





Electrochemistry

The Extraction of Aluminium from Bauxite – Electrolysis of Molten Aluminium Oxide



 The metallic element aluminium has played an essential role in 20th and 21st Century manufacturing.

 From the ubiquitous aluminium foil, to the cases of electronic devices – from soft-drinks cans to motorcar chassis and window frames – aluminium impacts the standard of modern living.







- At 8.3% by mass, Aluminium is the most abundant metallic element in the Earth's crust.
- Because it is a relatively reactive metal, with a high affinity for oxygen, aluminium occurs naturally in the Earth's crust as aluminium oxide, formula Al_2O_3 .
- Aluminium oxide is mined from the Earth's crust as the mineral *bauxite*. Although compounds of aluminium are usually colourless, bauxite is reddishbrown in colour because it also contains the oxides of iron; *goethite*, FeO(OH) and *haematite*, Fe₂O₃.







• For elemental aluminium to be put to good use, it must first be chemically separated from the oxygen that it is bonded to in bauxite.

 Because aluminium is a relatively reactive metal, chemically separating it from oxygen is quite a difficult and expensive process.

 Back in 1855, obtaining pure aluminium was so difficult that it was valued more highly than gold.
Emperor Napoleon III gave his distinguished dinner guests aluminium cutlery, while less important guests
dined using knives and forks made 'only' of gold.

 Because aluminium is above carbon in the reactivity series, carbon cannot be used to reduce aluminium and extract aluminium from its oxide.

 Instead, aluminium is obtained commercially through the *electrolysis of molten aluminium oxide* (alumina).



• Firstly, aluminium oxide must be obtained in its pure form (called *alumina*), *i.e.* it must be separated from impurities such as the goethite and haematite.



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 a) Bauxite is added to aqueous sodium hydroxide at 180 °C. The aluminium oxide reacts to form an aqueous solution of sodium aluminate. Other chemicals in the bauxite remain undissolved, and are removed by filtration.

 $Al_2O_3(s) + 2NaOH(aq) \rightarrow 2NaAlO_2(aq) + H_2O(l)$



Note: This reaction relies upon the amphoteric nature of aluminium oxide.

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b) Aluminium hydroxide is crystallised from a supersaturated solution of sodium aluminate.

 $NaAlO_2(aq) + 2H_2O(l) \rightarrow Al(OH)_3(s) + NaOH(aq)$



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c) When heated in a rotary kiln, the aluminium hydroxide undergoes thermal decomposition to form pure aluminium oxide (alumina).

 $2Al(OH)_3(s) \rightarrow Al_2O_3(s) + 3H_2O(l)$

The pure aluminium oxide can now be heated until it is molten, and then electrolysed in order to obtain elemental aluminium.



Electrolysis of Aluminium



• Aluminium oxide (alumina) melts at 2072 °C. This is a very high temperature to maintain on an industrial scale. In practice, it is not feasible to carry out electrolysis at this temperature due to the extremely large amount of energy that is required.

To overcome this problem, the aluminium oxide is dissolved in *molten cryolite*, formula Na₃A*l*F₆, which melts at 1012 °C. In practice, the electrolysis is carried out at approximately 980 °C, because A*l*₂O₃ serves as an *impurity* in the Na₃A*l*F₆, *lowering its melting point*.

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• Electrolysis of the aluminium oxide occurs as an electric current of between 100 000 and 300 000 A is passed through the molten electrolyte.

• Aluminium ions are reduced at the negative (–) cathode to produce molten aluminium.

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

Note: Aluminium melts at 660 °C, and is therefore a *liquid* at the temperature of the electrolysis (980 °C).

• Oxide ions are oxidised at the positive (+) anode to produce gaseous oxygen.

 $2O^{2-}(l) \rightarrow O_{2}(g) + 4e^{-}$

 Note: Due to the high temperature that the electrolysis is carried out at, most of the oxygen that is produced at the graphite (an allotrope of carbon) anode reacts with the anode to produce carbon dioxide.

 $C(s) + O_2(g) \rightarrow CO_2(g) \Delta H = -394 \text{ kJ / mol}$

 As a consequence, the graphite anode needs to be frequently replaced. Although this seems inconvenient, oxidation of the graphite anode is actually desirable because it is an *exothermic reaction*, and the heat energy that is released helps to keep the electrolyte in its molten state.

 The electrolysis of molten aluminium requires a large amount of thermal energy to keep the aluminium oxide molten and also a large amount of electrical energy to cause reduction of the aluminium ions and oxidation of the oxide ions.

• This makes the electrolysis of aluminium oxide expensive and also *polluting* due to the CO(g), CO₂(g) and SO₂(g) produced during combustion of fossil fuels.

 Consequently, it is important to recycle aluminium in order to reduce atmospheric pollution and conserve the Earth's natural resources.

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