Metal extraction

The occurrence of metals in the Earth's crust
•Rocks that contain a high enough percentage of a metal to be extracted commercially are known as ores .
•Aluminium and iron are the most abundant metals in the Earth's crust.
•Most compounds are found as **oxides** or **sulphides**, but sulphides are usually converted to oxides before extraction.

Converting sulphides to oxides
Sulphides ores are usually converted to oxides before extraction by roasting with oxygen.

The most important ore of zinc is mostly zinc sulphide

$$2\,ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

or copper can be extracted from copper(I) sulphide

$$Cu_2S + 2O_2 \rightarrow 2CuO + SO_2$$

The oxide is then reduced with a suitable reducing agent such as carbon.
Sulphur dioxide is an acidic gas that can form acid rain if released into the atmosphere.
The sulphur dioxide can be used, however, to form sulphuric acid by the contact process

Methods of extraction
The extraction of metals involves **reduction**, usually of metal oxides.
This reduction of the metal compound is usually done in one of the following ways:
•by heating with carbon (in the form of coke)
•by heating with hydrogen
•by heating with a more reactive metal (active metal)
•by electrolysis

Which method is used depends on:

•the energy requirements
extraction uses large amounts of energy (electricity and / or heat)

•the cost of the reductant
Carbon , which is cheap, is widely used, but sometimes more reactive metals are required which are very costly

•the metal purity required
the higher the required purity, the greater the cost in obtaining that purity

Method 1: Reduction of metal oxides with carbon

Carbon and carbon monoxide are cheap, effective and readily available reducing agents

Iron, manganese and **copper** are extracted using C and CO

In theory all metals can be extracted this way, but for some
- the temperature required is excessively high
- metal carbides are formed rather than the metal itself (e.g. tungsten, titanium)

$Fe_2O_{3(s)} + 3\,CO_{(g)} \rightarrow 2\,Fe_{(l)} + 3\,CO_{2(g)}$ Occurs at about 1200ºC

$Fe_2O_{3(s)} + 3\,C_{(s)} \rightarrow 2\,Fe_{(l)} + 3\,CO_{(g)}$ Occurs at higher temps

excess C is easily removed in the steel making process

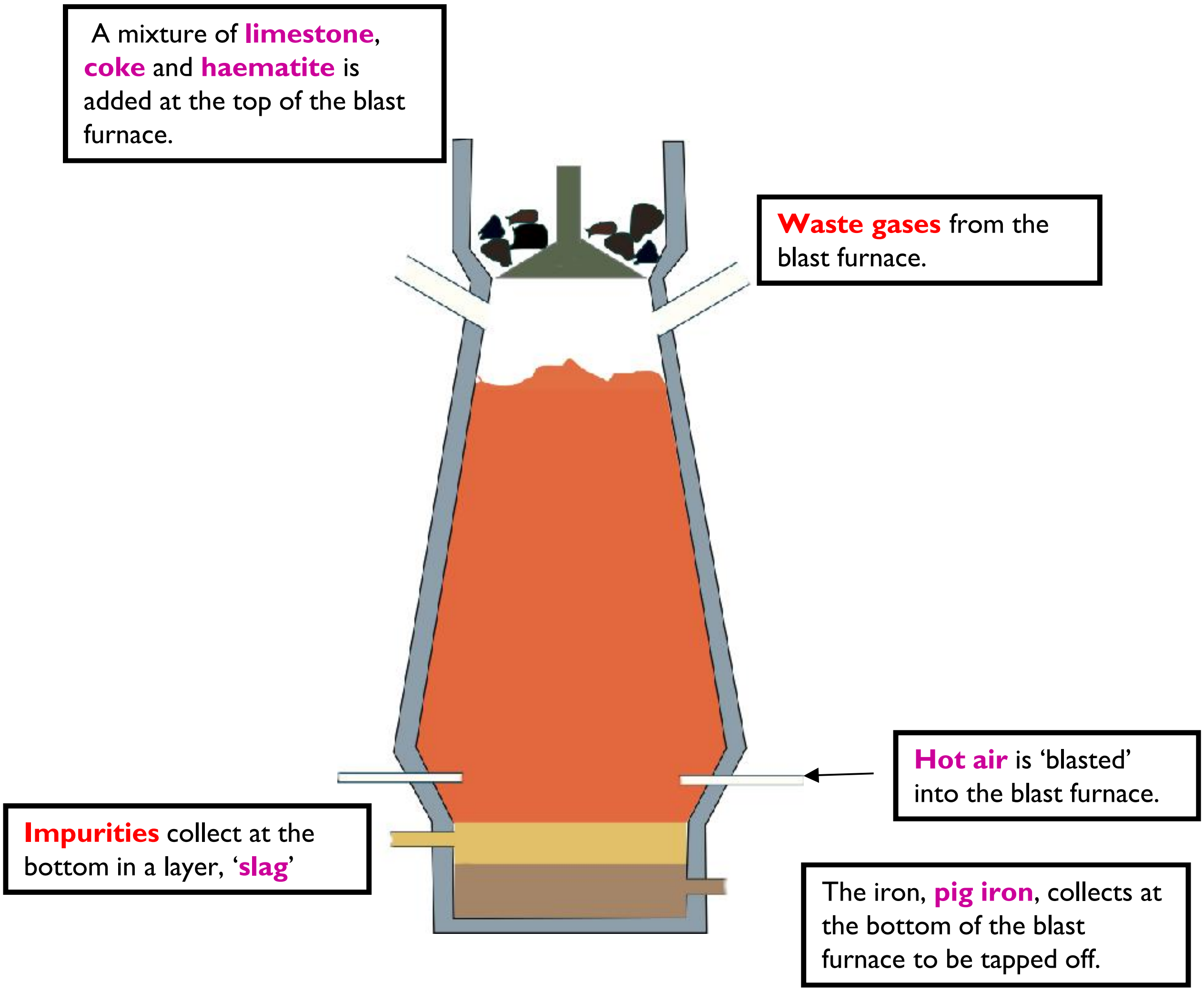
$MnO_2 + C \rightarrow Mn + CO_2$

$2\,CuO + C \rightarrow 2\,Cu + CO_2$

The CuO comes from the thermal decomposition of malachite

$CuCO_3 \rightarrow CuO + CO_2$

Pollution problems arise from using carbon, giving CO_2 (a greenhouse gas) and CO (toxic)



Method 2: Extraction by electrolysis

When a metal is more reactive than carbon (e.g. aluminium), it can not be extracted by reduction with carbon; electrolysis is usually used. Electrolysis is not used if the metal has to be very pure.

The main cost in this process is the electricity – so a cheap supply is needed – plants are often built near hydroelectric power stations.

The raw materials for the extraction of aluminium are purified aluminium oxide (Al_2O_3) and cryolite (Na_3AlF_6).

The aluminium oxide must be molten or dissolved to conduct electricity.

It is dissolved in molten cryolite (this lowers the melting point of the aluminium oxide, increases conductivity and therefore reduces cost).

Without using the cryolite, the aluminium oxide melts at too high a temperature which makes the process uneconomic.

Electrode Reactions

cathode $Al^{3+} + 3e^- \rightarrow Al$

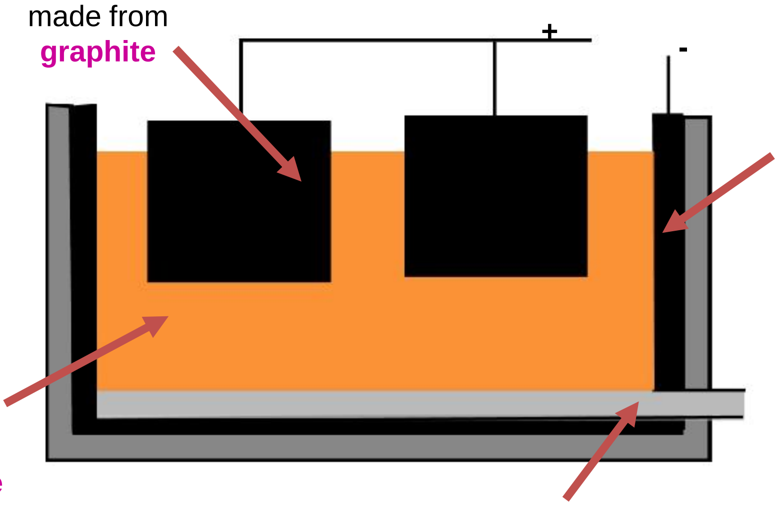
anode $2O^{2-} \rightarrow O_2 + 4e^-$

The oxygen gas formed at the anode then reacts with the graphite (carbon) anode and forms carbon dioxide

$$C + O_2 \rightarrow CO_2$$

The anode therefore disintegrates and has to be replaced frequently.

Oxygen gas formed at the anode, reacts with the carbon to form CO_2. The anode disintegrates and has to be replaced frequently.



Method 3: Reaction with a more reactive metal

Titanium is a very useful metal because it is abundant, has a low density and is corrosion resistant – it is used for making strong, light alloys for use in aircraft for example.

Titanium is extracted by reaction with a more reactive metal (e.g. Mg, Na).

Titanium cannot be extracted with carbon because titanium carbide (TiC) it is formed rather than titanium (similar reactions take place for vanadium, tungsten and molybdenum). Titanium cannot be extracted by electrolysis because it has to be very pure.

Steps in extracting Titanium

1. TiO_2 (solid) is converted to $TiCl_4$ (liquid) at 900°C:
2. The $TiCl_4$ is purified by fractional distillation in an Ar atmosphere.
3. The Ti is extracted by Mg or Na in an Ar atmosphere at 500°C

$$TiO_2 + 2\,Cl_2 + 2\,C \rightarrow TiCl_4 + 2\,CO$$

$$TiCl_4 + 4\,Na \rightarrow Ti + 4\,NaCl$$

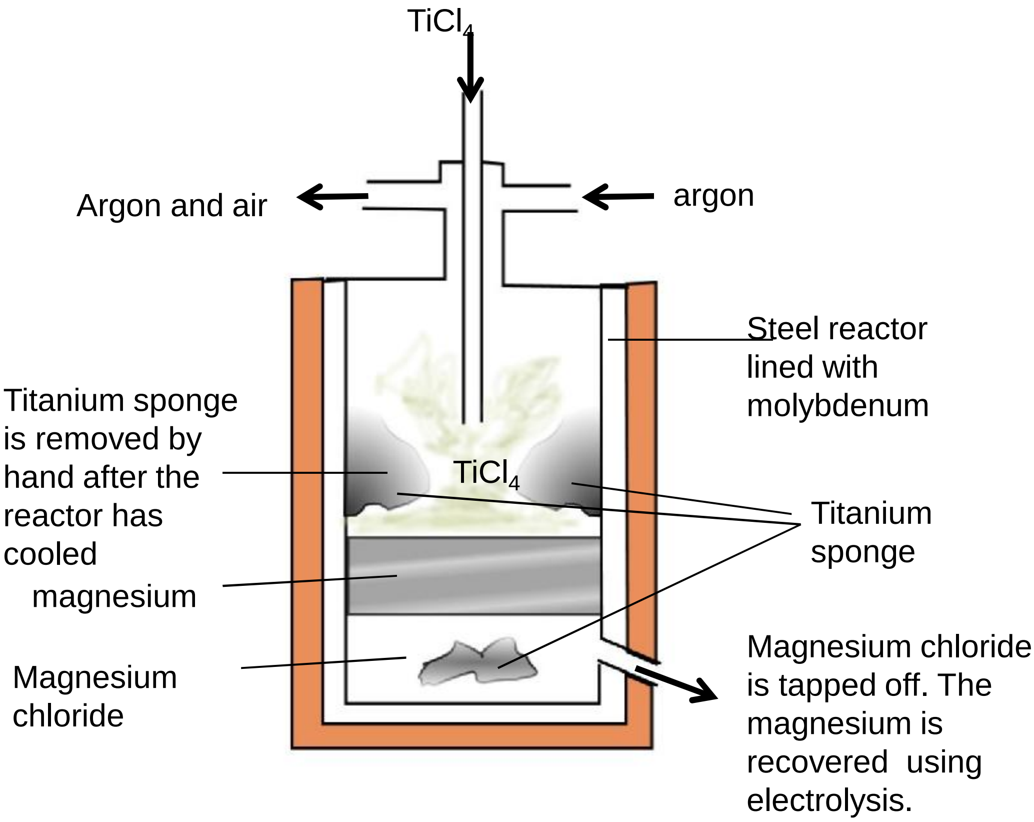
$$TiCl_4 + 2Mg \rightarrow Ti + 2\,MgCl_2$$

Titanium is expensive because

1. The expensive cost of the Na or Mg
2. This is a batch process which makes it expensive because the process is slower (having to fill up and empty reactors takes time) and requires more labour and the energy is lost when the reactor is cooled down after stopping
3. The process is also expensive due to the Ar, and the need to remove moisture (as $TiCl_4$ is susceptible to hydrolysis).
4. High temperatures required in both steps

TiO_2 is converted to $TiCl_4$ as it can be purified by fractional distillation, $TiCl_4$ being molecular (liquid at room temperature) rather than ionic like TiO_2 (solid at room temperature).

This all makes titanium expensive even though it is a relatively abundant metal. It is only therefore used to a limited amount even though it has useful properties



Method 4: reduction by hydrogen (e.g. W)

Tungsten cannot be extracted with carbon because tungsten carbide (WC) is formed rather than tungsten.

$WO_3 + 3 H_2 \rightarrow W + 3 H_2O$ Tungsten (VI) oxide (WO_3) is heated with hydrogen at 900°C.

Hydrogen is a **reducing agent** in this reaction

There are risks of explosions and problems with storage with using hydrogen that must be carefully managed

Advantages of using hydrogen

no pollution (from CO, CO_2)
readily available from H_2O or CH_4

Will give higher purity than using Carbon

Most methods (except electrolysis) are variations of displacement reactions, where a reducing agent is added to the metal ore. You should be able to construct equations for unusual combinations of ores and reducing agents e.g. $2V_2O_5 + 5Si \rightarrow 4V + 5SiO_2$ $AlCl_3 + 3Na \rightarrow 3NaCl + Al$

Environmental aspects of metal extraction

We need to recycle metals as supplies will not last for ever

Recycling metals:
- saves resources (e.g. metal ores)
- creates less waste (e.g. mining waste)
- saves energy resources (less energy to re-cycle than make from ore, e.g. recycling Al uses 5% of energy used to extract)
- Scrap removed from countryside or from landfill
- reduces air pollution (e.g. CO_2 – greenhouse effect, SO_2 – acid rain, CO - toxic)

However, there are costs associated with collecting, sorting and transporting metals to be recycled that have to be factored into the overall financial and energy costs.

Extracting copper with scrap iron

Copper can also be extracted by using the displacement reaction of **scrap iron** with an aqueous solution of copper. This solution can be made by reacting sulphuric acid with copper ores (can be done with low grade ores). The **more reactive iron** displaces the copper by **reducing the copper ions.**

$Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Compared to the high temperature carbon reduction of copper oxide this
- uses less energy,
- can work with lower grade ores and so is more sustainable
- Would work with low quality scrap iron so saves this being wasted.

The copper solution can be formed from low grade ores or from scrap recycled copper