Topic 2.7

EXTRACTION OF METALS

Extraction of Iron Extraction of Aluminium Extraction of Titanium Recycling

EXTRACTING METALS FROM THEIR ORES

Most metals do not occur native. They exist in compounds, usually oxides or sulphides. These compounds are known as **minerals**. A rock which contains this mineral is called an **ore**.

A number of methods are used to extract metals from their ores.

The best method to use depends on a number of factors:

- Will the method successfully extract the metal?
 - This depends on the reactivity of the metal
- How much do the reactants cost?
 - Raw materials vary widely in cost
- What purity is needed, and are the purification methods expensive? Some metals are not useful unless very pure, others are useful impure
- How much energy does the process use? High temperatures and electrolysis use a lot of energy
- How efficiently, and in what quantities, can the metal be made? Continuous processes are more efficient than batch processes
- Are there any environmental considerations?
 - Some processes produce a lot of pollutants

Three different methods will be considered in this topic:

Reduction of metal oxides with carbon: this is used in the extraction of **iron**.

Reduction of metal halides with more reactive metals: this is used in the extraction of **titanium**.

Electrolysis of the metal ore: this is used in the extraction of **aluminium**.

Reduction of the metal oxide with hydrogen: this is used in the extraction of **tungsten**.

As these extraction processes are expensive and the supply of ore is not infinite, it is essential to **recycle** the metal as much as possible.

SULPHIDE ORES

Sulphide ores cannot be converted directly into the metal. Instead they must be converted to the oxide. This is achieved by **roasting them in air**:

- $2ZnS + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$
- $2PbS + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$

This process causes problems because of the large quantity of sulphur dioxide produced. Sulphur dioxide is one of the principal causes of acid rain.

However if the sulphur dioxide can be collected before being released into the atmosphere, it can be used to make sulphuric acid.

REDUCTION OF METAL OXIDES WITH CARBON

Metals which are below carbon in the reactivity series are often extracted from their ores by reacting the ores with carbon and carbon monoxide -a cheap and effective method. Iron is the most important example of this.

1. Extraction of iron

The cheapest reducing agent capable of reducing iron from its principal ore, haematite (Fe_2O_3) , is carbon monoxide. Iron is extracted from haematite by reaction with CO in the **Blast Furnace**.

Coke and haematite are added continuously to the top of the blast furnace. Hot air is blown into the base of the furnace.

The following reactions constitute a summary of the chemical processes taking place in the blast furnace:

a) heating the furnace

The coke reacts with the oxygen at the base of the furnace to produce carbon dioxide. This is an exothermic reaction and keeps the furnace hot:

• $C(s) + O_2(g) \rightarrow CO_2(g)$

b) making the reducing agent

The carbon dioxide rises up the furnace and reacts with more coke to produce carbon monoxide. This is an endothermic reaction:

• $C(s) + CO_2(g) \rightarrow 2CO(g)$

c) reducing the iron oxide

The carbon monoxide is a reducing agent and reduces the haematite to iron:

• $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$

The liquid iron sinks to the base of the furnace and is tapped off.

Some of the haematite is reduced directly by the carbon:

• $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$

The ore often contains other oxides such as Fe_3O_4 or FeO, which are also reduced by carbon:

- $Fe_3O_4(s) + 4C(s) \rightarrow 3Fe(s) + 4CO(g)$
- $FeO(s) + C(s) \rightarrow Fe(s) + CO(g)$

2. Extraction of manganese and copper

Copper and manganese can also be extracted from their oxides in the blast furnace in a similar way:

 $MnO_{2}(s) + 2CO \rightarrow Mn(l) + 2CO_{2}(g)$ $MnO_{2}(s) + 2C(s) \rightarrow Mn(l) + 2CO(g)$

 $CuO(s) + CO(g) \rightarrow Cu(l) + CO_2(g)$ $CuO(s) + C(g) \rightarrow Cu(l) + CO(g)$

3. Advantages and disadvantages of the process

advantages:

- the raw materials are very cheap
- the reaction is exothermic, so less energy is needed to keep the furnace hot
- the purity of the iron is sufficient for most steel-making purposes
- it is a **continuous** process which means iron can be made more efficiently

disadvantages:

- the use of carbon does mean carbon dioxide is released (it is a greenhouse gas)
- metals which are higher than carbon in the reactivity series (eg aluminium) cannot be extracted in this way
- metals which react with carbon to form carbides (eg titanium and tungsten) cannot be extracted in this way
- metals that need to be very pure cannot be produced in this way, as the metal produced always contains significant quantities of carbon

REDUCTION OF OXIDES BY ELECTROLYSIS

Metals which form ionic oxides can be extracted by electrolysis of the metal oxides. As this is expensive it is generally used for metals which are too reactive to be reduced by any chemical means. Aluminium is one such example.

Aluminium is the third most abundant element in the earth's crust, and the most abundant metal. It occurs predominantly as bauxite, which is an impure form of aluminium oxide, Al_2O_3 .

Almost 800 million tonnes of aluminium are extracted each year from bauxite, and so the extraction of aluminium is of immense commercial importance.

The extraction of aluminium takes place in two principal stages; the purification of Al_2O_3 from bauxite and the electrolysis of purified Al_2O_3 .

1. Extraction of aluminium

Once the bauxite has been purified, electrolysis can start.

 Al_2O_3 has a melting point of 2000°C, which is too high to enable it to be electrolysed feasibly. It is thus dissolved in molten cryolite, Na_3AlF_6 , and the solution is electrolysed at 900°C.

Oxygen is liberated at the anode, which is made of graphite:

• $2O^{2-} \rightarrow O_2(g) + 4e$

Aluminium is liberated at the cathode, which is also made of graphite:

• $Al^{3+}+3e \rightarrow Al(l)$

The overall cell reaction is thus as follows:

• $2Al_2O_3 \rightarrow 4Al(1) + 3O_2(g)$

The cell can be drawn as follows:



The cylinders in the middle of the cell are the anodes. The sides and base of the container are the cathodes.

The molten aluminium sinks to the bottom of the cell and can be tapped off.

The oxygen liberated at the anode reacts with the graphite electrode, which burns slowly:

• $C(s) + O_2(g) \rightarrow CO_2(g)$

The anode must therefore be regularly replaced.

2. Advantages and disadvantages of the process

advantages:

- it is a **continuous** process, so is efficient
- it makes the metal in pure form

disadvantages:

- the cost of melting the aluminium and supplying the energy for electrolysis is very high
- it only works for ionic oxides

REDUCTION OF METAL HALIDES WITH MORE REACTIVE METALS

In many cases, carbon cannot be used to reduce the metal oxide to the metal as the metal reacts with carbon to form the carbide instead. This is the case with tungsten and titanium:

- $TiO_2(s) + 3C(s) \rightarrow TiC(s) + 2CO(g)$
- $2WO_3(s) + 9C(s) \rightarrow W_2C_3(s) + 6CO(g)$

A reactive metal could be reacted with the oxide, such as magnesium:

 $TiO_2(s) + 2Mg(s) \rightarrow Ti(s) + 2MgO(s)$

However it is very difficult to achieve pure titanium by this method as the magnesium forms an alloy with the titanium.

It is possible to avoid this problem by first converting the ore to the chloride, and then reducing the chloride with magnesium or sodium. This is the method used to extract titanium.

1. Extraction of titanium

i) conversion of ore into chloride

TiO₂ is heated in a stream of chlorine, in the presence of coke, to produce TiCl₄.

• $TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow TiCl_4(g) + 2CO(g)$

The TiCl₄ is covalent and volatile. It can be separated from the other products by fractional distillation.

ii) reduction of the chloride

The Ti is extracted from its chloride by reduction with magnesium or sodium:

- $TiCl_4(g) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$
- $TiCl_4(g) + 4Na(l) \rightarrow Ti(s) + 4NaCl(l)$

These reactions are exothermic and keep the reaction vessel at a very high temperature. This process is known as the Kroll process. **An inert atmosphere of argon is used to prevent the magnesium or sodium reacting with oxygen**.

2. Advantages and disadvantages of the process

advantages:

- it produces very pure titanium

disadvantages:

- it is a batch process, which means the titanium is not produced continuously. This adds to the cost of the process.
- the sodium/magnesium are expensive
- the energy costs are very high

Due to the high cost of this process, titanium is not widely used, despite is useful properties. Steel is used instead unless the special properties of titanium are specifically needed.

REDUCTION OF METAL OXIDES WITH HYDROGEN

Hydrogen can also be used as a reducing agent and is the main method for the extraction of tungsten from its oxide:

1. Extraction of tungsten

Tungsten is reacted with hydrogen gas at a high temperature:

 $WO_3 + 3H_2 \rightarrow W + 3H_2O$

2. Advantages and disadvantages of the process

advantages:

- it produces very pure tungsten
- hydrogen is a cheap reagent

disadvantages

- the energy cost are high
- using a flammable gas such as hydrogen at high temperatures is very dangerous

RECYCLING

Reasons for recycling

Aluminium oxide, titanium oxide and iron oxide are all very abundant in the earth's crust, and shortages are not anticipated. There are, however, a number of important reasons why recycling is desirable:

- Recycling generally uses less energy than extraction
- Mines and quarries are unsightly
- The extraction process produces polluting gases like sulphur dioxide and carbon dioxide
- Disposing of scrap metal is difficult
- Most scrap contains a high percentage of the desired metal, so the process can be quite efficient

Problems with recycling

i) collection of scrap metal

Scrap metal needs to be collected from wherever it is used. There are costs involved in doing this.

ii) removing the desired metal from the rest of the scrap

Once collected, the desired metal needs to be separated from the other metals. Unless the metal is magnetic, this needs to be done manually. There are costs involved in doing this.

iii) purifying the desired metal

One separated, the metal needs to be returned to the purity required for it to be useful. There are costs involved in doing this.

Methods of recycling

i) Aluminium

Most of the recycled aluminium is from drinks cans and foil. The cans are collected at recycling points. The cans are shredded and the paint is removed. The metal is melted down into large ingots The ingots are rolled into sheet metal from which more cans are cut.

ii) Iron

Most of the recycled iron is from old trains, ships and cars.

Because of the large size of these objects, the collection is done by specialist metal reclaiming companies.

The objects are cut into a manageable size.

The iron is separated from the other metals using a large magnet.

The scrap is melted and purified in the Basic Oxygen Process.

The purity required for the commercial use of **titanium** and **tungsten** means that recycling is not commercially viable.

USING SCRAP IRON TO EXTRACT COPPER

A recent low-energy innovation for extracting copper is to convert copper compounds into aqueous form and react them with scrap iron.

The process can be summarised as follows:

- copper ores are converted into solutions containing Cu²⁺ ions using dilute sulphuric acid and a specialised bacterium
- the copper ions are then reduced to copper using scrap iron: $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$

Advantages of this process:

- it uses very little energy (although energy would have been used to make the iron)
- it works on very low grade copper ores, including copper mining waste
- iron is much cheaper than copper