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
\[ 2 \text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2 \]
or copper can be extracted from copper(I) sulphide
\[ \text{Cu}_2\text{S} + 2\text{O}_2 \rightarrow 2\text{CuO} + \text{SO}_2 \]
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.

\[
\begin{align*}
\text{Fe}_2\text{O}_3(s) + 3 \text{CO}(g) & \rightarrow 2 \text{Fe}(l) + 3 \text{CO}_2(g) \quad \text{Occurs at about 1200°C} \\
\text{Fe}_2\text{O}_3(s) + 3 \text{C}(s) & \rightarrow 2 \text{Fe}(l) + 3 \text{CO}_2(g) \quad \text{Occurs at higher temps}
\end{align*}
\]

excess C is easily removed in the steel making process

\[
\text{MnO}_2 + \text{C} \rightarrow \text{Mn} + \text{CO}_2
\]

The CuO comes from the thermal decomposition of malachite

\[
\text{CuCO}_3 \rightarrow \text{CuO} + \text{CO}_2
\]

Pollution problems arise from using carbon, giving CO2 (a greenhouse gas) and CO (toxic)

A mixture of limestone, coke and haematite is added at the top of the blast furnace.

Waste gases from the blast furnace.

Impurities collect at the bottom in a layer, ‘slag’

The iron, pig iron, collects at the bottom of the blast furnace to be tapped off.

Hot air is ‘blasted’ into the blast furnace.
The cathode is made from graphite. The anode is made from graphite. The electrolyte contains molten aluminium oxide dissolved in molten cryolite, at a temperature of 950°C. The anode is made from graphite. The cathode is made from graphite. The aluminium ions are attracted to the cathode, gain three electrons to form liquid aluminium. Oxygen gas formed at the anode, reacts with the carbon to form CO₂. The anode therefore disintegrates and has to be replaced frequently. The oxygen gas formed at the anode then reacts with the graphite (carbon) anode and forms carbon dioxide. The anode therefore disintegrates and has to be replaced frequently. 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 (Al₂O₃) and cryolite (Na₃AlF₆). 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. When a metal is more reactive than carbon (e.g. aluminium), it cannot be extracted by reduction with carbon; electrolysis is usually used. Electrolysis is not used if the metal has to be very pure. Method 2: Extraction by electrolysis

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

The raw materials for the extraction of aluminium are purified aluminium oxide (Al₂O₃) and cryolite (Na₃AlF₆).

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.

Oxygen gas formed at the anode, reacts with the carbon to form CO₂. The anode disintegrates and has to be replaced frequently.

Electrode Reactions

cathode: \[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \]

anode: \[ 2\text{O}^{2-} \rightarrow \text{O}_2 + 4e^- \]

The oxygen gas formed at the anode then reacts with the graphite (carbon) anode and forms carbon dioxide. C + O₂ → CO₂

The anode therefore 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).

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

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

Titanium cannot be extracted with carbon because titanium carbide (TiC) 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.
Method 4: reduction by hydrogen (e.g. W)

W\text{O}_3 + 3 \text{H}_2 \rightarrow \text{W} + 3 \text{H}_2\text{O} \quad \text{Tungsten (VI) oxide (WO}_3\text{) is heated with hydrogen at 900°C.}

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

Hydrogen is a reducing agent in this reaction

Advantages of using hydrogen
no pollution (from CO, CO\textsubscript{2})
readily available from H\textsubscript{2}O or CH\textsubscript{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\textsubscript{2}O\textsubscript{5} + 5Si → 4V + 5SiO\textsubscript{2} \quad \text{AlCl}_3 + 3\text{Na} → 3\text{NaCl} + \text{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\textsubscript{2} – greenhouse effect, SO\textsubscript{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.

\[ \text{Cu}^{2+}(\text{aq}) + \text{Fe(s)} \rightarrow \text{Cu(s)} + \text{Fe}^{2+}(\text{aq}) \]

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

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.