

## General questions in metallurgical processes

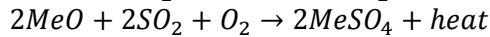
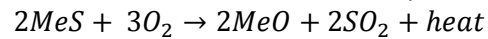
1. *Metal occurs mostly in two types of ores: oxide and sulphide ores. To extract metals from these two type of ores, different processes are applied. Please state briefly typical processing routes for both types of ores.*

**Oxide:** for example iron oxide: first sintering of the iron oxide before reduction in a blast furnace. The reduction takes place in multiple steps during different reactions. Eventually pig iron is created and this is further processed in a BOF to remove impurities and add other additives for a better steel alloy. It's then casted and can be sold.

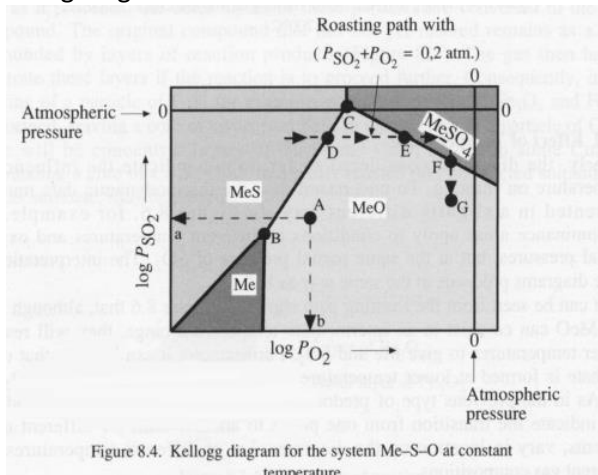
**Sulfides:** for example ZnS: The ore has to be roasted first to oxidize the Sulphide to an oxide. Than the Zink oxide is leached with Sulphate to get an ZnSO<sub>4</sub> solution. During the leaching some impurities are removed. Than the solution is going through some purification processes to remove more impurities, like adding Zn dust to remove more noble metals. When the solution is purified, it goes to the electrolysis plant. A current is put on the solution and cathodic zink is created. This goes to the melting and casting plant before it can be sold.

2. *What are the purposes and main reactions of roasting sulphide concentrates? What products you could expect from the sulphide roasting? Please explain how to the use of the Kellogg diagram in sulphide roasting process(see separate figures for reference.*

The purpose of roasting in this case is the oxidation of metal sulphides. The main reactions are:



Kellogg diagram:



At constant T, the lines between 2 compounds are calculated based on equilibrium constant and the partial pressure of O<sub>2</sub>, and/or SO<sub>2</sub>

For line BC: MeS – MeO (reaction 1):

$$K_1 = \frac{(P_{\text{SO}_2})^2}{(P_{\text{O}_2})^3}$$

$$\log p_{\text{SO}_2} = \frac{1}{2}(\log K_1 + 3\log P_{\text{O}_2})$$

3. *What is the Ellingham Diagram(see separate figure for reference)? How it is used in the evaluation of metallurgical processes, please give one example.*

**Kellogg Diagram:** Stability Diagram

It gives an indication about which phases can exist, at given Temperature, and partial pressure of O<sub>2</sub> and SO<sub>2</sub> (This is needed for the thermodynamics part of Sulphide roasting, a feed preparation operation)

Ellingham Diagram: Is an Oxide system

Ellingham diagram is in the metallurgical operation, important for the Pyrometallurgical extraction systems.

4. *Please describe briefly the essential pyrometallurgical and hydrometallurgical unit operations.*

- **Pyrometallurgical process**  
Chemical reaction at HT  
Iron and Steel, lead and tin, copper (85%), titanium, majority nickel.

- **Hydrometallurgical process**  
Chemical reactions in aqueous solutions normally below 100°C (Except pressure hydrometallurgy)  
Zinc (80%), Copper (15%), Partly cobalt and nickel.
- **Electrometallurgical process**

5 *Cost for metals production and metals price are affected by many factors. Please describe these factors and explain how these factors could affect the production cost and market price.*

- **Properties of the metals** (strength, toughness, corrosion resistance and thermal conductivity, etc.)  
Depends on the purity or the value of specific properties. (e.g. the electrical conductivity of copper)
- **Formability**  
The effect of this factor is the cast or wrought which it is marketed
- **Surface appearance**
- **The cost to the costumer** (major Factor)  
The selling price of metals varies over a very wide range from gold and the precious metals at one extreme to iron at the other

6 *What are typical feed preparation operations? What types of chemical reactions are involved?*

Typical Feed preparations operations are:

- **Drying**  
 $Me_x[complex]_y \cdot zH_2O \xrightarrow{heat} Me_x[complex]_y + zH_2O$  (for chemical bounded water)  
Or just heat to evaporate water from the ore that is not chemically bounded
- **Calcination**  
removing of CO<sub>2</sub> or removing of hydroxide-group  
 $CaCO_3 \xrightarrow{Heat(1000^\circ C)} CaO + CO_2$   
 $CaCO_3 \cdot MgCO_3 \xrightarrow{heat(1200^\circ C)} CaO \cdot MgO + 2CO_2$   
 $2Al(OH)_3 \xrightarrow{heat(1100^\circ C)} Al_2O_3 + 3H_2O$
- **Roasting**
  - Oxidatising:  $2MeS + 3O_2 \rightarrow 2MeO + 2SO_2 + heat$
  - Sulphatising:  $2MeO + 2SO_2 + O_2 \rightarrow 2MeSO_4 + heat$
  - Chlorising (CaCl<sub>2</sub> used):  
 $MeS + CaCl_2 + \frac{3}{2}O_2 \rightarrow MeCl_{2(g)} + CaO + SO_2$   
 $MeO + CaCl_2 \rightarrow MeCl_{2(g)} + CaO$   
 $MeS + Cl_{2(g)} + O_2 \rightarrow MeCl_{2(g)} + SO_2$   
(Cl<sub>2</sub> gas used):  
 $MeO + Cl_{2(g)} \rightarrow MeCl_{2(g)} + \frac{1}{2}O_2$
- **Sintering:** partial melting and re-solidification of ores to create better porosity and strength.

7 *What metallurgical processes are normally used to extract metals from oxide ores and sulphide ores?*

Oxide ores: pyrometallurgical route (reductive smelting)

Sulphide ores: pyrometallurgical, hydrometallurgical route or a combination of those two

8 *What are electrowinning and electro-refining, and where they are used in metallurgical industry?*

Electrowinning from aqueous solutions:

- Part of hydrometallurgical operation/plant
- $ZnSO_4 + H_2O = Zn + \frac{1}{2} O_2 (g) + H_2SO_4$  (under DC current)

Electro-refining:

- Operating in aqueous solutions, but as part of pyrometallurgical processes.
- $Cu_{(impure\ anode)} = Cu_{(pure\ cathode)}$  (Under DC current)

Electrowinning and Electro-refining are used in Electrometallurgy.

9 What types of leaching processes are available, according to chemical reactions? What types of ore or minerals are suitable for those leaching processes.

Types of leaching processes:

- Acid dissolution:  $ZnO_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_2O$ 
  - Suitable: Metal oxides (or sulphides under pressure.)
- Alkali dissolution:  $ZnO_{(s)} + 2(OH^-)_{(aq)} \rightarrow ZnO_2^{2-}_{(aq)} + H_2O$ 
  - Suitable: Metal oxides forming complex anions soluble in water. ( $Al_2O_3$ ,  $ZnO$ )
- Anion exchange:  $CaWO_4_{(s)} + CO_3^{2-}_{(aq)} \rightarrow CaCO_3_{(s)} + WO_4^{2-}_{(aq)}$
- Complexation (used to increase solubility):  $CuO_{(s)} + 2(NH_4^+)_{(aq)} \rightarrow Cu(NH_3)_2^{2+}_{(aq)} + H_2O$
- Redox reactions:  $ZnS_{(s)} + 2(Fe^{3+})_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2(Fe^{2+})_{(aq)} + S_{(s)}$
- Bacteria Leaching:
  - Suitable: Metal sulphides.

10 Please write down the different components of the cell voltage and their relative importance in electrowinning of metals.

Theoretical decomposition voltage: the potential that is needed to get a certain reaction going in theory.  
Overpotential: the potential that is in practice needed to get a reaction going. This can be more than the theoretical decomposition voltage. The energy is mostly lost in heat but can also be lost by the evolution of gas at the anode or the cathode. This reduces the current area and thus more energy is needed.

## Hydrometallurgical

Leaching algemeen: het oplossen van een vaste feed t.b.v. purificatie of concentratie verhoging.

1. Leaching is one of the most important unit operations in hydrometallurgical processes. Please describe what types of leaching processes can be identified? What are their main characteristics and chemical reactions?

- **Dissolution of salt in water**  
 $[CuSO_4]_{solid} = (Cu^{2+})_{aq} + (SO_4^{2-})_{aq}$   
 Beperkt door oplosbaarheid.  
 Niet altijd mogelijk, bijvoorbeeld bij de winning van aluminium, waar water tijdens de electrowinning eerder reageert dan het aluminium.  
 Bijvoorbeeld: sulphates and chlorides.
- **Acid solution**  
 $[ZnO]_{solid} + 2(H^+)_{aq} = (Zn^{2+})_{aq} + H_2O$   
 Bijvoorbeeld: metal oxides, eventueel sulphides under pressure.
- **Alkali solution** (basisch)  
 $[ZnO]_{solid} + 2(OH^-)_{aq} = (ZnO_2^{2-})_{aq} + H_2O$   
 Bayer process: metal oxides forming complex anions soluble in water.
- **Anion exchange**  
 $[CaWO_4]_{solid} + (CO_3^{2-})_{aq} = [CaCO_3]_{solid} + (WO_4^{2-})_{aq}$
- **Complexation**  
 $2[Au]_{solid} + 4(CN^-)_{aq} + H_2O + 0.5(O_2)_{gas} = 2(Au(CN)_2^-)_{aq} + 2(OH)^-$   
 Let op, vorming  $OH^-$ . De het basisch worden van het oplosmiddel kan de reactie beperken, eventueel met zuur te compenseren.  
 $[CuO]_{solid} + 2(NH_4^+)_{aq} = (Cu(NH_3)_2^{2+})_{aq} + H_2O$
- **Redox reactions**  
 $[ZnS]_{solid} + 2(Fe^{3+})_{aq} = (Zn^{2+})_{aq} + 2(Fe^{2+})_{aq} + [S]_{solid}$   
 Eventueel geforceerd (met elektrische stroom/spanning).
- **Bioleaching** (bacterial leaching)  
 $MS + Fe_2(SO_4)_3 = 2FeSO_4 + MSO_4 + S$   
 Bijvoorbeeld: metal sulphides.

Dit kan in een reactor, maar ook *heap leaching* (*in situ leaching*) van ertsbergen bij de mijn is mogelijk. Een dergelijke berg erts kan tot 25 jaar nodig hebben!

2. *Where precipitation processes are used in hydrometallurgical processes? What are their basic principles and main chemical reactions?*

**Precipitation** = solid phase formation from an aqueous solution.

**Where is it used?** : For solution purification, metal concentration (upgrading) and recovery of metals (e.g. H<sub>2</sub> reduction, cementation)

**basic principles:**

\* Lowering the solubility (physical process) :  $Me^{(n+)} + n(OH^-) \rightarrow Me(OH)_n$

Methods to induce super-saturation

\* Chemical Reactions (precipitation of metals):

- cementation :  $Cu^{(2+)} + Fe(s) \rightarrow Cu(s) + Fe^{(2+)}$

- Precipitation with gas:  $Ni^{(2+)} + H_2(g) = Ni(s) + 2H^+$  (1)

$H^+ + NH_3(g) = NH_4^+$

-Electrowinning:  $Zn^{2+} + 2e^- = Zn(s)$  (cathode)  $H_2O - 2e^- = 2H^+ + 0.5O_2$ (anode)

3. *What are the functions of leaching operation in hydrometallurgical processes?*

Selectieve oplossing van het gewenste metaal, waarna scheiding van de ongewenste (vaste) fase kan plaatsvinden.

4. *How the leaching solutions (containing target metal ions and impurities) are purified in hydrometallurgical processes?*

- **Precipitation & crystalisation**

Scheiding van de vloeistof, via filtratie of centrifuges.

- **Supersaturation**

Oplosbaarheid wordt overschreden, waardoor een (fijne) neerslag ontstaat.

Kan opgewekt worden door: afkoeling, verhitting, verdamping, door toevoeging van een ander zout (ion-activiteit) of de toevoeging van een reactant.

- **Nucleation**

Binding rond seed-kristal.

- **Addition of a chemical reagent** (Eh-pH)

Bijvoorbeeld: metal hydroxides & metal sulphides.

- **Addition of a second solute** (*salting out*)

Door toevoeging van andere ionen (waardoor oplosbaarheid daalt).

- **Solution in a second aqueous phase** (solution extraction)

5. *How the targeted metals are precipitated as metal products in hydrometallurgical processes?*

Bijna zelfde antwoord als bij vraag 2:

Chemical Reactions (precipitation of metals):

- cementation :  $Cu^{(2+)} + Fe(s) \rightarrow Cu(s) + Fe^{(2+)}$

- Precipitation with gas:  $Ni^{(2+)} + H_2(g) = Ni(s) + 2H^+$  (1)

$H^+ + NH_3(g) = NH_4^+$

-Electrowinning:  $Zn^{2+} + 2e^- = Zn(s)$  (cathode)  $H_2O - 2e^- = 2H^+ + 0.5O_2$ (anode)

process parameters: Equipment and control: tanks, batch or continuous, temperature, acidity (pH), agitation etc.

6. *Please describe the unit operation for hydrometallurgical extraction of zinc metal from its sulphide concentrates (if it involves a non-hydrometallurgical operation, please describe it also). Please write down the main chemical reactions, major raw materials and products/by-products.*

Typische 'leach' oplossingen bevatten in g/L:

Zn 130-150

Cu 0.2-0.4

Cd 0.5-0.7

Co 0.01-0.04

Ni 2-7 mg/L

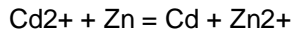
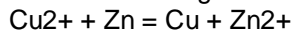
As 0.2-0.4 mg/L

Sb 0.3-0.4 mg/L

## Verwijdering van Cu, Ni, Cd en Co

### stap 1 verwijdering van Cu en Cd (dmv cementatie)

Zink stof toevoegen met temperatuur 50 - 60 graden celsius



### stap 2 verwijdering van Co en Ni (dmv precipitatie)

toevoeging  $\text{CuSO}_4$  hierdoor oxidatie  $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$

toevoeging  $\text{C}_2\text{H}_5\text{OCSSK}$  bij 38 - 45 graden celsius

Nu heb je een bijna pure vorm van zink As en Sb te verwaarlozen.

## Electrometallurgy

1. *What are electro-winning and electro-refining operations? Please use copper to explain the electrowinning and electro-refining processes in sulphate solution systems.*

Reaction offers the possibility that a metal will be converted from an ionic species to elemental metal if the ionic species is present in a conducting liquid or can be rendered into that condition

Electro winning : When the electrolyte is a aqueous solution

Electro refining: extensively for the refining of metals produced by pyrometallurgical means.

2. *Please use zinc to explain the electrowinning.*

Cathode (Al):  $\text{Zn}^{2+} + 2e = \text{Zn}$ , in competition with  $\text{H}_2$  evolution

Anode (Pb, Pb-Ag):  $\text{H}_2\text{O} - 2e = 0.5 \text{O}_2 + 2\text{H}^+$

Total reaction:  $\text{ZnSO}_4 + \text{H}_2\text{O} = \text{Zn} + \text{H}_2\text{SO}_4 + 0.5\text{O}_2$

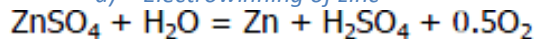
3. *What is molten salt electrolysis, and where it is used for metals extraction? What are the differences compared to electrowinning of metals in aqueous solutions.*

Non-aqueous electrolyte: molten salt (halides)

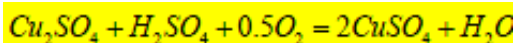
Molten salt electrolysis: Al, Mg, Ca, K, Na, REEs

4. *Please write down the electrochemical reactions of:*

a) *Electrowinning of zinc*

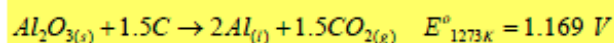
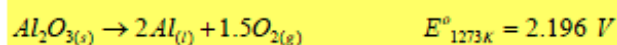


b) *Electrorefining of copper*



c) *Molten salt electrolysis of aluminium*

Overall reaction



5. *What are the principles of electrolysis? What types of electrolytic processes are available for metals extraction and refining? Please give ONE example for each of the electrolytic process in extractive metallurgy.*

Principles: There must be transfer possible of electrons between two reacting species. So that the reactions occurs spontaneously. At the cathode a reduction process takes place called cathodic reaction and at the anode an oxidation process called anodic reaction. The two electrodes must be electrical connected through an external circuit.

Type of processes:

1. Electro-winning (Zn) 2. Electro-refining (Cu) 3. Molten salt refining (Al)

6. *Electrical power is the most important cost factor for electrolysis process. What physical law and operating parameters are determining the power consumption of the electrolysis for metals extraction or refining?*

$P = IV / \eta = V / \eta q$  (kWh/kg),  $q$  = theoretical amount of produced metal,  $I$  = cell current,  $V$  = voltage,  $n$  = Tafel's

law =  $a + b \cdot \log(i)$

7. How current efficiency and energy efficiency are linked together in the electrowinning or electrorefining of metals? What are your ideas to increase current efficiency and reduce the energy consumption for electrowinning of metals.

Current efficiency is the percentage of the current that results in the deposition of the targeted metal. And the energy efficiency is coming from the half reactions of the interface. The Energy is more positive than the reaction more anodic and the metal will dissolve.

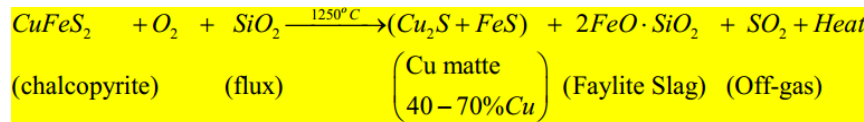
## Copper smelting and refining / copper making

1. Copper occurs in majority as sulphide ores. Please describe the main extraction and refining steps and their functions of copper-making: from concentrates to refined copper as final metal product.

**(Step 0) Copper ore  $\text{CuFeS}_2$  has a grade of 20-30%.**

### Step 1: Matte smelting, grade goes to 40-65%

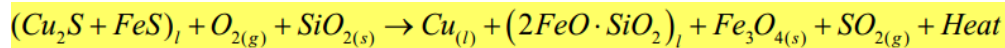
Partial removal of S



Products:  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  and matte: Cu, Fe

Waste: Off gass  $\text{SO}_2$  and slag  $\text{FeOSiO}_2$

### Step 2: Matte converting, grade 98.5-99%

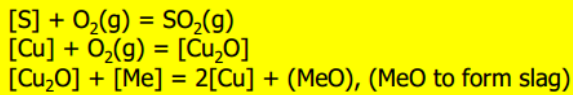


Products: Blister copper

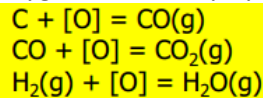
Waster:  $\text{SiO}_2$ , slag and  $\text{Fe}_3\text{O}_4$

### Step 3: Fire-refining, grade 99-99,5%

Oxidation of S



Oxygen removal by hydrogen

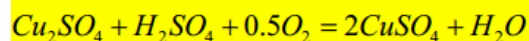
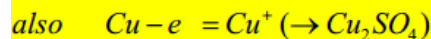
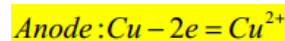


Products: Cu

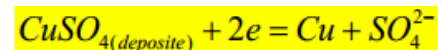
Waste: MeO,  $\text{SO}_2$

### Step 4: Electro-refining, grade to 99,99%

Half reactions



Total reaction



Products: Cu

Waste: As, Sb (impurities) and  $\text{SiO}_7$

2. Copper matte converting is carried out at about  $1200^\circ\text{C}$ . Please use Gibbs free energy functions below to indicate clearly:

a) The oxidation order of the 2 sulphide compounds of  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  in the matte(which is first)

$T=1200^\circ\text{C} \Rightarrow 25^\circ\text{C}=298^\circ\text{K}$  dus  $1200^\circ\text{C}=1473^\circ\text{K}$

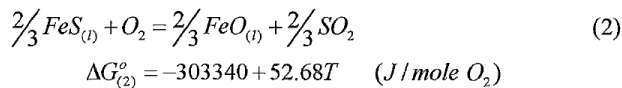
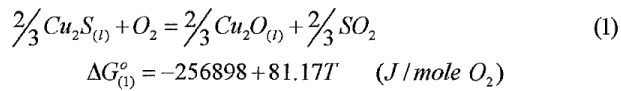
T invullen bij  $dG_1$  en  $dG_2$ :

$dG_1 = -256898 + 81,17 \cdot 1473 = -137334,59 \text{ J/mol}$

$$dG_2 = -303340 + 52,68 \cdot 1473 = -225742.36 \text{ J/mol}$$

$dG_2 > dG_1$  dus reactie 2 is eerder geneigd om te verlopen dan reactie 1.

b) *Cu<sub>2</sub>O initially formed is unstable if there is substantial amount of FeS in the matte. The Gibbs free energy of the following 2 oxidation reactions as function of temperature is given below:*



**Niet beantwoord, mist deel vd vraag?**

## Refining

1. *What types of impurities can be identified in metals during their extraction processes?*

### Impurities in metals

- Non-metallic elements: S, O, C, N, H (gas dissolution to metals)
- Metallic impurities: reduced from ores (good or bad)
- Trace metals: Ag, Au, PGM – can also be of economical value ! (e.g. Cu-, Ni- ores)
- Non-metallic inclusions: slag entrainment or reactions
- Impurities brought by scrap recycling

*Harmful to properties (mechanical, electrical)*

- S and P in steel reduce ductility and toughness!

*Good for properties – Alloying elements*

- Adding “impurities” to gain special properties
- Steel: Fe-based alloys
- Stainless steel: Cr, Mo, V, Nb, Ni etc.
- Alloys of non-ferrous metals: e.g. brass and bronze

2. *What are typical refining operations(including their principles) before the metals could be sold to the end-users?*

### Types of refining processes

*Metal-to-slag*

- **Fire refining:** selective oxidation of metal impurities (forming slag)
- **Electro-slag refining:** for special steel refining, metal droplets through refining slag (CaF<sub>2</sub> based, low melting, less viscous)

*Metal-to-metal*

- **Liquid – liquid separation:** decreasing solubility of A in B upon cooling (separation of Zn and Pb: Zn condensation by Pb splashing)
- **Liquation:** impurity solidifying upon cooling, separation from purer liquid metal (removal of Fe from Sn)
- **Zone refining:** melting and re-solidification extra purity (Si, Ge for electronics industry), repeating operation

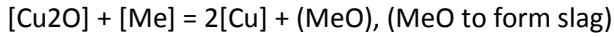
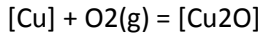
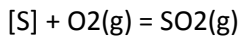
*Metal-to-gas*

- **Vacuum refining:** reducing partial pressure of product gas  
Steel converting: e.g. [C]<sub>metal</sub> + [O]<sub>metal</sub> = CO<sub>gas</sub>
- **Inert gas purging:** removal gas product (e.g. CO) by diluting the partial pressure with inert gas (Ar or N<sub>2</sub>).

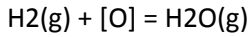
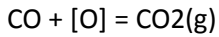
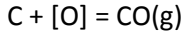
3. Please explain how blister copper is refined? What are the steps and main chemical reactions in the operation?

“Blister” copper cannot be cast to anode properly for electro-refining:  $[S] + 2[O] = SO_2(g)$  bubble!

- Fire-refining needed: 2 stages
- Oxidation of S, together with other impurities (e.g. Fe, Ni) using O<sub>2</sub>



- Removal of oxygen: reduction with e.g. carbon, hydrogen, and hydrocarbons



- Temperature control: 1130 – 1150oC (both stages)

4. What are the objectives of steelmaking? What are the main differences between BOF and EAF steelmaking processes?

**Objectives:** Removing C and other impurities by oxidation (blowing O<sub>2</sub>) → converting

**BOF:**

- Mostly used steelmaking process
- Batch process, 20 – 40 minutes cycle
- 50 – 350 ton capacity
- Temperature: ~1600oC
- No fuel is needed! (Can melt max 90% charge scrap)
- Slag formation: FeO-SiO<sub>2</sub>-CaO based.
- Partly recycled to BF
- Partly used as constituents in cement kilns, and construction industry
- 4 steps: Scrap charging, hot metal charging, O<sub>2</sub> blowing, tapping

**EAF:**

- Raw Materials
- Steel scrap, DRI, cold pig iron
- Energy resource (20-50 MV.A)
- Electrical power
- Both AC arcs and DC arcs
- Capacity: 80-150 ton
- Share: >30% total steel

The biggest difference is that BOF uses 90% scrap and 10% hot pig iron, which is already hot from the Blast Furnace. EAF uses 100% scrap, DRI, or cold pig iron and heats this up to the needed temperature. For that it needs an electrical power system to generate heat.

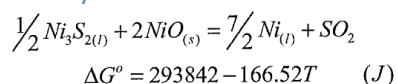
This means that EAF only is used for recycled or cooled down material, BOF is used as a system directly after the Blast Furnace system to directly refine the pig iron further.

## Sulphide smelting

1. Sulphide smelting of nickel is similar to sulphide smelting of copper. However, during nickel converting in practice, only high grade nickel matte(Ni<sub>3</sub>S<sub>2</sub>) is produced instead of metallic nickel. Metallic nickel is produced in the end through electrolysis of nickel sulphide.

*Please use the thermodynamic data below and proper thermodynamic calculations to explain why it is neither appropriate nor advisable to convert nickel matte directly to metallic nickel in a conventional P-S converter? (please think about minimum operating temperature for the reaction).*

Note that the melting point of nickel, nickel oxide and nickel sulphide are: 1455°C, 1955°C and 789°C, respectively.



According to the thermodynamic data and the formula:



$$\Delta G^0 = \Delta H - T\Delta S$$

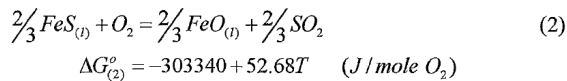
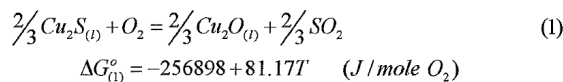
a reaction occurs if the Gibbs energy is negative. This occurs at:

$$0 = 293842 - 166,52T$$

$$T = 2037 \text{ }^\circ\text{C}$$

This would mean that the operating temperature for the reaction should exceed 2037 °C in order to smelt all the material. This is very inefficient and therefore uneconomic. Furthermore, the smelting container should be made of materials capable of these temperatures which would only add up to the costs. It is more advisable to melt the nickel sulphide and then use electrolysis as this would only require temperatures of 789 °C.

2. *During copper converting, the FeS in the copper matte is firstly removed in the slag-making stage. After that copper is converted from the white metal(almost pure Cu<sub>2</sub>S) into metallic copper by blowing air or oxygen into the converter. Please use the following thermodynamic data to calculate the equilibrium partial pressure of oxygen for conversion of pure Cu<sub>2</sub>S to pure Cu at 1300°C, if pSO<sub>2</sub>= 0,1 atm.*



First we calculate the Gibbs energies:

$$\Delta G_{(1)}^0 = -256898 + 81,17 \cdot 1300 = -362419 \text{ J/mol O}_2$$

$$\Delta G_{(2)}^0 = -303340 + 52,68 \cdot 1300 = -371824 \text{ J/mol O}_2$$

$$\Delta G_{tot}^0 = \Delta G_{(2)}^0 - \Delta G_{(1)}^0 = -1627 \text{ J/mol O}_2$$

This translates to:

$$k = e^{-\frac{\Delta G_{tot}^0}{RT}} = 1,13$$

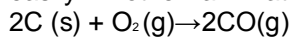
Because the partial pressure  $k = \frac{p\text{SO}_2}{p\text{O}_2}$  this yields:

$$p\text{O}_2 = 0,09 \text{ atm}$$

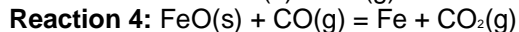
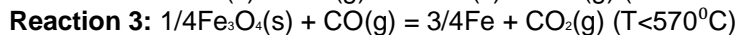
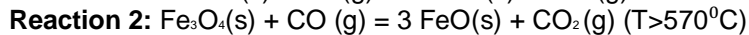
## Ironmaking and steelmaking

1. *Please describe how metallic iron(hot metal) is produced in Blast Furnace Process. Please also state: the raw materials, main chemical changes of feed along the movement in the furnace, various zones in the blast furnace and different products of smelting operation. What are the roles of metallurgical coke in ironmaking blast furnace process?*

Metallic iron is produced in a blast furnace, due to reduction of iron ore. The ore is charges into the blast furnace in the form of pellets and sinter. Pellets are little balls with a diameter of 10-25 mm and sinter has a diameter of 5-50 mm. They have a high permeability, so the CO gas can move through the furnace easily. Another raw material is coke, it provides the carbon for the CO gas.



The CO gas reduces the iron ore in four steps:



These four reactions take place in the stack of the furnace. In the heart, the temperature is high enough to melt the iron and the liquid iron can be tapped from the bottom of the furnace. All the impurities that were present in the iron ore form a slag. This consist of SiO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub>. It has a lower density than metallic iron, so it floats on top of it. This means it can be tapped from the furnace and separated from the iron.

2. *What are the main impurities in steelmaking process(brought by both hot metal and steel scrap)? How are they removed from the steel melt, and what are the main chemical reactions of these impurities removal? What are the benefits to use steel scrap, and what kind of consequences you could expect if you use only hot metal as the main feed(no use of scrap) in BOF converter process?*

Main impurities are (non-metallic elements) : S, O, C, N, H (gas dissolution to metals). Metallic impurities (reduced from ores). Trace Metals (Ag, Au) e.g. Cu-, Ni, ores. Non-metallic inclusions (from reactions with the slag).

Sometimes the metal gains special properties because of these impurities (stainless steel, brass, bronze etc.)

The impurities can be removed in 3 (metal-to-slag, metal-to-metal and metal-to-gas) refining. ways. main chemical reactions are  $2[Me] + O_2 = 2[MeO]$  and  $[MeO] + [Me'] = (Me'O) + [Me]$  (where Me is bulk metal). If you don't use scrap you won't get any special properties. Another benefit of using steel scrap is that it's cheaper.

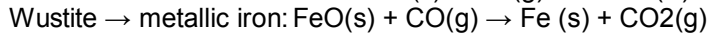
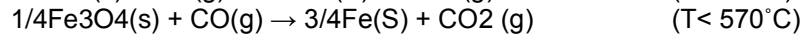
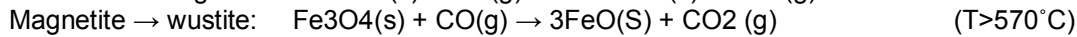
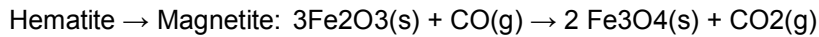
3. *What are the important steelmaking processes? What are the main objectives of these steelmaking processes? Please describe the main refining reactions during steelmaking.*

The blast furnace process, which is divided into two main processes: Oxygen Steelmaking and EAF Steelmaking.

Oxygen steelmaking is also known as Blast Oxygen Furnace (BOF); it uses 70-75% liquid iron and 25-30% scrap; it covers 60% of the steelmaking in the world.

EAF stands for Electric Arc Furnace. It uses 100% scrap and some are with DRI. DRI is the direct reduced iron. This production is increasing. The EAF steelmaking covers now 40% of the world iron production.

The main reactions:



4. *Please describe the raw materials used in blast furnace ironmaking process and how they are prepared before feeding to the blast furnace. What are the roles of metallurgical coke in ironmaking blast furnace process?*

There are three raw materials used in a blast furnace, iron ore, coke and limestone.

Coke: Coal is pulverized and is put in a slot type oven. This oven is heated to a temperature of 900 - 1100°C. The coal gets plasticized and gasses are released. In the end, all the gasses are released and the coke consists only out of carbon. The coke is cooled down and transported to the blast furnace.

Pellets: The iron ore is first pulverized to a fine powder with a diameter of 0,01 to 0,1 mm. This is mixed with water and binders, such as clay and limestone. This powder mixture is then transformed into little balls in a big rotating drum. These pellets are then baked in a rotary kiln to get the perfect porosity for the blast furnace.

Sinter: In a sintering process, ore is transformed into very porous pieces with a diameter of 5 to 50 mm. The ore is first broken to a grain size of 6 mm. This powder is mixed with a fuel, like coke. This coke is then burned and it releases a lot of heat. Due to this heat, the ore melts to form a big porous mass. This mass is cooled down and broken in pieces with the right diameter.

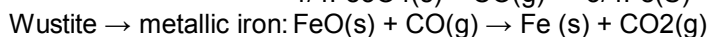
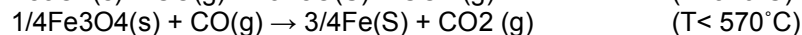
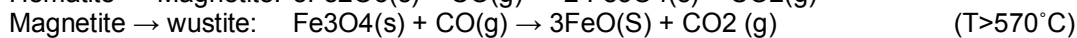
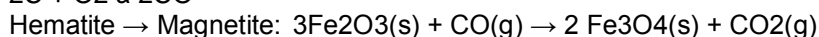
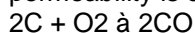
Limestone is added to remove the silica from the iron ore and doesn't need a preparation.

5. *What are the various zones of the blast furnace, and the main physical – chemical changes in these zones?*

The main chemical reactions are  $\text{MeO} + \text{C} \rightarrow \text{Me} + \text{CO}(\text{g})$ . This is reduction. By now, of course, we all know the four reactions belonging to iron making. the various zones are the start of the softening front (of the ore+reductant), the end of the cohesive zone (where mixture becomes fully liquid), the granular zone (before softening front).

6. *What are the functions of metallurgical coke in ironmaking blast furnace process? Please describe all possible reactions involved coke from top to the bottom of the furnace? Are all coke and pulverized coal fed into the blast furnace consumed in the blast furnace? If not, where the rest of them in the form of carbon go?*

Coke is used to optimize the reaction to metallic iron. Because of the size of the cokes a layered structure of coke and ferrous burden is created. Because of this structure permeability is created and this permeability is critical for the process, because now hot air can go up, through the permeable layers.



Not all coke and pulverized coals is consumed in the blast furnace, as seen in these reactions there is carbon that reacts to carbondioxide-gas.

7. *What are the two most important types of steelmaking processes? What are their general principles of operation(raw materials, heat supply, main reations, products and by-products or wastes, furnace types etc.)?*

There are 2 steelmaking processes, EAF and BOF. Carbon has to be removed from the metallic iron. BOF: It consists of 4 steps: scrap charging, hot metal charging, oxygen blowing and tapping. oxygen is blown through liquid iron and this reaction takes place:  $C + \frac{1}{2} O_2(g) = CO(g)$ . C is removed from the iron and 98-99% Fe remains. EAF: 100% scrap is used to make steel. The scrap is melted using electrical power. The temperature can rise to 7000°C. The product is steel.

8. *What are the main impurities in steelmaking process (brought by both hot metal and steel scrap)? How are they removed from the steel melt? What are the main differences between BOF and EAF steelmaking processes? Please state why do we use the steel scrap as part of the raw materials in BOF steelmaking.*

The main impurities are carbon and liquid slag. There is always some silicon, sulphur, phosphorus, manganese and titanium as impurity, but the last few cover a really small amount. The liquid slag is removed easily because it floats on the hot metal. The carbon can be removed by using oxygen. The carbon will react into the gas carbonmonoxide and will remove itself from the iron.

Oxygen steelmaking is also known as Blast Oxygen Furnace (BOF); it uses 70-75% liquid iron and 25-30% scrap; it covers 60% of the steelmaking in the world.

EAF stands for Electric Arc Furnace. It uses 100% scrap and some are with DRI. DRI is the direct reduced iron. This production is increasing. The EAF steelmaking covers now 40% of the world iron production.

The scrap metal mostly comes from previous processes. Not all hot metal was suitable. This scrap metal isn't bad, so they use it again in the blast furnace. It will melt again and it will be made into metallic iron. To reduce the costs they can use the scrap metal.

## Roasting

1. *What are the objectives of roasting for processing sulphide ores? What types of sulphide roasting processes are available in industrial practice? What are the main roasting reactions for each types of sulphide roasting? What kind of roasting furnace is normally used in industry?*

Types of roasting:

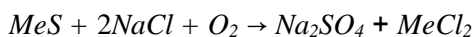
Oxidising            sulphides to oxides  
Sulphating        sulphides to sulphates

Objectives for roasting is preparing of the feed before extraction of metal. Important parameters: particle size, residence time, T, gas compositions

Furnaces: Fluidized-bed roaster, multi-hearth roaster, rotary kilns.

Dead roasting:             $2MeS + 3O_2 \rightarrow 2MeO + 2SO_2 + \text{heat}$         forming oxide  
Sulphate roasting:         $2MeO + 2SO_2 + O_2 \rightarrow 2MeSO_4 + \text{heat}$         forming sulphate  
Gas forming:                 $S_2 + 2O_2 \rightarrow 2SO_2$                                         tapped away leaving pure metal  
                                       $2SO_2 + O_2 \rightarrow 2SO_3$

Chloridising roasting:    changes metal sulphides to more water soluble chlorides.



2. *What is sintering and sintering roasting? What kinds of ores are suitable for sintering, and what kinds of ores are suitable for sintering-roasting? Please indicate the main difference between these two, using examples of ore.*

Is an agglomeration process of partial melting of fined-grained and dust like ore and re-solidification.

Sintering:            iron ore and lead sulphide

Sinter roasting: sulphide ores

Main difference is that sinter roasting is a self-heating process.

## Phase diagrams

1. *Gegeven is het onderstaande binaire fasendiagram A-AB-B. De temperatuur(T) is verticaal uitgezet. De druk (P) wordt constant verondersteld. Het diagram bevat de primaire fasenvelden E,F,G,H en I en het liquid-veld.*

a) Benoem de punten X en Y.

x: peritectic point

y: eutectic point

b) Welke fasen zijn stabiel in de velden E,F,G,H en I?

E: Solid A + Liquid

F: Solid A + Solid AB

G: Solid AB + Liquid

H: Solid B + Solid AB

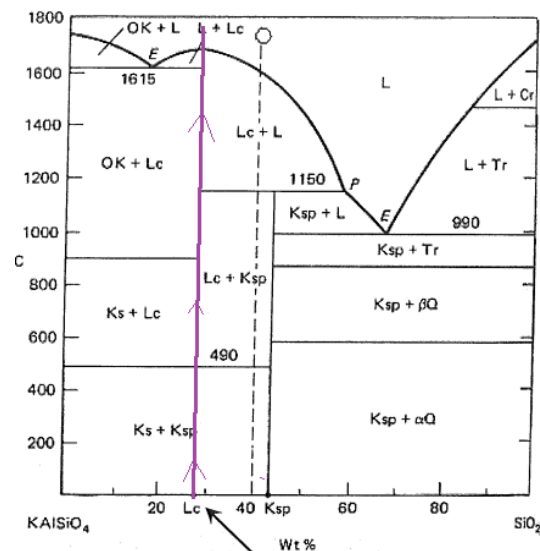
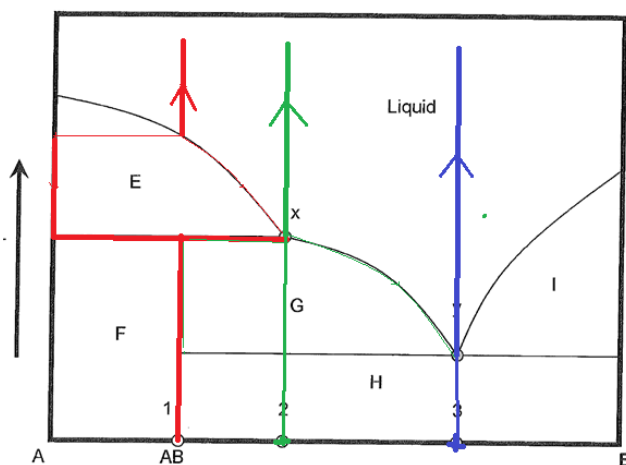
I: Solid B + Liquid

c) Beschrijf het smeltgedrag van de samenstellingen 1,2 en 3. Geef hierbij op een los vel de evolutie van vaste fase(n) en smelt aan.

Bij het smelten met compositie 1, beginnen we met precies de samenstelling van AB, Bij  $T_x$  (tevens het smeltpunt van AB) krijgen we deels solid A, en deels de Liquid samenstelling. Bij nog hogere temperaturen houden we nog alleen Liquid over.

Bij het smelten van compositie 2, beginnen we met een samenstelling van vaste AB en vaste B, tot het punt  $T_y$ . Hier houden we Solid AB en liquid over, in het punt x wordt dit volledig liquid(in dezelfde samenstelling als in punt 2)

Bij het smelten vanaf punt 3, beginnen we weer met een samenstelling van Solids AB en B, en in punt y(eutectic point) gaat dit over in volledig liquid(van samenstelling uit punt 3).



### Links bij vraag 1, rechts bij vraag 2

2. Below the phase diagram for the system kalsillite – Silica ( $KAlSiO_4 - SiO_2$ ) is given.

a) Indicate graphically the crystallization path of the melt composition indicated by the blue circle. Explain also in words what happens. You may use the separate sheet for graphically indicating the crystallization path. The diagram is printed larger on that sheet.

rond 1600 graden cristaliseert leuciet in de samenstelling, waarbij nog steeds liquid aanwezig is. Op 1150 graden(smeltpunt k-feldspar) kristalliseert ksp, en hebben we dus een vaste samenstelling van leuciet en K-veldspaat, rond 490 graden is leuciet echter overgegaan in kalsiliet. En ons eindresultaat is dus een vaste samenstelling van ksp en ks.

b) Describe in words what happens when the composition (Lc) is heated from room temperature to its melting point.

Bij deze samenstelling is leuciet niet stabiel op kamer temperatuur, echter hebben we de vaste compositie ks + ksp. Rond 490 graden vormt dit zich tot pure leuciet. Lc smelt rond 1700 graden, en is samenstelling van Lc liquid.

Below the ternary diagram of the system  $CaO - Al_2O_3 - SiO_2$  is given. (DIT DIAGRAM IS NIET BIJGEVOEGD BIJ DE OUDE TENTAMENS)

c) Indicate in this diagram at least two eutectical points and two peritectical points.

nvt(diagram niet gegeven)

d) *The straight lines in this ternary diagram are so called Alkemade lines. What is the definition of an Alkemade line?*

An Alkemade line is a straight line which connects two compositional points of which the **primary phase fields are adjacent**, and of which the **intersecting line is a boundary curve**.

3. *Beschouw het onderstaande ternaire diagram van het systeem A-B-C. Het betreft een systeem met smeltfasen en vaste fasen.*

a) *Hoe noemt men een lijn van het type A-BxCy? alkemade lijn*

b) *Als ik langs de lijn A-BxCy een binair fasendiagram zou tekenen, zou dat dan een echt binair systeem (true binary system) zijn of een pseudobinair systeem (pseudobinary system)? Verklaar uw antwoord.*

pseudobinair, omdat de alkemade lijn niet de boundary curve van de primaire fasen doorsnijdt. (wanneer die dat wel zou doen zou het true binair zijn)

c) *Benoem de punten 1,2,3, 4, 5, en 6.*

1: Ternaire peritectic

2: Ternaire Eutectic

3: Binair peritectic

4: Binair eutectic

5: binair eutectic

6: binair eutectic

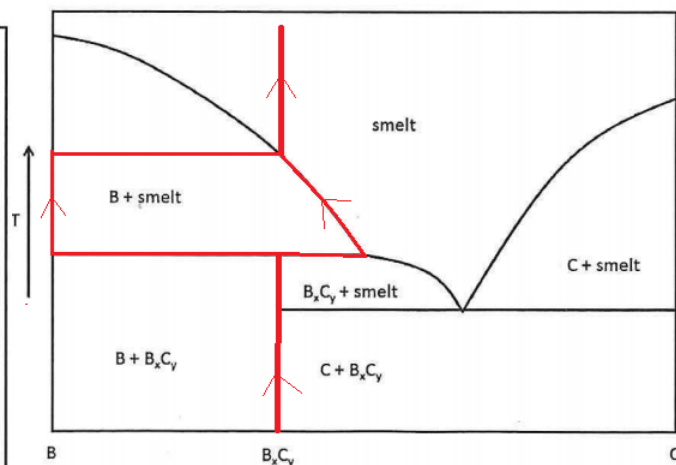
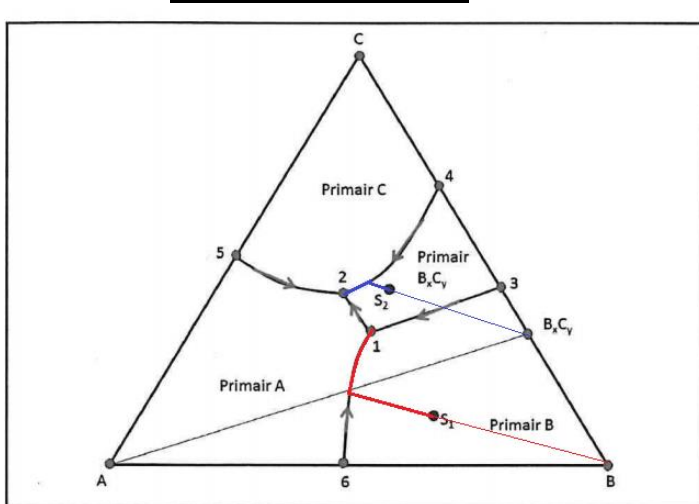
d) *Teken op een apart vel (bijgeleverd) het kristallisatiepad van de smelten met de samenstelling S<sub>1</sub> en S<sub>2</sub>.*

S<sub>1</sub>: vanaf S<sub>1</sub> kristalliseert steeds meer B, en komt zo op de peritectische lijn 6-1 terecht. In punt 1 is er geen liquid meer en is nog alleen vaste stof. De lijn stop in dit peritectisch punt omdat het punt S<sub>1</sub> zich aan de andere kant van de alkemade lijn bevindt, en dus in die driehoek.

S<sub>2</sub>: dit punts kristallisatie route bereikt wel het eutectisch punt. S<sub>2</sub> beweegt zich van het punt B<sub>x</sub>C<sub>y</sub> af (omdat het zich in dat vak bevindt) en vind al gauw het eutectisch punt. Hiet is alle liquid op en is er een vaste samenstelling over

e) *In het onderstaande diagram vindt u een schetsmatige voorstelling van de snede BC. Stel, ik verhit een vaste stof met de samenstelling B<sub>x</sub>C<sub>y</sub> zodat deze gaat smelten. Geef m.b.v. dit diagram (op een apart vel (bijgeleverd)) het gehele smeltproces weer, en verklaar wat er steeds gebeurt.*

**Links vraag 3d, rechts 3e**



**4. oefenopgaven (volgens Jack wordt niet een figuur in**

**deze vorm gevraagd, aangezien dit niet behandelde stof bevat)**

a) solvus

b) Eerst kristalliseert  $\alpha$ , en hebben we de samenstelling  $\alpha$ +liquid. Bij verdere afkoeling wordt dit  $\alpha$ +eutectic composition.

c) -