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Chem!stry

The Industrial Extraction of Aluminium from Aluminium Oxide

Introduction:

Pure aluminium (A*l*) is a silvery-white metal with many desirable properties:

- It has a low density (the density of aluminium is 2.70 g cm^{-3} compared to the density of iron 7.86 g cm^{-3}).
- Aluminium is non-toxic.
- Aluminium can be highly polished (aluminium has a good metallic lustre).
- Aluminium is a very good electrical and thermal conductor.
- Aluminium is not magnetic.
- Aluminium is the second most malleable metal (after gold) and the sixth most ductile metal.
- Many of aluminium's alloys have high mechanical and tensile strength.
- Although a reactive metal ($E^{\ominus}$ Al^{3+}/Al = –1.66 V) aluminium is resistant to corrosion because its surface is coated with an inert layer of aluminium oxide (Al_2O_3). The protective oxide layer may be artificially thickened by a process called *anodising*. When aluminium is anodised, it is placed in an aqueous solution of sulphuric acid and made the *positive* terminal or *anode* of an electrolytic cell. The following reaction then takes place:

$$2Al + 3O^{2-} \rightarrow Al_2O_3 + 6e^-$$

Figure 1 gives the various uses of aluminium in North America:

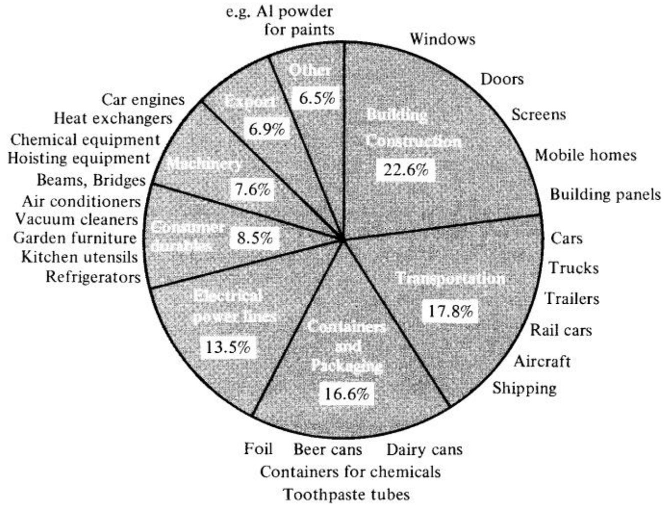

Figure 1

History:

Aluminium derives its name from *alumen*, a Latin word meaning "bitter salt". Aluminium is the most abundant metal in the Earth's (crust 8.3% by mass compared to iron 6.2% by mass). Although aluminium is so abundant, due to its high reactivity it has only recently (1854) been isolated as the pure metal on a commercial scale by electrolysis. Due to the initial difficulty encountered in extracting pure aluminium metal, it was once very expensive; it was exhibited next to the crown jewels during the Paris Exposition of 1855 and the Emperor Louis Napoleon III used aluminium cutlery on state occasions.

Aluminium can now be obtained from its oxide very cheaply. This is for two reasons:

- Electricity is now generated very cheaply.
- Aluminium oxide is dissolved in molten cryolite (Na_3AlF_6) which reduces its melting point from 2040°C to 950°C.

Occurrence of Aluminium Ore:

Aluminium is mined as the ore bauxite, aluminium oxide-2-water ($Al_2O_3.2H_2O$) which contains silicon(IV) oxide and iron(III) oxide as impurities. Bauxite is approximately 50 - 70% aluminium oxide. Because bauxite occurs close to the surface, it is simply obtained by open-cast mining.

The extraction of aluminium from bauxite can be considered in two stages:

- Separation of anhydrous aluminium oxide from the bauxite (removal of the silicon(IV) oxide and iron(III) oxide impurities).
- Electrolysis of the anhydrous aluminium oxide.

Purification:

Pure aluminium oxide is obtained from the ore by using the fact that it is *amphoteric* (has both acid and base properties) whereas the impurities are acidic (silicon(IV) oxide) and basic (iron(III) oxide). After being ground, the bauxite is heated with concentrated sodium hydroxide. This gives a solution of tetrahydroxoaluminate(III):

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$$

The silicon(IV) oxide also reacts to form a solution of sodium silicate, but the iron(III) oxide does not dissolve and is removed in settling tanks:

$$2NaOH(aq) + SiO_2(s) \rightarrow Na_2SiO_3(aq) + H_2O(l)$$

Hydrated aluminium oxide crystals are next added to the aqueous solution of tetrahydroxoaluminate(III). This encourages crystallisation of hydrated aluminium oxide from the solution. The solid hydrated aluminium oxide is removed from the solution of sodium silicate by filtration, washed and then heated at 1000°C to remove water of crystallisation. This leaves pure, anhydrous aluminium oxide. The process is outlined below:

Ground Bauxite

↓

Heat with conc. NaOH

↓

Solution of A*l*(OH)$_4^-$ and Na_2SiO_3

↓

Addition of hydrated A*l*$_2$O$_3$ to encourage crystallisation

↓

Hydrated A*l*$_2$O$_3$ heated at 1000°C

↓

Pure anhydrous A*l*$_2$O$_3$ ready for

Electrolysis:

Aluminium is obtained from its oxide by electrolysis. Because the melting point of aluminium oxide is very high (2040°C) it is dissolved in molten cryolite (sodium hexafluoroaluminate - Na_3AlF_6) with calcium fluoride (CaF_2) and aluminium fluoride (AlF_3) added to lower its melting temperature. This allows the anhydrous aluminium oxide to be electrolysed at 950°C therefore saving energy. **Figure 2** shows the Hall-Héroult cell used for the electrolysis of anhydrous aluminium oxide. A current of 40 000 - 100 000 A is used in this cell:

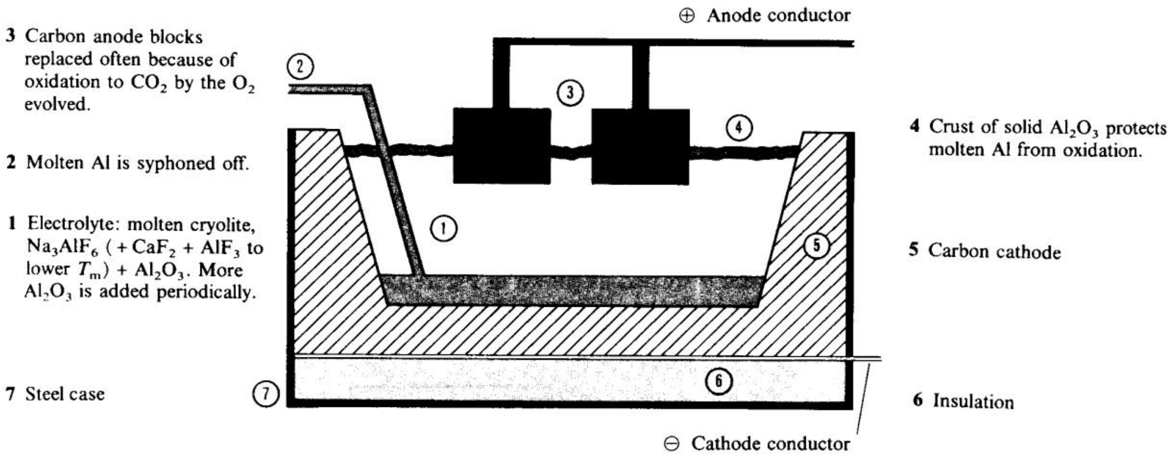

Figure 2

The reactions at the electrodes are:

At the Cathode (Negative)

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

At the Anode (Positive)

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

In addition to oxygen gas being produced at the anode, fluorine gas may also be produced:

$$2F^{-} \rightarrow F_2 + 2e^{-}$$

The anode is a block of graphite (carbon). This reacts with the oxygen gas produced at the anode to form carbon dioxide gas:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

This reaction is *exothermic* and therefore produces heat energy required to keep the electrolyte molten. As a consequence of this reaction, the carbon anode must be replaced frequently.

Molten aluminium is syphoned out of the Hall-Héroult cell and stored in a furnace before casing into shape.

Electrolysis is an expensive method of extracting a metal from its ore. The reason why electrolysis, and not reduction of the ore using carbon, is used for the extraction of aluminium can be seen from the Ellingham diagram in **Figure 3**:

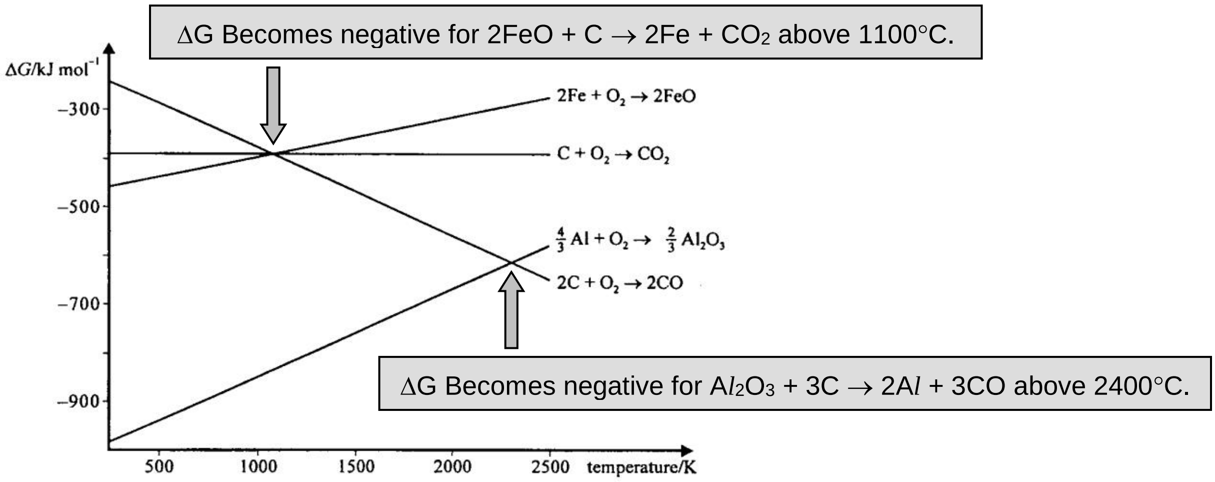

Figure 3

Whereas reduction of iron(II) oxide by carbon is feasible (–ΔG) at about 1100°C, reduction of aluminium oxide by carbon is only feasible (–ΔG) at about 2400°C. To reach such a high temperature requires a huge amount of energy and is therefore not financially viable.

Location of the Process:

The aluminium extraction plant should be sited close to a deep-water seaport to allow import of the bauxite and export of the aluminium metal. The plant should also be located close to a cheap source of electricity (*e.g.* nuclear or hydroelectric).

Importance of Recycling Aluminium:

Even though aluminium is the most abundant metal in the Earth's crust, it is also one of the most widely used metals and consumes a lot of energy in its manufacture. To conserve energy and prevent unnecessary mining of bauxite, aluminium should be recycled. To melt aluminium so that it can be cast into a new shape and reused requires a temperature of 660°C. This is much lower than the temperature required for the electrolysis of bauxite, and in addition, does not require a large electric current.