Chem Factsheet

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Metal Extraction and Recycling

Prior knowledge

You need to be familiar with the following terms: oxidation, reduction, reducing agent (reductant), oxidising agent (oxidant) and redox reaction.

You need to be able to write chemical formulas and balance both full equations and half-equations.

After working through this Factsheet you should be able to understand:
- how sulphide ores are treated and understand the associated environmental problems and the link to the Contact Process
- types of reaction involved in the extraction of metals
- use of solid C / gaseous CO to smelt only certain metals; be able to write the equations and state the conditions
- conditions, the energy involved and the equations at each electrode in extracting aluminium from purified bauxite
- conditions and equations for the extraction of titanium from rutile (TiO_2)
- conditions, equation and the risks involved in the extraction of tungsten from WO
- environmental aspects and the economics of recycling compared to extraction of metals
- environmental advantages of extracting copper by the use of scrap iron over smelting.

How certain metals occur in the Earth' crust

Metals rarely occur in the earth's crust as the element. They need to be extracted from compounds found naturally in various ores.

An ore may be defined as: a (finite) mineral from which a metal can be extracted *economically*.

Such extractions are all *chemical processes*, in fact *reductions*. In general, metals were "discovered" only when suitable reducing agents became available.

The ores of many metals are oxides and sulphides. Although only one sulphide ore is shown below they are the main source of metals such as zinc (from sphalerite, ZnS/FeS) and lead (from galena, PbS).

Initial treatment of sulphide ores

Sulphide ores are not reduced directly to the metal but are roasted in air to convert them to oxides.

e.g. $\mathbf{ZnS(s) + 1\tfrac{1}{2}O_2(g) \rightarrow ZnO(s) + SO_2(g)}$

Note. The zinc oxide can be reduced to zinc using carbon at high temperatures.

If the sulphur dioxide is allowed to escape into the atmosphere it forms acid rain which causes erosion to buildings and is harmful to vegetation and aquatic life by making the water too acidic. Thus, for environmental reasons, the sulphur dioxide gas is trapped and, for economic reasons, then used to manufacture sulphuric acid by the Contact Process. This acid may be sold or used in the metal extraction process. This is a good example of "green economics".

Reduction of metallic oxides to metallic elements

Metals occur in positive oxidation states in compounds in ores. Thus metals are obtained by reduction processes, the electrons being supplied by either

A) an effective chemical reducing agent or
B) electrically.

Metals in increasing order reactivity	Cu	W	Fe	Mn	Ti	Al
Main ore(s)	Chalcopyrite Malachite	Wolframite Scheelite	Haematite Magnetite	Pyrolusite	Rutile	Bauxite
Main compounds	$CuFeS_2$ $CuCO_3$. $Cu(OH)_2$	$FeWO_4/MnWO_4$ $CaWO_4$	Fe_2O_3 Fe_3O_4	MnO_2	TiO_2	Al_2O_3
Date of discovery	≈ 4000 BC	1783	≈ 1500 BC	1774	1791	1827
Reductant(s)	C(s) / Scrap Fe	$H_2(g)$	Solid C or gaseous CO		Na / Mg	Electricity

A) An effective chemical reductant

1. Carbon or carbon monoxide as the reductant

These are the cheapest reducing agents and hence are used whenever possible. (The carbon comes from coke which is made from coal.)

Carbon and carbon monoxide will reduce oxides of iron, manganese and copper, in continuous processes, to the respective metal. The essential condition for these reductions is a high temperature (>1000°C). For each of the processes several redox equations can be written depending upon the ore, the reductant and the gaseous product.

a) The extraction of iron from an iron ore (e.g. haematite) in a Blast Furnace

Possible equations are:
(i) $Fe_2O_3(s) + 3C(s) \rightarrow 3CO(g) + 2Fe(s)$
(ii) $2Fe_2O_3(s) + 3C(s) \rightarrow 3CO_2(g) + 4Fe(s)$
(iii) $Fe_2O_3(s) + 3CO(g) \rightarrow 3CO_2(g) + 2Fe(s)$

Reduction has occurred since the oxidation number of iron decreases, from +3 in Fe_2O_3 to 0 in Fe.

b) The extraction of manganese from manganese(IV) oxide in a Blast Furnace or an Electric Arc Furnace

e.g. $MnO_2(s) + 2CO(g) \rightarrow Mn(s) + 2CO_2(g)$.

c) The extraction of copper from malachite, ($CuCO_3.Cu(OH)_2$)

The malachite is heated to produce copper(II) oxide, carbon dioxide and steam.

$CuCO_3.Cu(OH)_2(s) \rightarrow 2CuO(s) + CO_2(g) + H_2O(g)$ (1)

The copper(II) oxide is then reduced to copper by carbon at high temperatures.

e.g. $2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g)$ (2)

Note. If the carbon is added directly to the malachite then a single equation may be written:

$CuCO_3.Cu(OH)_2(s) + C(s) \rightarrow 2Cu(s) + 2CO_2(g) + H_2O(g)$ (1) + (2)

The copper(II) ion is reduced to copper since electrons have been gained:

$Cu^{2+} + 2e^- \rightarrow Cu$

The reductant is carbon since its oxidation number increases from 0 (in C) to +4 (in CO_2).

2. Sodium or magnesium as the reducing agent

Either of these reactive metals is used for the extraction of titanium by a batch process called the Kroll Process.
The ore rutile, TiO_2, is heated with carbon in a stream of chlorine gas to produce titanium(IV) chloride.

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

Note: This is **not** a reduction as far as titanium is concerned because its oxidation state remains unchanged at +4.

The titanium(IV) chloride is purified by distillation and then reduced by either sodium or magnesium.

The essential conditions for either reductant are an atmosphere of argon and a high temperature. If air was present the Mg / Na would react with oxygen.

$TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti$
or $TiCl_4 + 4Na \rightarrow 4NaCl + Ti$

3. Hydrogen as an effective reducing agent

Tungsten ores are converted to tungsten(VI) oxide and reduced by hydrogen at a high temperature.

$WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$

Hydrogen in the presence of air (O_2) is highly flammable so there is a risk of hydrogen gas igniting and an explosion occurring. All sources of ignition, e.g. sparks, flames, must be eliminated.

B) Electrical Reduction

Aluminium is extracted from purified Bauxite, which is dissolved in molten cryolite (Na_3AlF_6) and electrolysed using direct current in a continuous process.

Half-equations at the electrodes

Negative steel electrode (cathode). $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

This is a reduction of Al^{3+} because electrons are gained

Positive carbon electrode (anode). $O^{2-}(l) - 2e^- \rightarrow \frac{1}{2}O_2(g)$

This is an oxidation of O^{2-} because electrons are lost.

Since the temperature is high the oxygen reacts with the carbon anode: $C(s) + O_2(g) \rightarrow CO_2(g)$

These expensive carbon anodes burn away and have to be periodically replaced. This adds to the already high cost of the process resulting from the use of expensive electricity for heating and electrolysis - hydroelectric power is usually the chosen source of electric energy as it is the cheapest. Furthermore, the carbon dioxide adds to global warming!

The essential conditions for this electrolytic reduction are:

(a) The electrolyte must be molten for the ions to be able move to the electrodes.This requires a high temperature.

(b) The electrolyte must be at as low a temperature as possible so the process can be economic; hence purified bauxite is mixed with cryolite, which melts at about 850^0C. (Pure Al_2O_3 melts at 2072^0C.)

(c) Direct current electricity must be used.

Why carbon reduction cannot be used for the extraction (a) titanium and tungsten and (b) aluminium

(a) The metal would react with the carbon and form a metal carbide. e.g. Ti form TiC and W forms WC. These carbides make the metals brittle and reduce their corrosion resistance. Thus more expensive reducing agents (Na or Mg for TiO_2) and (H_2 for WO_3) are used instead of carbon to obtain a metal free from carbide.

(b) The temperature required is too high. At > 2000^0C the energy cost for the reduction of Al_2O_3 by C exceeds the high energy cost of electrolysis.

Recycling of scrap metals compared with their extraction for ores

The advantages of recycling scrap metals	The disadvantages of recycling scrap metals
• energy used in extracting the metal from the ore is saved. This is especially true for Al where reduction of Al_2O_3 requires much expensive electrical energy. (The total cost of prospecting, mining, transporting the ore, extracting the metal, (etc) are more expensive than the costs of collecting, separating, transporting and reusing scrap.) • ores are finite resources. Using scrap metal extends the life of the ore deposits. • employment is provided for people who collect, separate and transport the scrap. • less ore needs to be mined so there is less spoiling of the landscape; land reclamation by mining companies is very expensive. • less polluting gases are generated if less ore is reduced to the metal since less fossil fuel is burnt to produce the high temperatures needed for the reductions and less carbon is used as a reductant. Thus in a Blast furnace the high temperature required is produced by burning coke and this releases CO_2 (a greenhouse gas), CO (toxic), some SO_2 (see above) due to sulphur impurities in the fossil fuel. It also produces oxides of nitrogen (NOx) because some atmospheric nitrogen and oxygen react at the high temperatures involved. There is also more CO_2 and CO when the iron ore is reduced!	• The mines are often in Third World countries. Hence the reduction in mining or closure of a mine can have serious economic consequences for the people in such countries as a whole and not just those in the mining and exporting industries. • Metals have to be separated from each other and from non-metallic substances (plastics, paint etc). This is relatively easy with ferrous metals as they are magnetic but not for other metals.

Comparing the impact on the environment of two of the ways of extracting copper

Method 1: The reduction of copper(II) oxide by carbon.

$$2CuO(s) + C(s) \rightarrow 2Cu(s) + CO_2(g)$$

Method 2: The reduction of a copper(II) solution by scrap iron, the solution having been produced by leaching copper(II) ores using hydrochloric acid or sulfuric acid.

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

Method 2 is preferred because:

- Leaching can use *low grade ores* and even the waste material in copper mine dumps.
- The reduction using iron produces no gases whereas high temperature carbon reduction always produces gases such as SO_2, CO_2, CO and NOx that are harmful to the environment.
- it occurs at ambient ("air") temperatures. No fuel is burnt to generate high temperatures with the accompanying negative impact on the environment.

Practice questions

1. Define reduction in terms of a) electrons b) oxidation numbers.
   Write a half-equation for the reduction of an aluminium ion.

2. Write equations for the reduction of Fe_3O_4 using i) a solid reducing agent (two equations may be written) and ii) a gaseous reducing agent (one equation). What condition is essential for these reductions to occur?

3. Write two different equations for the reduction of manganese(IV) oxide by carbon.

4. (a) Write the equation for reaction of titanium(IV) oxide with carbon and chlorine.
   (b) Explain why the titanium is not reduced in this reaction.

5. To produce tungsten, the ore scheelite ($CaWO_4$) is reacted with hydrochloric acid to give tungsten(VI) oxide, calcium chloride and water. The oxide is then reduced at high temperature by hydrogen to the metal.
   (a) Write equations for both reactions.
   (b) Why is carbon not used as the reducing agent for WO_3?
   (c) State one environmental advantage of using hydrogen rather than carbon as the reductant.
   (d) State one risk associated with the use of hydrogen

6. In Japan, where the cost of electricity is very high, attempts have been made to reduce aluminium oxide with carbon to aluminium and carbon monoxide. The method met with failure because, at the temperature required, the aluminium oxide began to vaporise. How is aluminium usually extracted? In your answer include
   (a) the name of the ore,
   (b) the nature of the electrolyte
   (c) the half-equation for the reaction that produces aluminium
   (d) which electrode has to be periodically replaced, explaining why and including an appropriate equation.

7. The deep blue mineral azurite ($2CuCO_3.Cu(OH)_2$) is formed by weathering of discarded copper ore on mine dumps. When dilute sulphuric acid is used to leach the copper from the azurite it may be considered to react with the copper carbonate and the copper hydroxide in the azurite separately.
   (a) Write an equation for each of reaction.
   (b) Write an ionic equation showing how copper is extracted from the leached solution and state the conditions for this reaction.

8. When extracting metals the reduction method chosen depends upon several factors including:
   (a) the cost of the reducing agent
   (b) the cost of the energy required for the process
   (c) the required purity of the metal.

   Give examples to illustrate each of these factors.

Answers

1. (a) Gain of electrons
   (b) Decrease in oxidation number. $Al^{3+} + 3e^- \rightarrow Al$.

2. e.g. (i) $Fe_3O_4(s) + 4C(s) \rightarrow 4CO(g) + 3Fe(s)$
   or $Fe_3O_4(s) + 2C(s) \rightarrow 2CO_2(g) + 3Fe(s)$

   (ii) $Fe_3O_4(s) + 4CO(g) \rightarrow 4CO_2(g) + 3Fe(s)$.

   Essential condition. High temperature.

3. $MnO_2(s) + 2C(s) \rightarrow Mn(s) + 2CO(g)$ & $MnO_2(s) + C(s) \rightarrow Mn(s) + CO_2(g)$

4 (a) $TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + 2CO(g)$

   (b) The oidation number of Ti is +4 in both TiO_2 and$TiCl_4$. It must decrease for reduction.

5. (a) $CaWO_4 + 2HCl \rightarrow WO_3 + CaCl_2 + H_2O$
   $WO_3 + 3H_2 \rightarrow W + 3H_2O$

   (b) Carbon produces tungsten containing tungsten carbide which makes the metal brittle.

   (c) The other product is steam (water) which is not harmful to the environment. If C is used, poisonous CO and / or CO_2 (a greenhouse gas) are produced.

   (d) Hydrogen is highly flammable – there is a danger of an explosion.

6. (a) Bauxite

   (b) Molten purified bauxite dissolved in cryolite

   (c) $Al^{3+} + 3e^- \rightarrow Al$

   (d) The positive carbon electrode since it burns away in the oxygen produced.
   e.g. $C + O_2 \rightarrow CO_2$.

7. (a) $CuCO_3(s) + H_2SO_4^-(aq) \rightarrow CuSO_4(aq) + H_2O(l) + CO_2(g)$
   $Cu(OH)_2(s) + H_2SO_4^-(aq) \rightarrow CuSO_4(aq) + 2H_2O(l)$

   (b) $Cu^{2+}(aq) + Fe(s) \rightarrow Cu(s) + Fe^{2+}(aq)$. Room/air temperature.

8. (a) Carbon is the cheapest reductant and is used wherever possible. However it is not used if the temperature required is too high (e.g. Al) or the metal produced would be brittle due to contamination by the metal carbide, (e.g. Ti / W).

   (b) It is cheaper to reduce bauxite to aluminium electrically rather than use carbon reduction because the temperature required is too high.

   (c) Tungsten is made by using more expensive hydrogen to reduce WO_3 rather than cheaper carbon. This produces a metal free from carbide which would make the W brittle.

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