3$; $T_m = 1063\text{ }^\circ\text{C}$; $T_v = 2530\text{ }^\circ\text{C}$
- soft, ductile, formable
- good castability

- chemically and corrosion resistant
- purity: ‰,carat = 1000/24‰

Raw materials:

- raw metal, polymetallic telurides and selenides, quartz veins
- sulphide ores of Cu, Pb, Zn or Sb – Au is produced as by-product from processing heavy metals

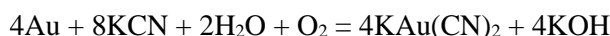
Production:

Amalgamation:

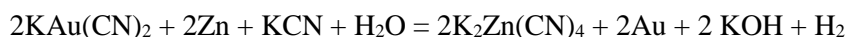
- dissolution of Au in Hg - the formation of amalgams
- filtrations and distillation → crude Au metal –60-85% (Ag, Cu)
- refining using salts (Na₂CO₃, NaNO₃, borax Na₂B₄O₇·10H₂O)

Cyanizing:

- leaching in cyanide solutions in air

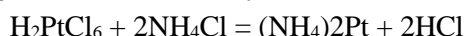


- elution, filtration
- precipitation using Zn



Affination:

- removing mixtures and isolating noble metals
- quartation (Ag:Au =3:1) → dissolving in HNO₃
- chlorination – Cl₂ → removing chlorides
- **electrolysis** - two stages (1st →Ag, Au in sludges → melting 2nd → Au)
 - solution of AuCl₃ + HCl, at 55-65 °C, 1.5V, 13 A/dm³
 - regeneration of electrolyte - Pt



Other procedures use sorption on active coals, methods of ion exchanges and extraction – leaching in HCl + Cl₂ and followed by extraction in amine solution.

Use and alloys:

- jewellery
- glass-making, porcelain decoration
- laboratory instrument components
- jet nozzles for the production of artificial silk
- Ag-Au-Cu nibs
- orthodoxy: Pt-Au
- mechanical and galvanic coating
- electrotechnics – contacts
- alloys with Pd, Ag, Cu, Ni, Pt – a change of colours.

6.11 Silver

Properties:

- $M = 107.87 \text{ g/mol}$; $\rho = 10.49 \text{ g/cm}^3$; $T_m = 960 \text{ }^\circ\text{C}$; $T_v = 2212 \text{ }^\circ\text{C}$
- high thermal and electrical conductivity
- good formability
- relatively stable even in weak oxidizing agents and salt solutions, diluted H_2SO_4
- dissolution in concentrated strong oxidizing acids - HNO_3 and hot H_2SO_4



→ in the presence of oxygen it dissolves in solutions of alkaline cyanides and forms cyanide-silver ion $[\text{Ag}(\text{CN})_2]^-$

- in dry and pure air silver is indefinitely stable,
- very low amounts of hydrogen sulphide H_2S are sufficient for silver to begin to blacken (the formation of black Ag_2S layers on the surface)

Raw materials:

- native metal, compounds AgCl , Ag_2S , complex ores of As and Sb
- sulphide ores (Cu, Pb, Zn, Sn) - raw materials from the production of these metals –using Patinson and Parkes processes

Pyrometallurgical production:

1. Parkes process:

- in the production of Pb, based on the formation of intermetallic compounds of Ag, Au and Zn – high temperature of melting and low density → non-dissolvable
 - adding Zn at $500 \text{ }^\circ\text{C}$, cooling at $350 \text{ }^\circ\text{C}$ → first foam - *without* Ag
 - adding other Zn → second foam *with* the main portion of Ag
 - removing Pb – by segregation at 600°C
 - by pressing + Zn distillation
 - cupellation – oxidation of Pb ($1000 - 1100 \text{ }^\circ\text{C}$)
 - refining by deoxidation and reduction with charcoal

2. Electrolytically from Cu raw materials, waste treatment

Hydrometallurgical production:

1. Amalgamation:
 - dissolution of Ag in Hg -the formation of amalgams,
 - firstly decomposition from AgCl (Fe, Cu) to Ag – otherwise loses of HgCl
 - filtration and distillation
4. Cyanizing:
 - leaching in the cyanide solution in air

$$4\text{Ag} + 8\text{KCN} + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{KAg}(\text{CN})_2 + 4\text{KOH}$$

$$\text{AgCl} + 2\text{KCN} = \text{KAg}(\text{CN})_2 + \text{KCl}$$
 → the safety of forming HCN - preventing the additive CaO
 - elution, filtration

- precipitation using Zn $2KAg(CN)_2 + Zn = 2K_2Zn(CN)_4 + 2Ag$

Refining:

- isolating noble metals
electrolysis – solution of $AgNO_3 + HNO_3$, at $T = 55-65\text{ }^\circ\text{C}$, 3V, 2-5A/dm³

Use and alloys:

- electrotechnics – contact materials Ag-Cu-Cd, W, Mo, Ag-Ni
- silver solders Ag-Zn-Cu(Cd), Ag-Sn-Cu
- photographic industry, galvanic metallization, table utensils and consumption products (Ag-Cu)
- orthodonty – silver amalgams (Ag-Sn-Hg)
- jewellery

**Summary of terms**

Pyrometallurgical production of copper, Hydrometallurgical production of copper, Pyrometallurgical production of nickel, Zinc production, Aluminate oxide electrolysis, Carbothermic processing of aluminium, Silicothermic processing of magnesium, Kroll method, Parkes' method, Amalgamation, Cyanizing

**Questions to the topic**

1. Which are the main reactions of matte smelting during copper production?
2. How many stadia does the bessmer process of copper matte include?
3. What are the methods of Ni-Cu separation?
4. Describe the refining process of lead.
5. What is the application of magnesium alloy?
6. What is the principle of Kroll method?
7. Which technologies are used for the gold and silver production?

**References**

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