

Tentamen van 3 juli 2015

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Part 1: Extractive metallurgy

1.1)

What are the pyrometallurgical, hydrometallurgical and electrometallurgical processes? What metals are mainly produced through the above 3 types of metallurgical processes or in the combination of different types of processes (with at least 1 example for each type)?

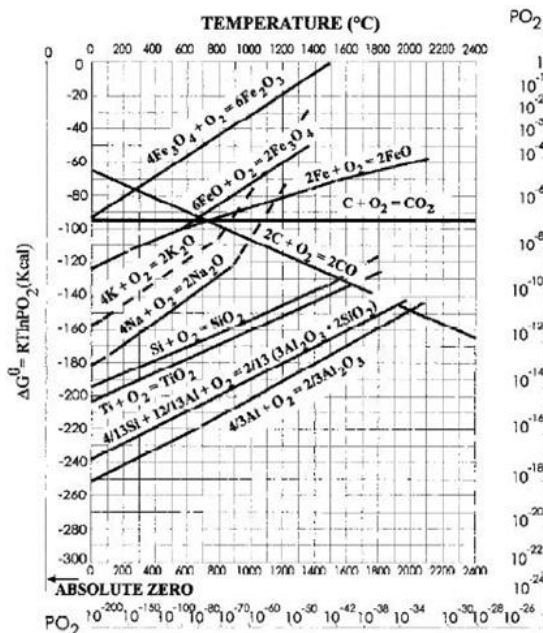
Pyrometallurgy are chemical reactions at high temperatures. The main metals that are produced with pyrometallurgy are Iron and steel, lead and tin, copper (85%), titanium and majority nickel.

Hydrometallurgy are chemical reactions in aqueous environment normally below 100 C (except pressure hydrometallurgy). The main metals produced with hydrometallurgy are Zinc (80%), Copper (15%), partly Cobalt and Nickel.

Electrometallurgy are chemical reactions through charge transfer. It's with an aqueous solution and molten salt. The main metals produced with Electrometallurgy are Aluminium, Magnesium, Copper electrorefining and electrowinning, Zinc electrowinning.

1.2)

What is Ellingham diagram? What are the two important parameters in the diagram? How is it used in carbothermic reduction of metal oxides and metal refining processes?



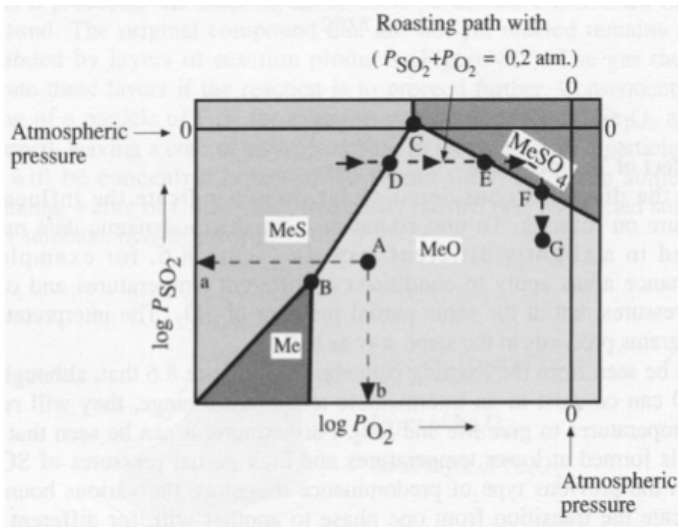
Purification of Mullite by Reduction and Volatilization of Impurities
A. Souto, F. Guisán, and S. de Aza, *J. Am. Ceram. Soc.*, 82 [10] 2660-64 (1999)

Ellingham diagram is a graph where ΔG (Gibbs energy) and T (temperature) are the two parameters. The Ellingham diagram is used to predict the equilibrium temperature between a metal, its oxide and oxygen.

In carbothermic reduction of metal oxides and metal refining processes the diagram is used to: determine if a reaction will take place at given temperature. A reaction will take place when the difference in Gibbs energy between the reaction of the metal and the carbon is negative (right of the cross-section between metal and carbon line).

1.3)

What is the Kellogg diagram? Where and how it is used In the evaluation of metallurgical processes, please give one example with a sketch of the diagram, indicating the key parameters (along X- and Y-axes) at a fixed temperature.



Kellogg diagram gives an indication about which phases can exist, at given Temperature and partial pressure of O_2 and SO_2 . (This is needed for the thermodynamics part of Sulphide roasting, a feed preparation operation)

Example Reaction along line BC: $2MeS + 3O_2 \rightarrow 2MeO + 2SO_2 + \text{heat}$

$$PO_2 \propto^3$$

$$PSO_2 \propto^2 / \propto$$

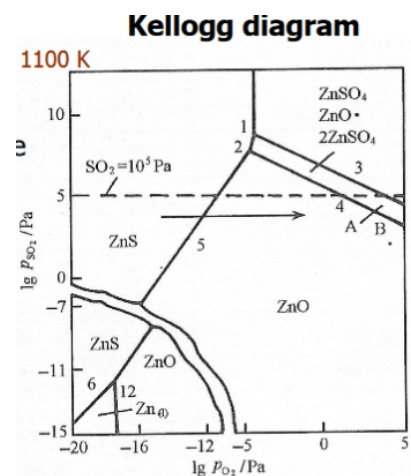
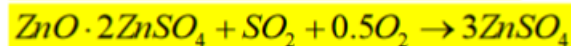
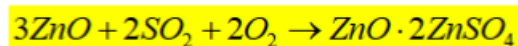
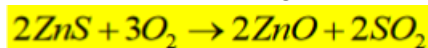
$$K = \propto$$

1.4)

What are the objectives and the main reactions of roasting zinc sulphide concentrates? What are sintering and pelletising? For Ironmaking, why do we need sinter and pellets in blast furnace process?

Roasting happens in a fluidized bed roaster. The reaction is exothermic (similar to coal combustion). Extra heat for roasting temperature, cooling is needed)

Main reaction roasting Zinc: $ZnS \rightarrow ZnO (+ZnSO_4)$



Sintering and pelletising :

Sinters zijn stukjes ore met additionalen erbij om de slag te controleren. Sintere "bake" je. Pellets bestaan alleen uit de ore. En "burn" je. Sintere en pellets worden niet tot het smeltpunt verwarmd, maar net daarboven. Daardoor is er geen chemische reactie en geen smeltpunt.

Waarom Sintering and Pelletising? □ In pyrometallurgical processing is het belangrijk dat de deeltjes niet te klein zijn die in de oven gaan, want dan kan de lucht er niet goed doorheen geblazen worden en dan krijg je stof vorming. Daarom moet je deze kleine deeltjes eerst aan elkaar binden. Deze gebonden deeltjes kan je in balletjes (pellets) of in grove brokjes (sinters) hebben. Verder worden er aan de sinters ook andere stoffen toegevoegd om de slag te controleren.

1.5)

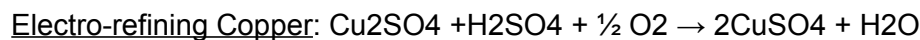
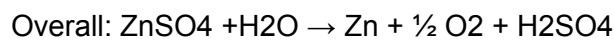
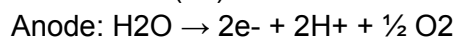
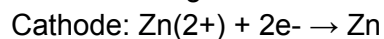
What are the principles of electrowinning and electro-refining? Please describe briefly electrochemical reactions on cathode, anode and overall reactions for: electrowinning of zinc; electro-refining of copper; molten salt electrolysis of aluminium.

Reactions offer 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.

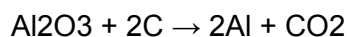
Electrowinning: When the electrolyte is an aqueous solution.

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

Electrowinning Zinc:



Molten salt electrolysis Aluminium:

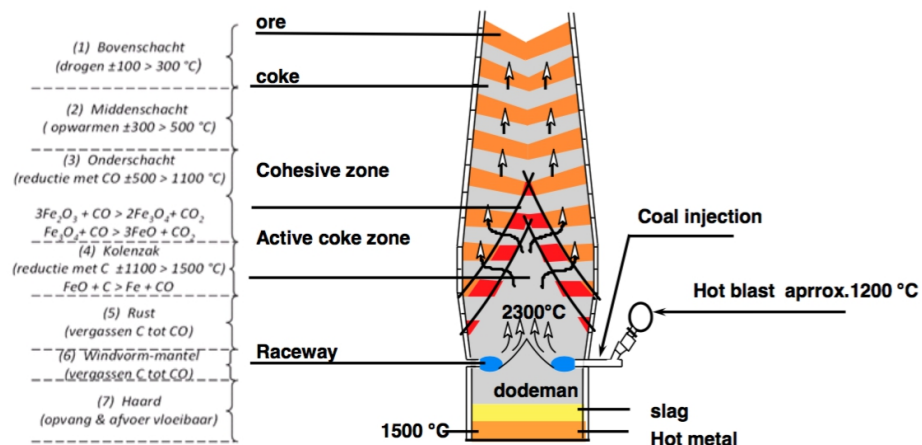
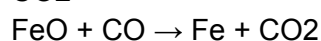
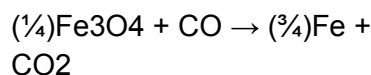
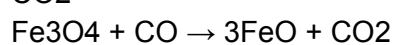
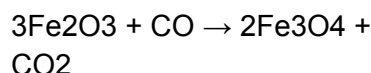


2.1) Ironmaking

Please describe the working principles of ironmaking blast furnaces.

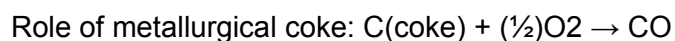
Raw materials and their preparation: coke, iron ore (pellets/sinters), limestone

Main chemical reactions:



Products of the process and their major compositions:

- Iron, hier wordt later staal van gemaakt, bestaat uit ijzer.
- Slag, dit wordt later cement en bestaat uit ...
- Gas, dit wordt schoongemaakt en wordt POWER! :)



2.2) Steelmaking

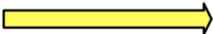
Please describe how crude (carbon) steel is produced with BOF steelmaking process.

Steelmaking fundamentals

- Feed: scrap + hot metal
- Objective: removing C and other impurities by oxidation (blowing O₂)
 - Reactions
 - $\frac{1}{2} \{O_2\}_{gas} = (O)_{metal}$ (Transfer of oxygen in BOF)
 - $(Si)_{metal} + 2(O)_{metal} = (SiO_2)_{slag}$
 - $(Mn)_{metal} + (O)_{metal} = (MnO)_{slag}$
 - $2(P)_{metal} + 5(O)_{metal} + 3(CaO)_{slag} = 3(CaO \cdot P_2O_5)_{slag}$
 - $(S)_{metal} + (CaO)_{slag} = (CaS)_{slag} + (O)_{metal}$ or
 - $(FeS)_{metal} + (CaO)_{slag} = (CaS)_{slag} + (FeO)_{metal}$
 - $(Fe)_{metal} + (O)_{metal} = (FeO)_{slag}$ (Transfer of oxygen in EAF)
 - Products:
 - Crude steel, slag, off-gas + flue dust

Removal chemistry of major impurities (to make the material stronger than Iron):

- Removal of C, Si and P (in oxidising environment)
- Removal of S (reducing environment)

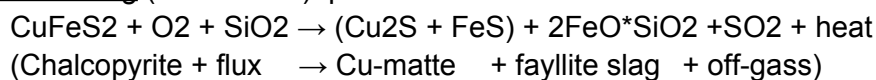
| pig iron |  | steel |
|-----------------|---|---------------|
| 1400°C | | 1600°C |
| 95% Fe | | 98-99% Fe |
| 4-4.5% C | | 0.1-2% C |
| Si, Mn, P & S | | Si, Mn, P & S |

2.3) Copper production

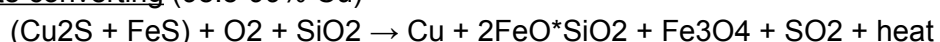
Copper occurs in majority as sulphide ores in the earth. Please describe the main extraction and refining steps and the main chemical reactions from copper sulphide concentrates to refined copper as final metal product. What is the average Cu content in the concentrates and final purity of copper?

0. Copper Ore (CuFeS₂) (20-30% Cu)

1. Matte smelting (40-60% Cu): partial removal of S



2. Matte converting (98.5-99% Cu)



Products: Blister copper

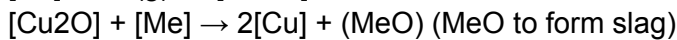
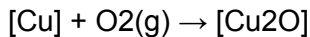
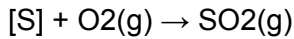
Waste: SiO₂, slag and Fe₃O₄

3. Fire Refining (99-99.5% Cu)

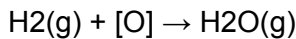
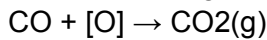
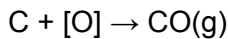
“Blister copper” : $[S] + 2[O] \rightarrow SO_2(g)$ bubbles impact castability (gietbaarheid).

Fire-refining needs 2 stages:

- I. Oxidation of S, together with other impurities (As, Sb, Sn, Bi and Fe) using O_2



- II. Oxygen removal by hydrogen: reduction with hydrocarbonds

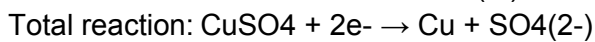
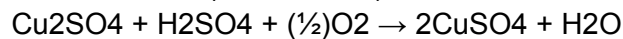
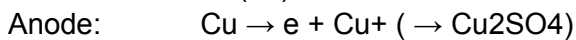
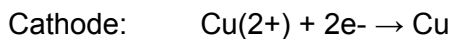


Products: Cu

Waste: MeO, SO_2

4. Electro Refining (99.5-99.9%)

Half reactions:



2.4) Aluminium production

How many steps are needed to produce Al metal from bauxite ore? Please explain the technologies used currently in industry (Bayer process and Hall-Hérout-process with key chemical reactions)? Please explain why we DO NOT use carbothermic reduction to produce Al metal from bauxite ore?

Two main steps to produce Al metal from bauxite ore:

1. Bauxite \rightarrow pure Alumina (Bayer process)
2. Alumina \rightarrow pure Al metal (Hall-Heroult process)

Bayer process: Bauxite \rightarrow Alumina (Al_2O_3)

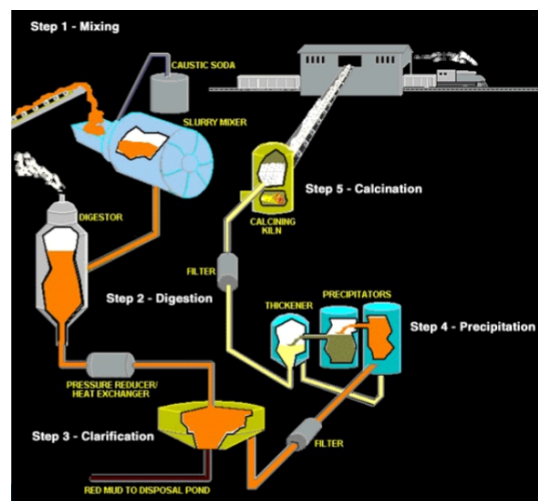
Step 1: Mixing

Step 2: Digestion: NaOH-leaching: $2Al(OH)_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$

Step 3: Clarification: solid-liquid separation

Step 4: Precipitation: $Al(OH)_3$ crystallization

Step 5: Calcination: $2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$

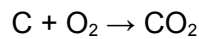


Hall-Héroult-process: (Molten Salt Electrolysis)

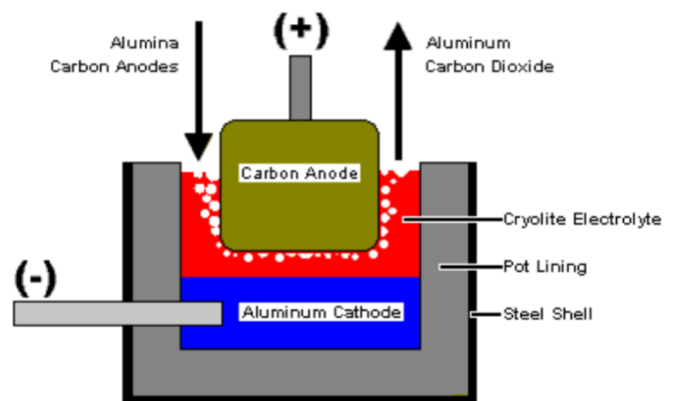
Electrowinning: deposition of metals under external current. At high temperatures

Standard electrode potential:

$$dG = -n \cdot G = F \cdot E = -R \cdot T \cdot \ln(K)$$



CO_2

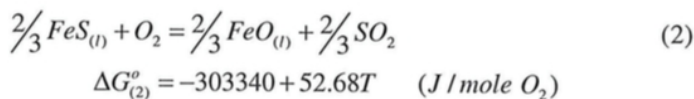
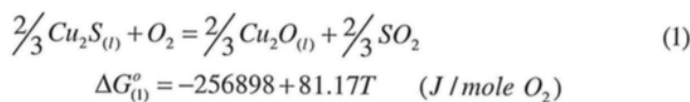


Why DO NOT use carbothermic reduction to produce Al metal from bauxite ore?

3.1)

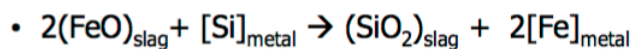
Thermodynamic evaluation of copper converting process:

Copper converting is carried out at about 1200°C in two steps: slag-making and copper-making. Oxidations of FeS and Cu₂S are two major competing reactions (see below). The standard Gibbs energy change for reactions (1) and (2) are given below.



a) Please write down the equilibrium constants for both reactions as the function of activity and/or partial pressure of chemical species in the system, and calculate the equilibrium constants for both reactions at 1200°C.

Example Equilibrium constant uit college:



$$K = \frac{a_{SiO_2} \cdot a_{Fe}^2}{a_{FeO}^2 \cdot a_{Si}}$$

$$\Delta G^{\circ} = -RT(\ln K)$$

Dus voor reactie (1):

$$K_1 = \frac{a_{Cu_2O}^2 \cdot a_{SO_2}^2}{a_{Cu_2S}^2 \cdot a_{O_2}^3}$$

Voor reactie 2:

$$K_2 = \frac{a_{FeO}^2 \cdot a_{SO_2}^2}{a_{FeS}^2 \cdot a_{O_2}^3}$$

Rewrite above reaction: $k = e^{-(dG/RT)}$

$R = 8.314 \text{ J/K}\cdot\text{mol}$

$T = 1200 \text{ C} = 1473 \text{ K}$

$dG1 = -256898 + 81.17 \cdot 1473 = -137334 \rightarrow k1 = 73242$

$dG2 = -303340 + 52.68 \cdot 1473 = -225742 \rightarrow k2 = 101254922$

b) Please use the values from the calculated standard Gibbs energy change to explain the oxidation order of the 2 sulphide compounds (CU₂S and FeS) in the matte: which oxide is oxidized first, and WHY?

$dG2 (\text{FeS}) < dG1(\text{Cu}_2\text{S})$, so FeS oxidizes first

3.2) Phase diagrams

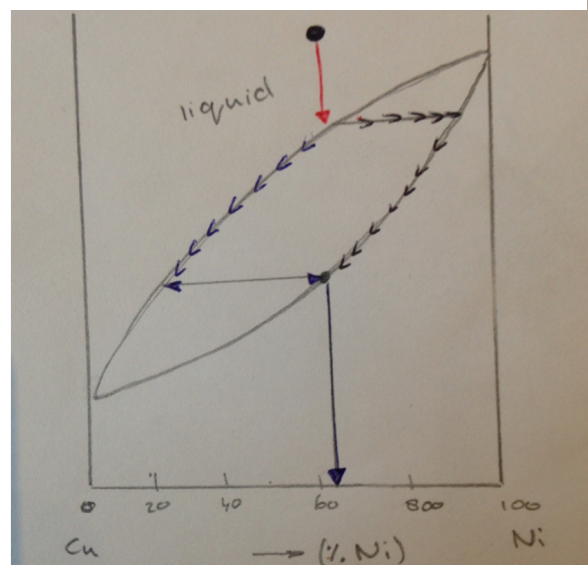
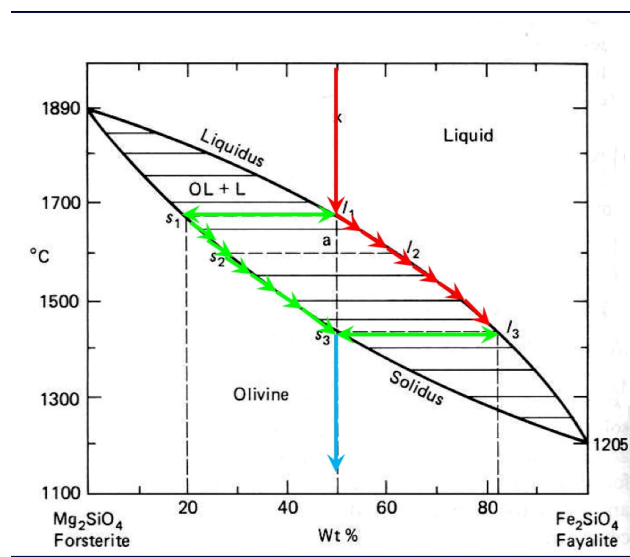
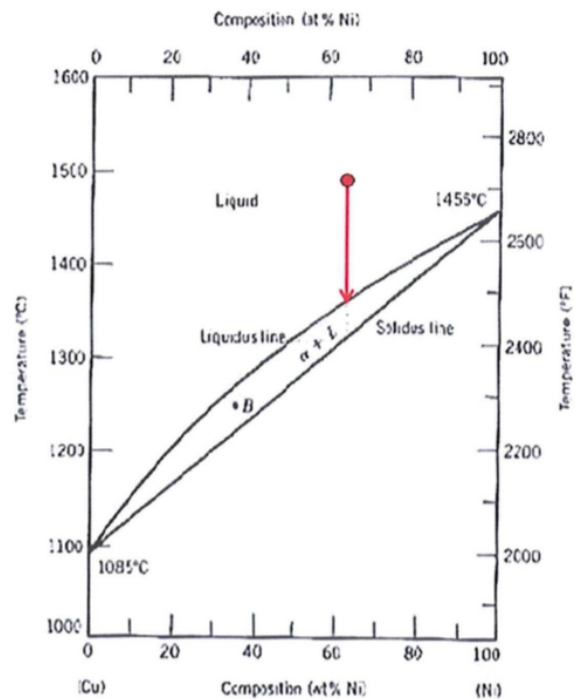
Above is shown the phase diagram of the binary system Cu - Ni. A certain liquid composition (given by the red dot), starts cooling, and the liquid composition reaches the liquidus. The liquid starts crystallising.
a) Draw on a separate sheet (provided) the crystallization path of the liquid.

b) What is the composition of the final liquid that will crystallise?

60% Ni

c) What is the exact name of this kind of phase relationship between Cu and Ni?

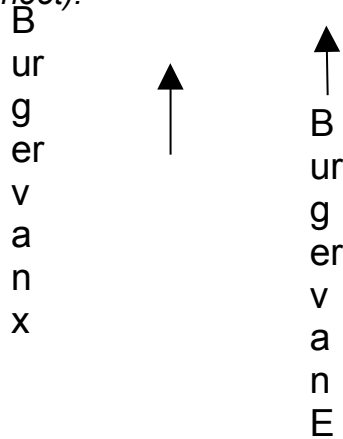
Continuous solid solution



Part 2: Physical Processing

1)

Consider the curved dislocation of mixed type drawn below. Indicate in point X the position of the Burgers vector, and explain your answer. (Redraw the image on your answer-sheet).



Bij een Edge dislocatie wijst de burger vector haaks op de dislocatielijn. Bij Screw juist parallel. X ligt precies op de helft tussen Edge en screw. Dus zal de burgers vector ook precies ertussen liggen. In dit geval is dat recht ophoog.

2)

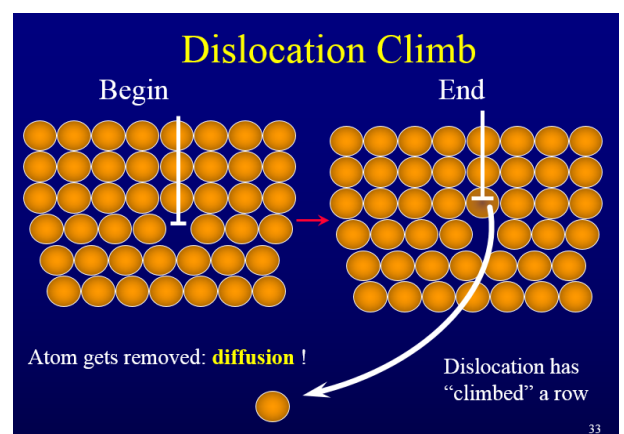
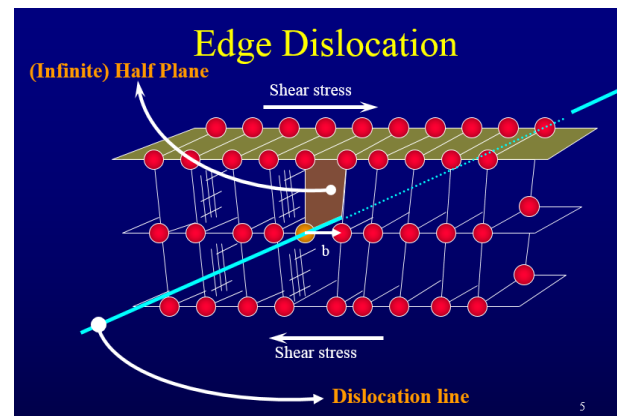
In the picture you see a schematic picture of an Edge Dislocation. The dislocation line is situated perpendicular to the plain of the drawing. Suppose the dislocation would climb out of its slip plane.

a) What process has to take place for this to happen?

Atom gets removed by diffusion

b) What physical quantity (fysische grootheid) is of fundamental importance for this process to take place, and is controlling the rate of this process? Explain your answer.

Diffusion is controlled by Temperature



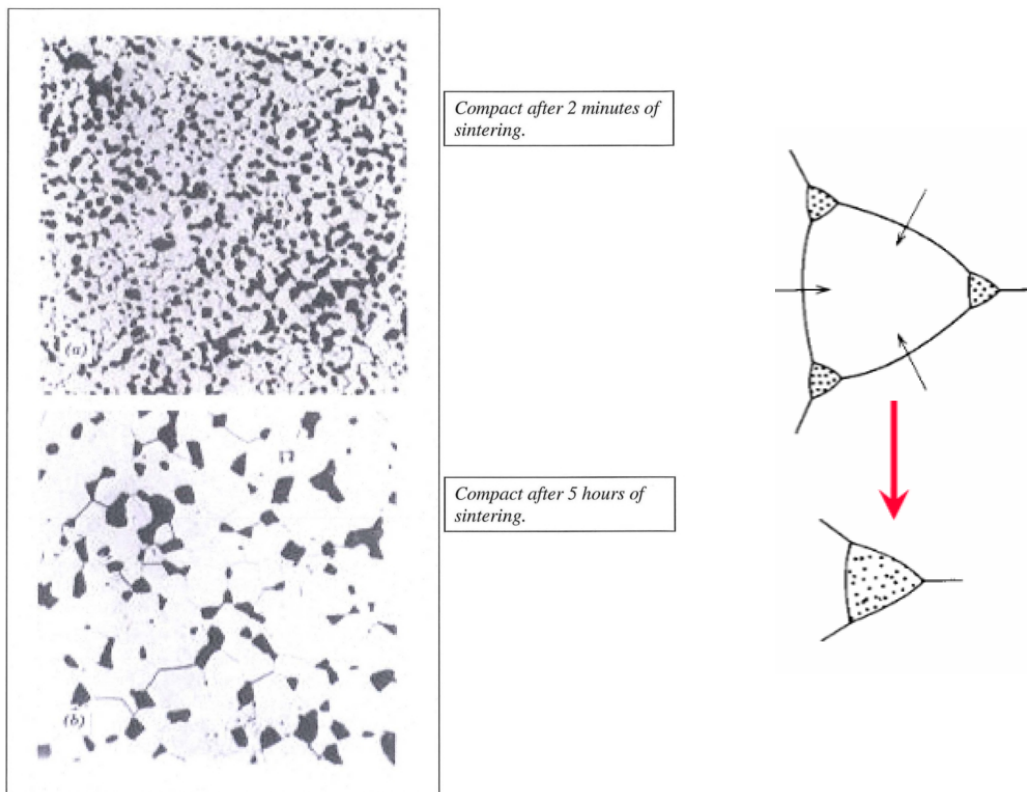
3) When heterogeneous material is ground, one may expect with respect to the grain sizes that each of the different minerals in the mixed and comminuted material will have its own grain size distribution. Explain this using the Hall-Petch Law:

$$\sigma = \sigma_0 + \frac{K_y}{\sqrt{d}}$$

You may assume that none of the minerals has cleavage.

Met de Hall-Petch Law berekenen je de grind limit (minimum grain size that can be reached). Doordat σ_0 en K_y constanten zijn die afhangen van welk mineraal je hebt, zal elk mineraal ook zijn eigen korrelgrote verdeling krijgen.

4) Consider the sintered compact depicted below. The number of pores (black areas) has significantly decreased after 5 hours, but the size of individual pores is considerably larger. This is called pore coarsening. Explain the mechanism of pore coarsening (use sketch drawings to illustrate the process).



5) Ore has a density of 2200 kg/m^3 . It requires sieving at 3 mm at a throughput rate of 600 t/hr. 20% of the material is within the difficult to sieve class (between 1.5 mm and 4.5 mm)
 a) How large is the screen surface area, using the screening equation in Appendix A

$$C = 1.4 \frac{\rho}{\gamma} D^{0.6}$$

C = Screen capacity in $\text{t/m}^2 \cdot \text{hr}$;
 D = mesh size in mm;
 1 foot = 12 inch = 0.3048 m

b) Design, using your above answer and the copies of Weiss (Appendix A, page 3E-10) the right width, length and number of screens.

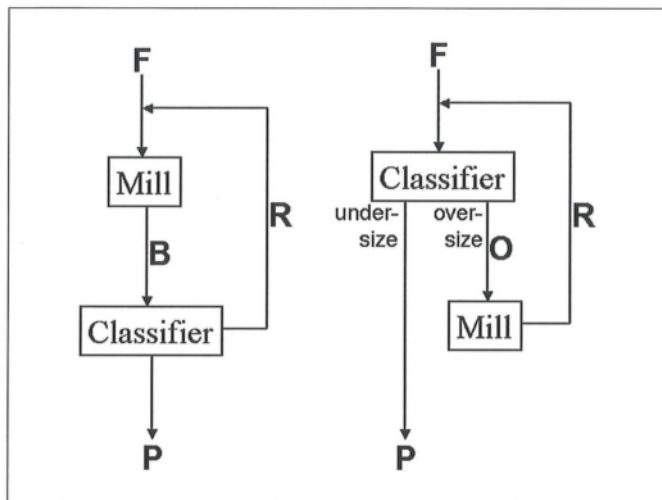
c) On page 3E-11, Weiss gives in chart A an alternative method to determine screen capacity of various materials. Argue why:

1. There is a difference between the 4 materials,
2. Why the lines are linear at large screen sizes and go curved towards zero at increasingly smaller screen sizes (so why has the curve the shape it has)

d) Draw a graph with screen capacity (y-axis) as a function of moisture content (x-axis) and argue the shape of the sketched curve.

e) Can I also use hydrocyclones as a separation technology for this ore and size? Base your arguments on the three major differences between the two separation technologies.

f) The screening is used in combination with a ball mill. You have two different flow sheet options (see below). Which one would have your preference and why?



Review Questions

Part I : Introduction to metallurgical processes

1-1: How a metals production process is organized (considering raw materials, energy use, products, wastes disposal, and equipment etc.). What are the main issues to consider if you are planning to design a metal production plant (a smelter)?

Raw materials:

- Primary resource of metals (ore and concentrates)
- Energy (fuels) and reductant
- Secondary resources of metals (scrap and waste)

Energy use: Coal, oil/gas, hydropower, nuclear power. Energy primary from ore is much more than secondary from scrap → recycling saves a lot of energy!

1-2: What factors determine the price of metals produced from a mine? Why the market of the metals industry is so dynamic and volatile?

- Grade of the ore
- How much left in the world
- Losses of resource during process
- Energy efficiency

| Ore | Economic content |
|-----------|-------------------|
| Iron | 25-70 % Fe |
| Aluminium | 50-65 % Al_2O_3 |
| Copper | 0.5-5 % Cu |
| Nickel | 1-6 % Ni |
| Lead | 1-12 % Pb |
| Zinc | 3-10 % Zn |

Industry is dependent on supply/demand, discovery of new ore bodies, new technologies to produce more efficient, amount of resource that is still left in the world.

1-3: What are the important minerals for production of iron, aluminum, magnesium, titanium, copper, nickel, cobalt, lead, zinc, tin, chromium and manganese?

- **Iron:** hematite (Fe_2O_3), magnetite (Fe_3O_4)
- **Aluminium:** bauxite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)
- **Magnesium:** dolomite ($(\text{Ca}, \text{Mg})\text{CO}_3$); magnesite (MgCO_3), MgCl_2
- **Titanium:** ilmenite (FeTiO_3), rutile (TiO_2)
- **Copper:** chalcopyrite (CuFeS_2), chalcocite (Cu_2S), bornite (Cu_5FeS_4), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$)
- **Lead:** galena (PbS)
- **Zinc:** sphalerite (ZnS)
- **Tin:** cassiterite (SnO_2)
- **Nickel:** pentlandite ($(\text{Fe}, \text{Ni})\text{S}$)
- **Cobalt:** carrolite (CuCo_2S_4), linnaeite (Co_3O_4)
- **Mercury:** cinnabar (HgS)
- **Chromium:** chromite (FeCr_2O_4)
- **Manganese:** pyrolusite (MnO_2), manganite (Mn_2O_3)
- **Tungsten:** Scheelite (CaWO_4), Wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$)
- **Uranium:** uraninite (UO_2)

1-4: A general overview how the following metals are produced in the world: their resource, productivity, main technology, the market. Please refer to the article collections "Metals Production Fundamentals".

Part II : Feed preparation

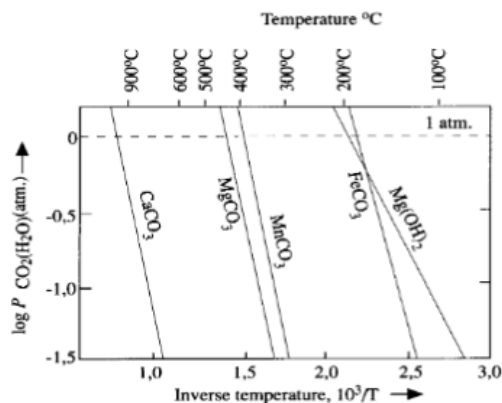
2-1: What types of calcinations processes are available? What are the similarities and the differences among them?

Calcination: "Thermal decomposition" process with gas evolution.

- Removal of CO_2 gas from carbonate:
 $\text{MeCO}_3 \rightarrow \text{MeO} + \text{CO}_2(\text{g})$
- Removal of chemically bounded water from hydroxides:
 $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O}(\text{g})$

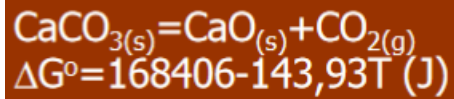
The calcination temperature is based on Gibbs free energy change of the reaction.

Important if reaction is endothermic or exothermic.



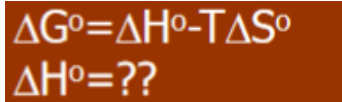
Effect of impurities: Increase decomposition pressure and decomposition at lower temperatures.

2-2: How to estimate at the required temperature for calcination of metal carbonates?



When $dG = 0 \rightarrow T = 1170 \text{ K}$

At a given temperature, how to calculate the heat (thermal energy) requirement for the calcination process? Please go through the example of calcination of limestone (CaCO_3) in the lecture and computer Practicals.



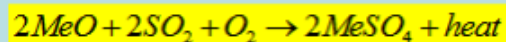
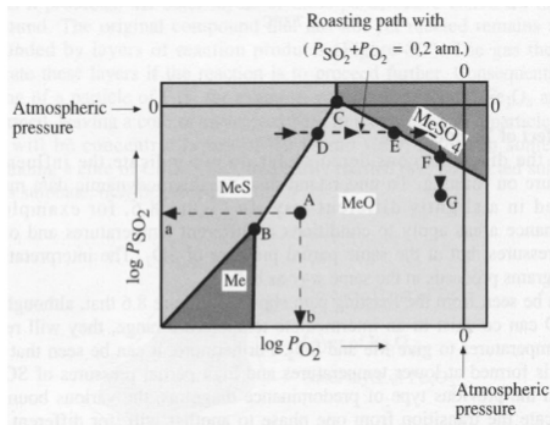
$dH = 168406 \text{ J/kg} \rightarrow 1 \text{ kg coke needs } 1684 \text{ kJ}$

2-3 What are the objectives of roasting for processing sulphide ores?

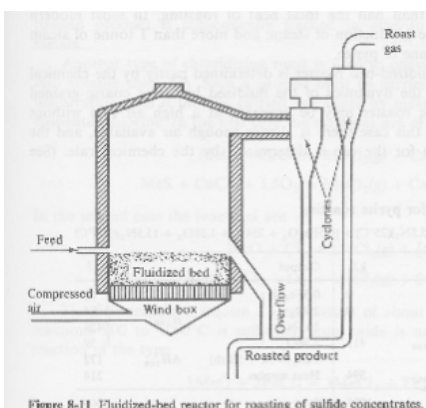
Controlled oxidation of metal sulphides below their melting points, usually between 500 and 1000 Celsius. Process control by manipulating: Temperature, Gas composition (partial pressure) and Residence time of solid particles.

What types of reactions are involved?

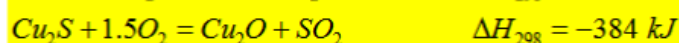
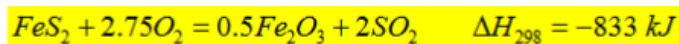
Kellog Diagram



What kind of equipment is normally used? What applications could you find in the metallurgical industry?

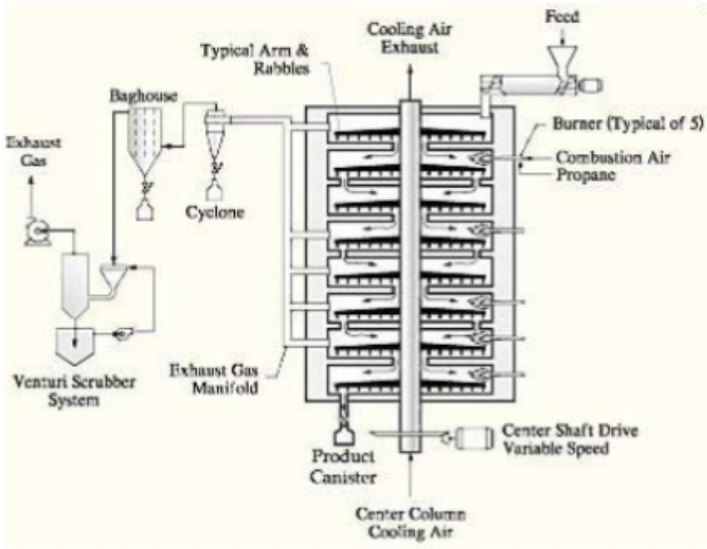


Fluidized bed roaster: Exothermic reactions, so cooling is needed.



Multi-hearth

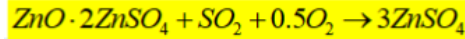
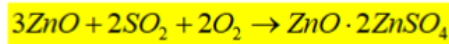
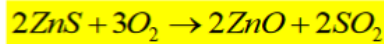
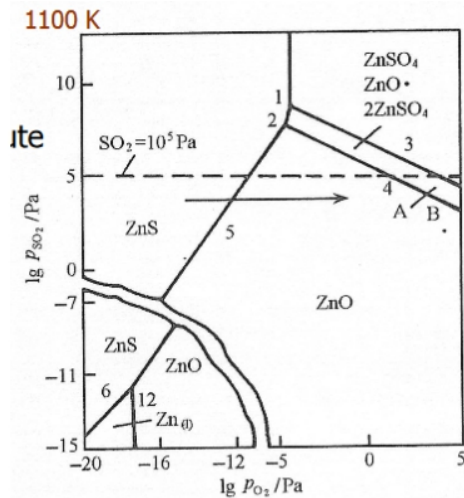
Figure 8-11 Fluidized-bed reactor for roasting of sulfide concentrates.



roaster: Rotating rabble arms stirring solids. Roasted concentrate falling from one hearth layer to the next.
 Applications: Pyrites, Copper sulphide concentrates, Zinc sulphide concentrates, Molybdenum sulphide concentrate.

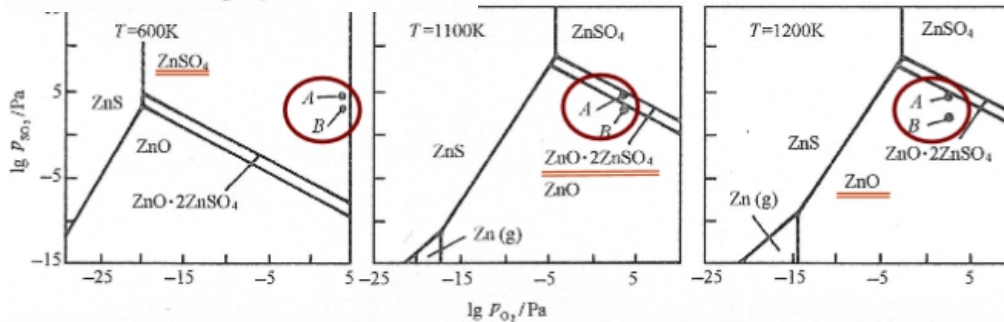
Rotary kilns: Multi-purpose furnace, versatile; drying, roasting, pre-reduction, incineration, cement production.

2-4: During roasting of zinc sulphide concentrates (ZnS), what different operating conditions prevail for the formation and ZnSO₄ in comparison with ZnO as the roasting product? Please give explanations by using the Kellogg Diagram of Zn-S-O system.



High temperature → ZnO

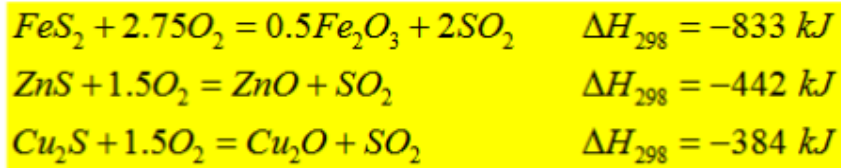
Lower temperature → ZnSO₄



2-5:

During roasting of zinc sulphide concentrates, what negative influences you could expect when the concentrates contains significant amount of pyrite FeS₂? To avoid

or reduce the negative effect, what could you recommend to the practice in maintaining certain operating conditions?

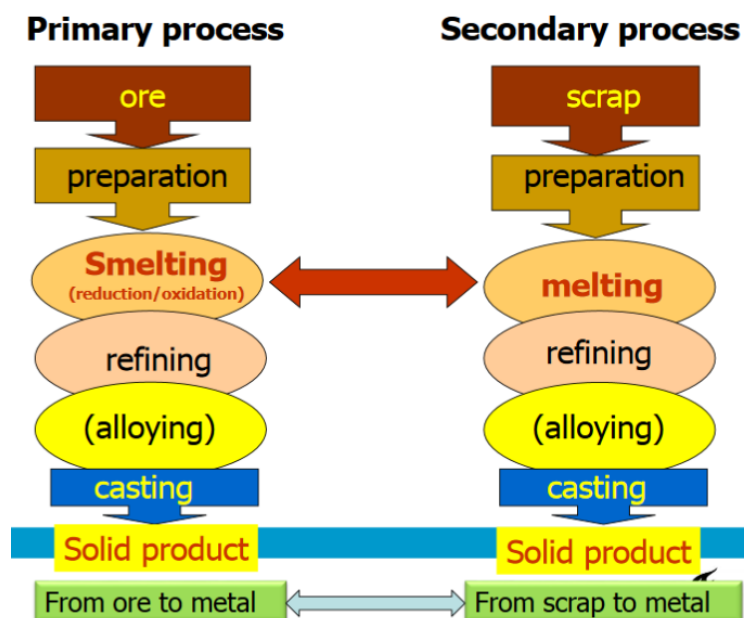


2-6: During zinc roasting, we get calcines (roasting products) at various locations of the system. Please explain why the sulphur and sulphate contents in the fine portion (collected in the waste heat boiler and cyclones, or electrostatic precipitator) are higher than the calcine collected from the fluidized bed furnace?

Part III : Metals Extractions

3-1: What are the basic unit operations for metal extractions? What are the main functions of each of them? Please give an indication or example about where they can be used for metals production?

- Preparation or pre-treatment stages
- Extraction stages
- Refining stages
- Recycling



3-2: What are the main differences between sulphide ore processing and oxide ore processing? Please draw a conceptual flowsheet

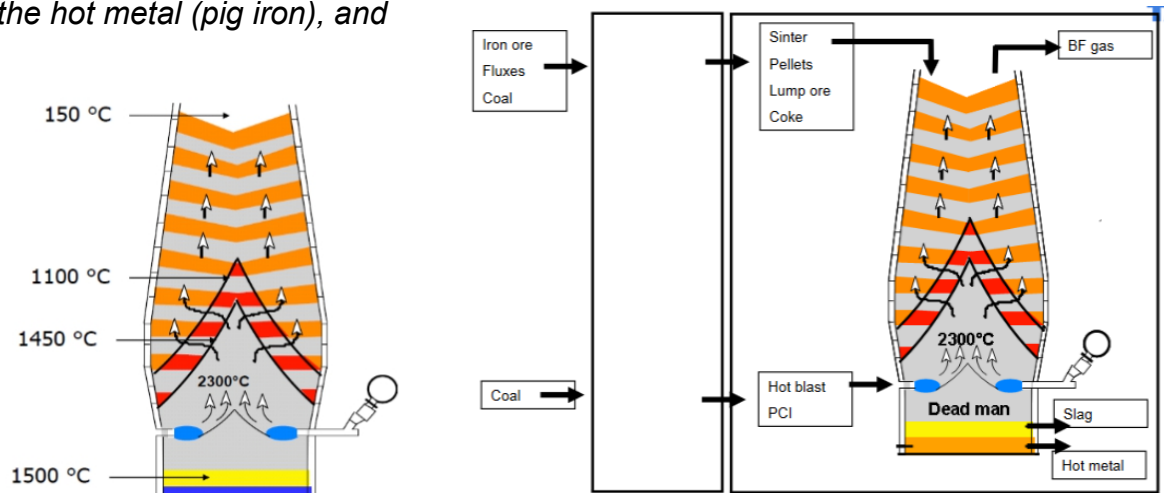
- (1) from iron ore (and steel scrap) to crude steel
- (2) from Pb-Zn sulphide concentrates to zinc and lead metals
- (3) from Cu sulphide concentrates to copper metal (99.99% purity)
- (4) from bauxite ore to aluminium metal

3-3: Please describe ironmaking blast furnace process, and indicating the raw materials and products and the auxiliary facilities. What are the different zones of the blast furnace, and what are the main chemical reactions in the ironmaking blast furnaces? Could you tell the main impurities in the hot metal (pig iron), and

>500 °C (dry zone):
 $\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow \text{Fe}_3\text{O}_4 + \text{CO}_2$
 $\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow \text{FeO} + \text{CO}_2$
 $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$

>1100 °C (wet zone):
 $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ (Boudouard)
 $\text{FeO} + \text{C} \rightarrow \text{CO}$

Raceway:
 $\text{C} + \text{O}_2 \rightarrow \text{CO}$
 $\text{H}_2\text{O} + \text{C} \rightarrow \text{H}_2 + \text{CO}$



where are they coming from?

Raw materials: Iron ore, coal, limestone and recycled steel.

Products:

Main impurities: C, Si and P and S

3-4: What are the essential feed preparation processes for iron making blast furnaces (iron ore agglomeration and coke making)? How coke, sinter and pellets are made?

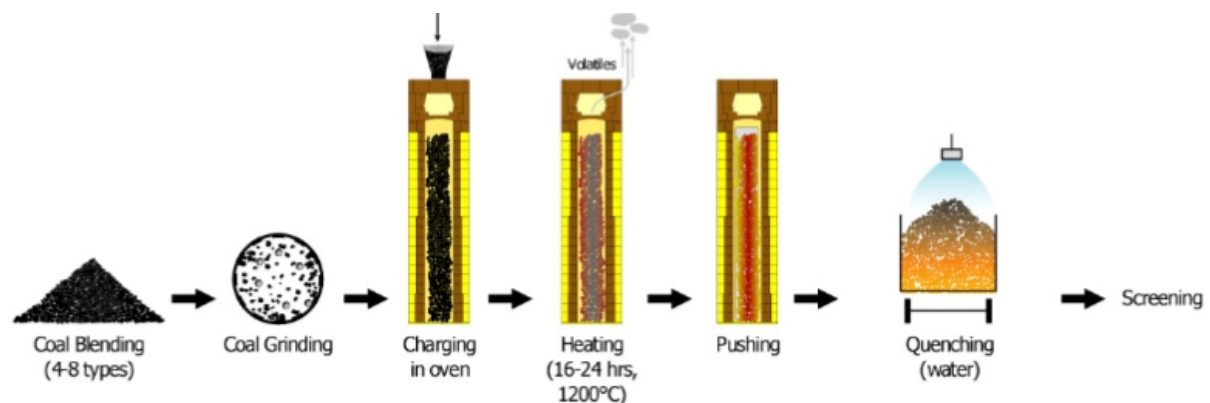
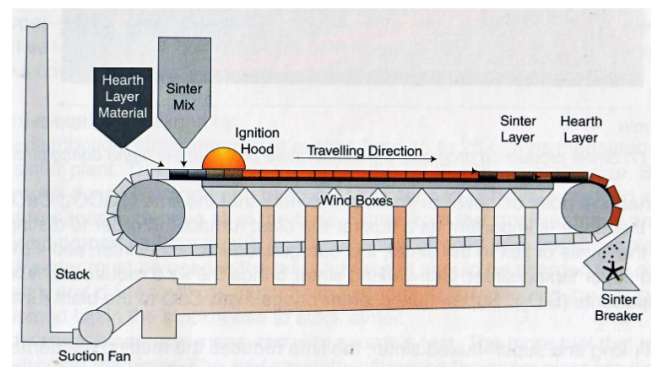


Sintering: Partial melting and re-solidification. Gasses going through a charge of solids.

Grate sintering:

Pelletising: Malen → Balling → Branden

Coke production:



3-5: What are alternative ironmaking technologies to the conventional blast furnace process? What is “Hlsarna” ironmaking process, and what are its main characteristics and advantages over blast furnace process?

Hlsarna: Direct use of coal and ore. No coking and agglomeration.

Economical benefits: Low cost coals, Lower grade iron ores, waste oxides, Lower Capex.

Environmental benefits: 20% CO₂ reduction, 80% CS and reduction of dust, NO_x, SO_x.

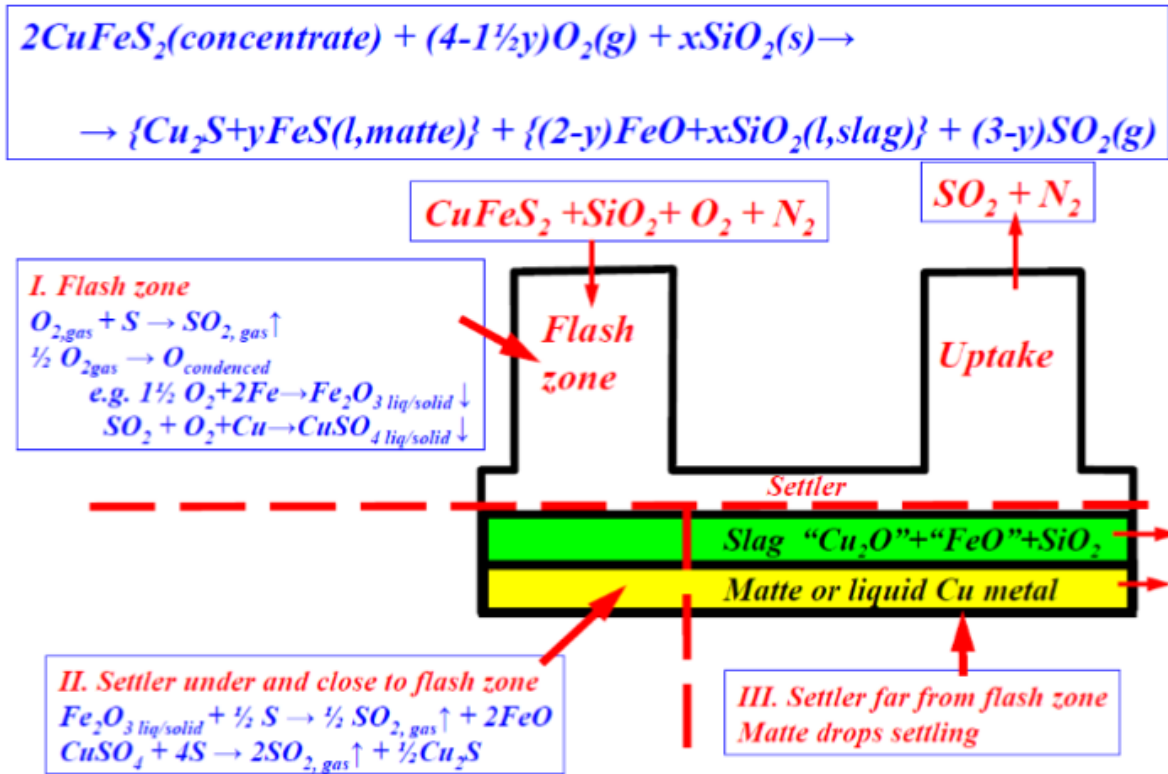
3-6: What are the main steps of extracting copper from its sulphide ores? Why it takes so many steps to get pure copper (99.99%)?

- Smelting
- Copper converting
- Fire refining
- Electro- refining

3-7: What are the objectives of copper matte smelting and matte converting? What are the main products of the matte smelting and converting operations? What are the main chemical reactions in both matte smelting and converting?

Copper matte smelting:

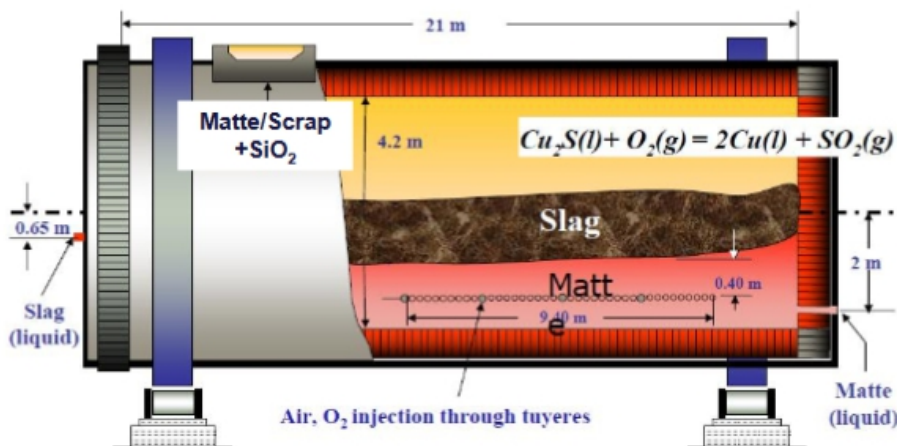
- From concentrates to a Cu-Fe-S mixture (matte) with proper grade and temperature for converting (Cu upgraded to 35-70%).
- Forming a silicate/ferrite slag, low in copper and fluid enough for easy tapping.
- Generating off-gas strong in SO₂ for acid production.



Smelting products:

- Copper matte: 35-70 wt% Cu. At high matte grade, copper in slag significantly increases. Smelting stops at 70 wt% usually adopted in industry.
- Smelting slag: FeO-SiO₂ (silicate slag), 35 wt% SiO₂, 0.5-0.9 wt% Cu in slag.
- Off-gas: SO₂ containing (10-15%) SO₂, N₂, H₂O, CO₂, O₂, H₂SO₄ acid production.

Copper matte converting: From matte to crude copper (98.5-99%)



Two stages:

Slag blow (Matte to white metal)– $\text{FeS} + 1.5\text{O}_2 + x\text{SiO}_2 \rightarrow \text{FeO} + x\text{SiO}_2 + \text{SO}_2$

Blister blow (Cu_2S to copper) – $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2$

Final products:

- Blister copper (98.5-99% Cu)
- Converter slag (Fe, total 35-50%, Fe_3O_4 15-25%, SiO_2 20-30%, Cu 2-15%)
- Off-gas

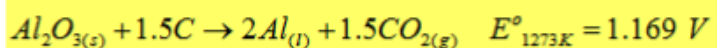
3-8: *What are the basic principles of molten salt electrolysis? What are the main aspects of the process? We know that it is more expensive than normal carbon reduction processes such as for ironmaking and lead extraction. Why we have to use it for a number of metals such as aluminium, magnesium, calcium, potassium or sodium, or rare earth metals?*

Nature of the process: Electrowinning, deposition of metals under external current.

Applications: More electro-negative metals than Mn, Aluminium, Magnesium, Calcium, Sodium and REE's.

3-9: *For molten salt electrolysis, the cell voltage is an important parameter which determines the specific power consumption (kWh/kg). Could you describe the various components which add up to the total cell voltage, and discuss the relative importance of them (using Al electrolysis as example)?*

Overall reaction



Anode: Carbon

Cathode: Molten Aluminium pool on carbon base.

- Carbon oxidation at anode: greatly reducing cell voltage, at expense of carbon consumption.
- The more positive the standard electrode potential in aqueous solutions, the easier to precipitate.
- Energy aspects electrolysis Aluminium:
 - Current: 50-300 kA
 - Cell voltage: 4-5 V
 - Current efficiency: 90-95%
 - Consumption: 15 kWh/kg + 3.6 kWh/kg for Alumina production
 - Anode consumption: 400 kg/t Al
 - Electric power: >35% cost of primary Al production

| Item | Volts/cell | Equivalent kWh/t ($\eta=86.5\%$) |
|---|-------------|---------------------------------------|
| Across the anode (anode drop) | 0.41 | 1414 |
| Across the cathode (cathode drop) | 0.46 | 1586 |
| Across the electrolyte (bath drop) | 1.87 | 6445 |
| Anode effects | 0.17 | 586 |
| Across cell conductors | 0.1 | 344 |
| Due to other circuits | 0.02 | 68 |
| Sub-total: various drops | 3.03 | 10443 |
| Effective electrolysis potential | 1.67 | 5757 |
| Grand total | 4.7 | 16200 |

Part IV : Metals Refining

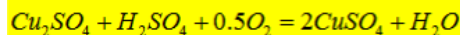
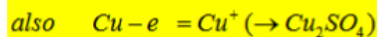
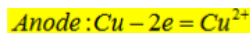
4-1: What are the basic types of metals refining operations? What are the main characteristics of each type of operation? Please give examples to illustrate the principles.

Electro-refining: Only targeted metal (anode) and precipitates (cathode).

Anode: $Me \rightarrow Me(n+) + ne^-$

Cathode: $Me(n+) + ne^- \rightarrow Me$

dissolves



4-2: What are the main objectives of steelmaking? What are the main impurities, and how are they removed during steelmaking? What are the main steelmaking processes and their key differences?

Main objectives:

Main impurities: C, Si and P are best removed in oxidising environment

S is best removed in a reducing environment

Steelmaking processes and their key differences:

Blast Furnace / Oxygen steel route

- Prime iron ore – 1400 kg/tcs
- Coal – 770 kg/tcs
- Limestone – 150 kg/tcs
- Recycled scrap – 120 kg/tcs
- Alloys

CO₂ impact ~ 2.0 t/tcs

Electric Arc Furnace route

- Recycled scrap – 880 kg/tcs
- Coal – 150 kg/tcs
- Limestone – 43 kg/tcs
- DRI or HBI
- Alloys

CO₂ impact ~ 0.7 t/tcs

Not yet suitable for all steel grades

BOF process: scrap charging → hot metal charging → O₂ blowing → tapping

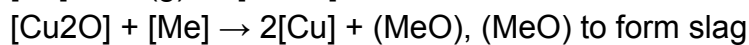
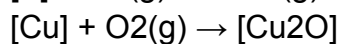
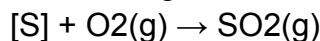
4-3: Why hot metal produced needs to be pre-treated to remove Sulphur (hot metal

desulphurization)? What are the main desulphurization reagents? What are their Sulphur removal principles (main chemical reactions and thermodynamic conditions)?

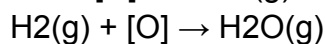
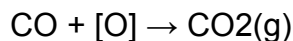
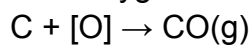
4-4: What are the objectives and chemical reactions of fire-refining of copper? How it is practiced in industry?

Fire-refining copper needs 2 stages:

Oxidation of S, together with other impurities, using O₂



Removal of oxygen: reduction with hydrocarbons

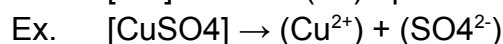


4-5: Why fire-refining of copper as well as steelmaking takes two general steps of impurity removal (oxidation and deoxidation)? Please explain what impurities have to be removed for both copper refining and steel refining?

Part V: Hydrometallurgy and electrometallurgy

5-1: Please explain the main unit operations of hydrometallurgical processes. Give one example for each type of operation.

1. Leaching: Transferring metals from solid feed into aqueous solutions.



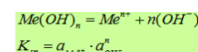
2. Purification of solution: Removing impurities, or separation of targeted metals.

Selective precipitation (hydrolysis, cementation); utilization of a carrier phase

(solvent extraction,

ion exchange,

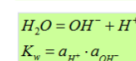
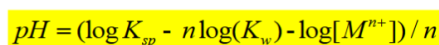
carbon-based



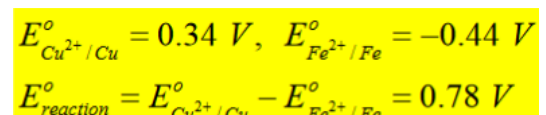
processes-

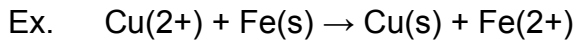
adsorption).

- Hydrolysis:



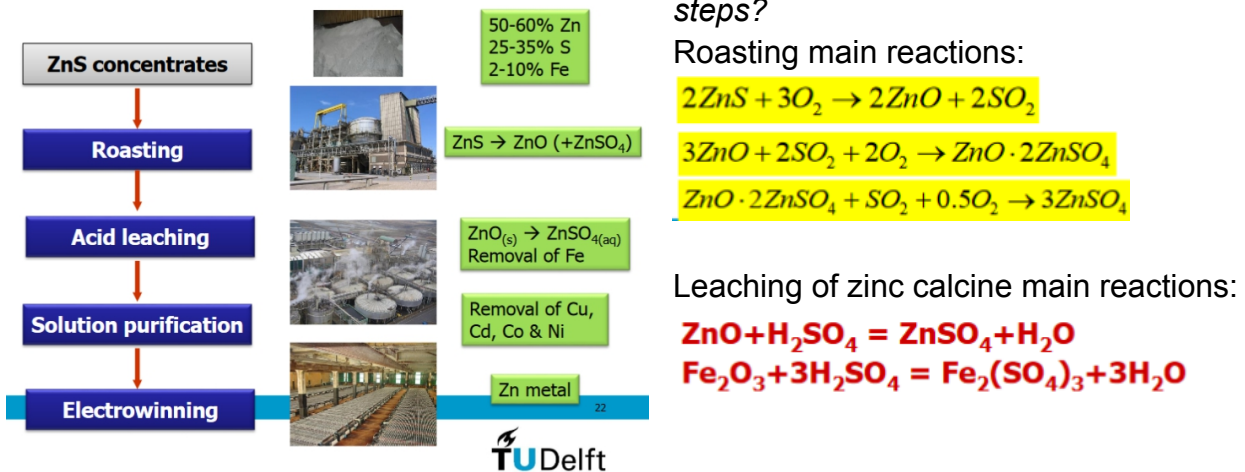
- Cementation:



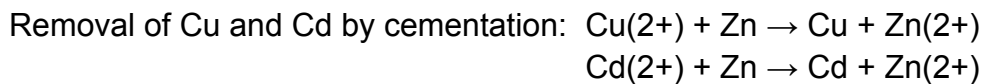


3. Metals recovery: Precipitation of metals (cementation, hydrogen reduction), electrowinning.

5-2: Please describe the complete flowsheet of hydrometallurgical zinc production from sulphide concentrates to pure zinc metal. How zinc metal is produced: the main chemical reactions for each main steps?

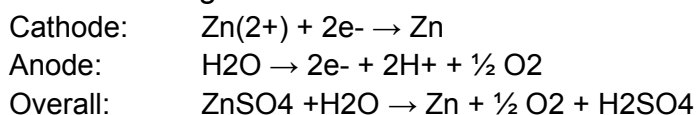


Solution purification:



Removal of Co and Ni by precipitation

Electrowinning:



5-3: Please describe the basic types of leaching processes for different types of minerals.

- Dissolution of salt in water: (sulphates and chlorides)
- Acid dissolution (metal oxides, or sulphides under pressure)
- Alkali dissolution (Bayer process, metal oxides forming complex anions soluble in water)
- Anion exchange
- Complexation increasing solubility
- Redox reactions (oxides, or sulphides under pressure of O_2 or another oxidant)

5-4: What thermodynamic and kinetic factors influence the leaching process?

Thermodynamics: Solubility, leaching reaction should be selective for the targeted metals □ Important factors: temperature, concentration of lixiviant (acidity or alkalinity), liquid to solid ratio.

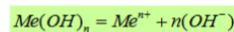
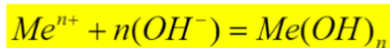
Kinetics: Surface reaction, diffusion of lixiviant in liquid and solid particles, product diffusion, mixing □ Parameters: particle size, mineralogy, temperature, pressure,

5-5: What is hydrolysis and where it is used in hydrometallurgical processes? What factors influence the hydrolysis?

Hydrolysis = hydroxide precipitation.

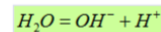
It is used in the hydrometallurgical process after the leaching step, for purification of the solution (selective precipitation).

Influenced by: pH and temperature

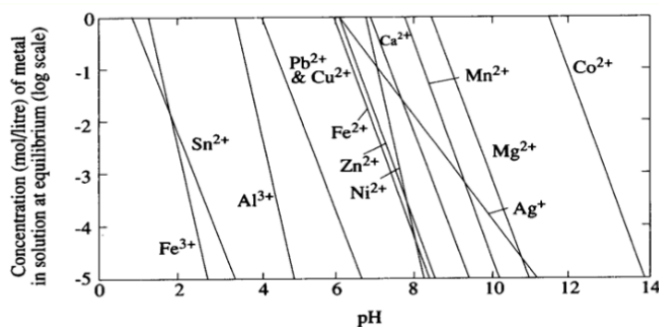


$$K_{sp} = a_{Me^{n+}} \cdot a_{OH^-}^n$$

$$pH = (\log K_{sp} - n \log(K_w) - \log[M^{n+}]) / n$$



$$K_w = a_{H^+} \cdot a_{OH^-}$$



30

5-6: What types of precipitation processes are available in hydrometallurgical processes? Using examples to explain how they are applied in hydrometallurgical processes (for metal extraction or precipitation of compounds)?

Hydrolysis

Cementation

5-7: What is the nature of electrometallurgy? What types of electrometallurgical processes are available and how they are used in extraction and refining of metals?

The nature of electrolysis (in aqueous solutions), reactions:

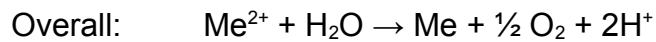
Cathode (-) : $Me^{2+} + ne^- \rightarrow Me$

Or $2H^+ + 2e^- \rightarrow H_2(g)$ // $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ □ important issue

Anode (+) : $H_2O \rightarrow \frac{1}{2} O_2(g) + 2H^+ + 2e^-$ (pH □) (for sulphate)

Or $2Cl^- \rightarrow Cl_2(g) + 2e^-$ (for chloride, no pH change)

Or $Me \rightarrow Me^{n+} + ne^-$ (for electro-refining)



Different electrometallurgical processes:

(All discussed in previous questions..)

- Electro-winning
- Electro-refining
- Molten salt electrolysis

5-8: What are the basic principles of electrowinning and electrorefining in aqueous solutions? Please explain how an electrolytic cell works (electrowinning and electrorefining). Please describe briefly the zinc electrowinning and copper electrorefining processes.

Electrolytic cell:

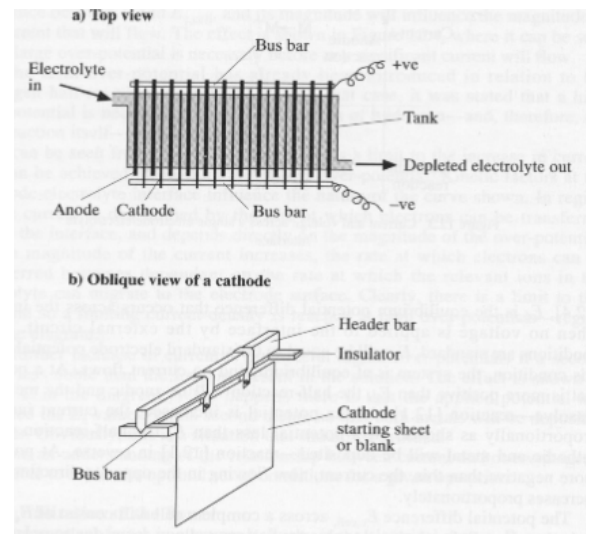
Cathode = sheet of the same metal or blank (steel/Al)

Anode = soluble metals, or sulphide, crude metal

Electrolyte = mostly sulphates/acidic, or chloride/acidic, alkaline (NaOH)

Electrowinning Zinc: (discussed in previous questions)

Electrorefining Copper: (discussed in previous questions)



5-9: What influences the cell voltage? How specific power consumption (kWh/kg metal) is determined for electrowinning process?

Influences on cell voltage:

- Standard electrode potentials
- Current efficiency

Specific power consumption: $P = \frac{V}{\eta \cdot q} = [kWh/kg]$

- V = cell voltage (Volts)
- η = current efficiency (%)
- q = theoretical amount of produced metal by passing 1 Ampere for 1h [g/(Ah)]

5-10: What is current efficiency? How current efficiency affect the electrowinning or electrorefining operation?

Current efficiency: percent current for deposition of targeted metal (due to side reactions, impurity or H₂ deposition, short circuit).

Effect:

5-11: Electrowinning of zinc: In order to produce 200,000 tones of zinc per year in an electrowinning plant, how much energy would be needed (kWh)? Suppose the plant is running in a year on average 300 net days, how big current needs to be supplied? Please use the following information as calculation basis:

(1) 1 tank house holds 40 cathodes (each cathode with 2 sides, and an area of 3 m² on each side);

(2) Current density on the cathode is 600 A/m².

(3) Please make a proper arrangement of the tank house (series or parallel and their combinations).

You can make other necessary assumptions (cell voltage, current efficiency etc.)

$$40(\text{cathodes}) \times 3 \text{ m}^2 = 240 \text{ m}^2 \text{ cathodes}$$

$$600(\text{A/m}^2) \times 240(\text{m}^2) = 144000 \text{ A}$$

$$q_{\text{zn}} = 1.2198 \text{ g/(Ah)} \text{ (from slides)}$$

$$\eta = 88\text{-}92\% \text{ (from slides)}$$

$$U = 3.3\text{-}3.4 \text{ V (from slides)}$$

$$P = \frac{U}{\eta q} = \frac{3.3}{0.9 \times 1.2198} = 3 \text{ kWh/kg}$$

Part VI: Phase diagrams

Please refer to Dr. Voncken's lecture notes and lecture presentations, and examples.

Part VII: Basic metallurgical calculations

7-1: You should be able to conduct basic thermodynamic calculations: for enthalpy change of a reaction, Gibbs free energy change of a reaction, thermodynamic equilibrium (compositions), and combustion of fuels.

Refer to various examples handled in the computer Practicals.

7-2: You should be able to read and use various types of graphical representation of metallurgical systems. Please read "chapter 2.3 Graphical representation of thermodynamic data" by Bodsworth, and other related chapters by Woolacott and Phase diagrams (binary and ternary) by Voncken as is supplied in the dictaat.

- Ellingham diagrams: understanding the oxide reduction process and metal refining through oxidation (thermodynamic conditions). How Ellingham diagram was constructed? How to judge the thermodynamic conditions (temperature, partial pressure ratio of CO₂ to CO) for oxide reduction with carbon (carbothermic reduction) and CO gas?
- Kellogg diagrams: understanding the sulphide roasting process and products. How Kellogg diagram is constructed, and please try to construct manually at

least part of the Kellogg diagram for Zn-S-O system? What are the chemical reactions of the border lines of the diagram?

- Phase diagrams: understanding, reading and drawing a liquid cooling process (refer to Part VI).