Unit 10 · Metallurgy

STUDY NOTES

Key terms

Native: found as the metal itself (gold, platinum; sometimes silver, copper). **Combined**: found as compounds.

Mineral: natural substance in the crust with a definite composition.

Ore: a mineral the metal can be extracted from **easily and profitably**.

Gangue: rock, sand and earth mixed with the ore.

Flux: added to join the gangue into a liquid. **Slag**: that liquid waste.

Metallurgy: extracting a metal from its ore and purifying it.

Roasting: heating strongly in plenty of air (sulphide ores). **Calcination**: with little or no air (carbonate, hydrated ores).

Smelting: reduction hot enough to melt the metal.

Pig iron: from the blast furnace, about 93–95% Fe, 3.5–4.5% C; hard, brittle.

Aqua regia: 3 conc. HCl : 1 conc. HNO_3, by volume.

Passive: an oxide film stops the reaction (Fe, Al in conc. HNO_3).

Formulas

$\%\ \text{Fe} = (\text{mass of Fe in formula} \div M) \times 100\%$	hematite $112 \div 160 = 70\%$ **Use:** magnetite 72.4%, siderite 48.3%
$\rho = m/V$	density test of gold **Use:** 19.3 g/cm^3 pure
$\text{pure gold} = \text{mass} \times \text{carat} \div 24$	24 carat pure **Use:** 1 tola (11.66 g) of 22-carat: 10.69 g

- 1 t of ore, 80% Fe_2O_3: $800 \times 112/160 = 560$ kg Fe; 600 L CO at STP per kg Fe
- 30 kg SiO_2 needs 50 kg $CaCO_3$, makes 58 kg $CaSiO_3$

Steps of metallurgy

1. **crushing, grinding**: crushers, ball mills; more surface
2. **concentration**: gravity (hematite), magnetic (magnetite), froth flotation (sulphides)
3. **roasting** $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$; **calcination** $ZnCO_3 \rightarrow ZnO + CO_2$
4. **reduction**: C or CO for Zn, Fe, Pb, Cu; electrolysis for Na, Mg, Al
5. **refining**: distillation (Zn, Hg), electro-refining (Cu)

- clay has aluminium but isn't an ore; bauxite is

Ores of iron

Ore	Formula	Fe
hematite	Fe_2O_3	70%
magnetite	Fe_3O_4	72%
limonite	$2Fe_2O_3 \cdot 3H_2O$	60%
siderite	$FeCO_3$	48%
iron pyrites	FeS_2	47%

- hematite mainly; pyrites not used (sulphur costly, SO_2 pollutes): for sulphuric acid
- Nepal: Dhaubadi, Nawalparasi, 2016, mostly hematite; no blast furnace yet

Extraction of iron

- **crushing**: jaw crushers, ball mills
- **concentration**: washing, hematite (about 5 g/cm^3) settles; magnet for magnetite
- **calcination** (little air):
  - $2Fe_2O_3 \cdot 3H_2O \rightarrow 2Fe_2O_3 + 3H_2O$
  - $FeCO_3 \rightarrow FeO + CO_2$
  - $4FeO + O_2 \rightarrow 2Fe_2O_3$ (else $FeO + SiO_2 \rightarrow FeSiO_3$, iron lost)
  - $S \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$
  - ore porous
- **smelting**:
  - blast furnace, 30 m or more, fire-brick lining
  - charge ore : coke : limestone about 8 : 4 : 1
  - hot blast about 1,000 °C (Cowper stoves) through **tuyeres**

Zone, bottom up	°C	Reactions
combustion	1,300–1,500	$C + O_2 \rightarrow CO_2$ + heat
fusion	1,200–1,300	$CO_2 + C \rightarrow 2CO$ − heat; iron melts; $3Fe + C \rightarrow Fe_3C$; $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
slag formation	700–1,000	$CaCO_3 \rightarrow CaO + CO_2$; $CaO + SiO_2 \rightarrow CaSiO_3$
reduction	400–700	$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ (spongy iron)

- **coke**: fuel and source of the reducing agent, CO
- slag floats, protects the iron from the blast; slag hole above, tap hole below; waste gases N_2, CO_2, CO heat the stoves
- slag used for cement, roads
- order matters, ranges differ between books: reduction top (coolest), combustion bottom (hottest)
- flow sheet: ore → crushing → concentration (gangue out) → calcination (H_2O, CO_2, SO_2, As_2O_3 out) → blast furnace (coke, limestone, hot air in; slag, gases out) → pig iron

	Cast iron	Steel	Wrought iron
carbon	2–4.5%	0.1–1.5% (to 2%)	under 0.1%
properties	hard, brittle; easy to cast	strong, tough; rolled, welded	purest, soft, tough
uses	manhole covers, stoves, karahis	rods, vehicles, tools	chains, gates

- steel: oxygen blown onto pig iron (basic oxygen process); + Cr, Ni = stainless steel
- hydrogen reduction: $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$, steam not CO_2; about 1,180 g CO_2 per kg Fe from reduction alone

Five metals

	Fe	Cu	Al	Ag	Au
color	silvery gray	reddish brown	silvery white	shiny white	yellow
density (g/cm^3)	7.87	8.93	2.70	10.5	19.3
melts (°C)	1,538	1,085	660	962	1,064
conductivity	5th	2nd	4th	1st	3rd
magnetic	yes	no	no	no	no

- **iron**:
  - steel for buildings, bridges, vehicles
  - stainless utensils
  - electromagnet cores
  - hemoglobin
- **copper**:
  - wires, motor coils
  - pipes, pot bottoms
  - gagri, karuwa
  - brass (Cu + Zn), bronze (Cu + Sn)
  - Patan's lost-wax statues
- **aluminium**:
  - oxide layer, no rust
  - pots, foil
  - aircraft (duralumin)
  - power lines (steel core)
  - cans
  - Hall and Héroult 1886
  - recycling saves about 95%
- **silver**:
  - best conductor and reflector
  - jewelry, coins, mirrors, contacts, solar panels
  - tarnishes black (sulphide)
- **gold**:
  - never tarnishes
  - most malleable
  - leaf about 10^{-4} mm
  - jewelry, reserves, contacts, dentistry

With acids

Reactivity: K, Na, Ca, Mg, **Al**, Zn, **Fe**, Pb, (H), **Cu**, Hg, **Ag**, Pt, **Au**. Above H: hydrogen from dilute HCl, H_2SO_4.

- $Fe + 2HCl \rightarrow FeCl_2 + H_2$; $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$ (pale green, Fe^{2+})
- $2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$; $2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2$ (slow at first: oxide coat)
- Cu, Ag: no reaction (slowly with air: $2Cu + 4HCl + O_2 \rightarrow 2CuCl_2 + 2H_2O$; no pickles in copper)
- hydrogen test: burning splinter, squeaky **pop**
- 2.7 g Al → 3.36 L H_2; 5.6 g Fe → 2.24 L

Nitric acid: an oxidizing agent; N (+5) reduced, **no hydrogen** (except Mg, Mn, very dilute, cold)

Product	N	Acid
NO_2, brown	+4	concentrated
NO, colorless	+2	dilute (about 1 : 1)
N_2O	+1	more dilute
NH_4^+ (NH_4NO_3)	−3	very dilute, cold

- $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$ (blue); 19.05 g Cu → 4.48 L NO
- $3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O$
- cold, very dilute: $4Fe + 10HNO_3 \rightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$; stronger: $Fe + 4HNO_3 \rightarrow Fe(NO_3)_3 + NO + 2H_2O$
- $Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + 2H_2O$ (slow); conc. HNO_3: Fe, Al passive
- brown fumes: $2NO + O_2 \rightarrow 2NO_2$
- check by electrons: 3 Cu give 6; 2 N (+5 → +2) take 6

Aqua regia

- $HNO_3 + 3HCl \rightarrow NOCl + 2H_2O + 2[Cl]$; $Au + 3[Cl] \rightarrow AuCl_3$; $AuCl_3 + HCl \rightarrow HAuCl_4$ (yellow)
- overall: $Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O$
- HNO_3 oxidizes; Cl^- holds gold as $AuCl_4^-$
- silver doesn't dissolve: AgCl coat
- de Hevesy, 1940: two Nobel medals dissolved, recast after the war

COMMON MISTAKES

✗ coke reduces the ore
✓ mostly CO does; coke is fuel and makes it.

✗ reduction zone at the bottom
✓ near the top, coolest.

✗ every mineral is an ore
✓ only if easily and profitably extracted.

✗ pig iron is soft
✓ hard, brittle.

✗ Fe_2O_3 is 56/160 iron
✓ 112/160.

✗ nitric acid gives hydrogen
✓ oxides of nitrogen.

✗ Fe + dilute acid → Fe^{3+}
✓ Fe^{2+} with HCl, H_2SO_4.

✗ aqua regia dissolves silver
✓ AgCl coat stops it.