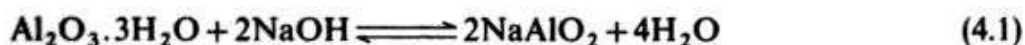


4.1 ELECTROWINNING

4.1.1 Aluminium extraction

In terms of scale of production (around 2×10^7 ton year⁻¹ worldwide) aluminium electrolysis is second in importance only to the chlor-alkali industry. This is because aluminium is both light and strong and therefore suitable for many engineering and construction applications, may readily and cheaply be treated by anodizing (section 8.3.1) to retard corrosion and is the principal alternative to copper as a conductor of electricity. Moreover, the known reserves of aluminium ores are relatively high.

Aluminium is normally produced from the ore, bauxite, which is a hydrated aluminium oxide containing silica and other metal oxides, particularly iron. It is converted to a pure alumina using the equilibrium:



The ore is first treated with sodium hydroxide under pressure. The aluminium largely dissolves as the aluminate, the iron oxide is insoluble and the silica also remains in the form of a sodium aluminium silicate, which leads to a loss of aluminium. Hence, the best bauxites are those low in silica. After filtration, the hydrated aluminium oxide is reprecipitated by seeding and the sodium hydroxide solution may be reused. The alumina is washed and then heated at 1200°C to remove water. The final step in the production of aluminium metal has to be electrolytic since the reduction of alumina with carbon is only possible at very high temperatures and the reverse reaction occurs on cooling. Moreover, because of the chemistry of aluminium, the electrolysis medium cannot be water; in fact, almost all commercial production of aluminium during the last 90 years has used an electrolysis in molten cryolite, Na₃AlF₆.

The process is based on the observation made concurrently and independently in 1886 by Hall in the USA and Héroult in France that, whereas alumina melts at 2020°C to give a non-conducting liquid, it will dissolve to the extent of 15 wt % in molten cryolite at 1030°C to give a conducting medium. Two years later, the second important step towards a viable process of aluminium extraction was made by Bayer who developed a method for leaching sodium aluminate to produce alumina. The high solubility of alumina in molten Na₃AlF₆ results from the near equality of size of fluorine and oxygen atoms in the aluminium complexes in the melt and, hence, facile formation of oxyfluoride ions on addition of the oxide to the Na₃AlF₆. Indeed, the aluminium is probably present as a mixture of several related species, although the exact chemistry of the system is not known and it is therefore difficult to write complete electrode reactions. Clearly, however, the cathode reaction is the reduction of an aluminium (III) species to the metal which is molten at the electrolysis temperature; the cathode is effectively a pool of liquid aluminium. Ideally, the anode reaction would be the oxidation of oxide ion to oxygen but it is difficult to

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find an anode material which is inert under the electrolysis conditions. Hence, the electrolysis has always been run with consumable carbon anodes so that the overall cell reaction is:



The carbon anode is consumed in a stoichiometric amount but the free energy for this reaction is $340 \text{ kJ mol}^{-1} \text{ Al}$ (at 1000°C) compared with 640 kJ mol^{-1} for the reaction:



i.e. the overall cell reaction if oxygen was evolved at the anode. In consequence, the sacrifice of the carbon anode leads to a much reduced cell voltage and energy consumption. Thus, the reversible cell voltage is -1.18 V compared with -2.21 V if the cell reaction was (4.3).

A cell for the Hall-Héroult process is shown in Fig. 4.1, and a block diagram of the whole process is shown in Fig. 4.2. Cell design is determined largely by the need to contain molten cryolite at high temperatures and to withstand attack by molten aluminium and also by sodium and fluorine formed as minor products at the cathode and anode respectively. Hence, the cell is a strong steel box lined first with alumina to act as a refractory, thermal insulator and then with carbon.

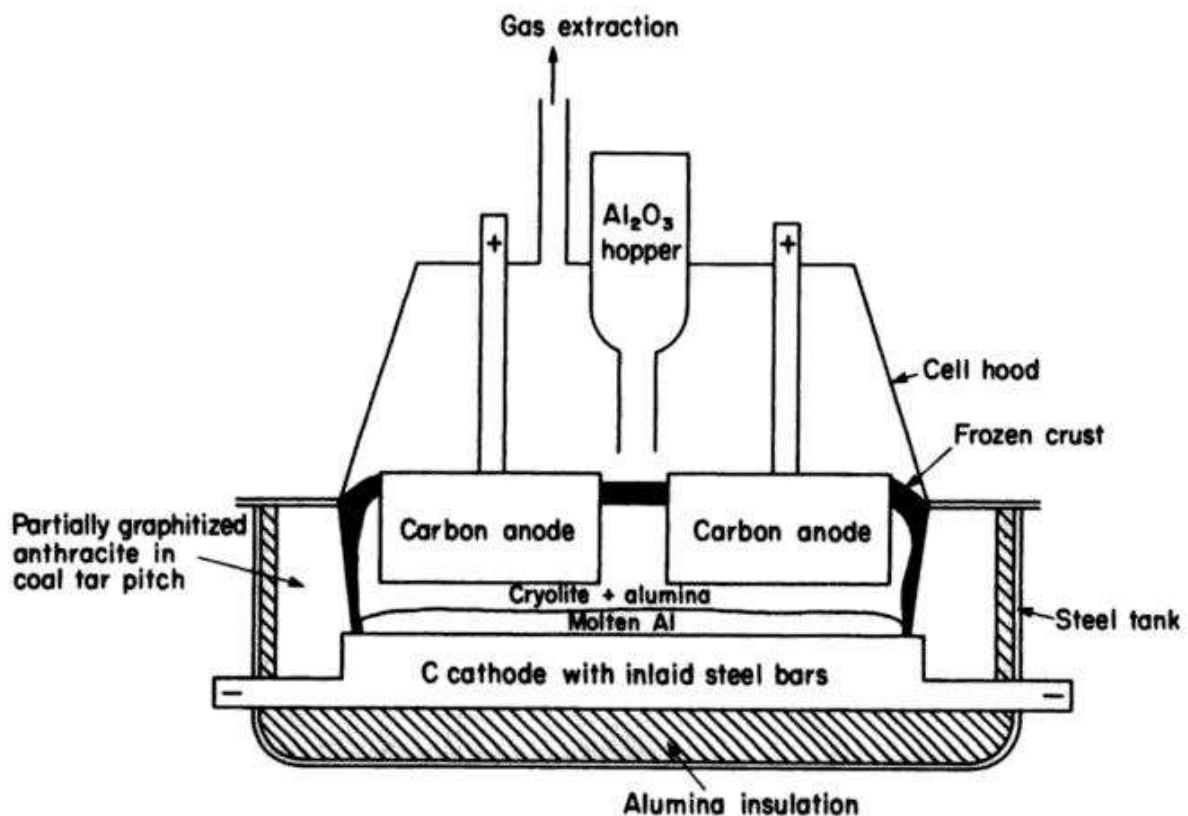


Fig. 4.1 Cell for the Hall-Héroult process for aluminium extraction.

In fact, the base of the tank is lined with prebaked carbon blocks which are inlaid with steel bars to reduce their electrical resistance and which act as current carriers to the molten aluminium cathode. The sides are lined with partially graphitized anthracite in coal-tar pitch. The process is then run so that there remains a layer of solid cryolite and alumina at the sides of the cell and a solid crust on the surface. This acts as a further barrier to corrosion and also to reduce the heat loss from the cell. The cell also has facilities for the periodic addition of alumina through the crust and for the removal of aluminium metal by suction. It is hooded with an extractor to vent the anode gases, mainly carbon dioxide, but also containing carbon monoxide from the unwanted back chemical reaction:



and particulate matter as well as in some cases fluorine or hydrogen fluoride. Reaction (4.4), of course, reduces the current efficiency for the electrolysis.

The carbon anodes are manufactured from a carbon source such as anthracite and a pitch binder mix. Two types have been used:

1. Prebaked carbon blocks of dimensions approximately $80 \times 100 \times 50$ cm deep.
2. Self-baking anodes (known as Soderberg anodes) usually one per cell and therefore of much larger dimensions. Such anodes are fed at the top with the ground carbon and pitch binder and this bakes *in situ* as it gradually descends into the molten electrolyte to form a hard, dense material which acts as the anode surface.

In both cases the anode is consumed and therefore must be lowered regularly (approximately 2 cm day^{-1}) to maintain a constant anode-cathode gap. Soderberg anodes were common in the late 1940s and the 1950s because they removed the anode-manufacturing step and, hence made the overall process cheaper to operate. Prebaked anodes were used in earlier cells and are again employed almost universally because they give a better energy performance and lead to less difficult environmental problems; the *in situ* baking causes fumes which are more difficult to control.

Except for the anodes, cell design has changed little since the introduction of the process in the last century. The cells have become larger, however, as the materials and construction techniques have improved, and typically a cell will now be $3 \text{ m} \times 8 \text{ m} \times 70 \text{ cm}$ deep with eighteen prebaked anodes. The inter-electrode gap must be rather wide, about 5 cm: (1) to prevent shorting because the small difference in density between the melt (2.1 g cm^{-3}) and the molten aluminium (2.3 g cm^{-3}) leads to an unstable cathode-electrolyte interface; and (2) to minimize the chemical reaction of the electrolysis products (reaction (4.4)) which causes loss in current efficiency.

While the electrolyte is essentially molten cryolite, certain additions are made and a typical electrolysis medium also contains excess aluminium trifluoride

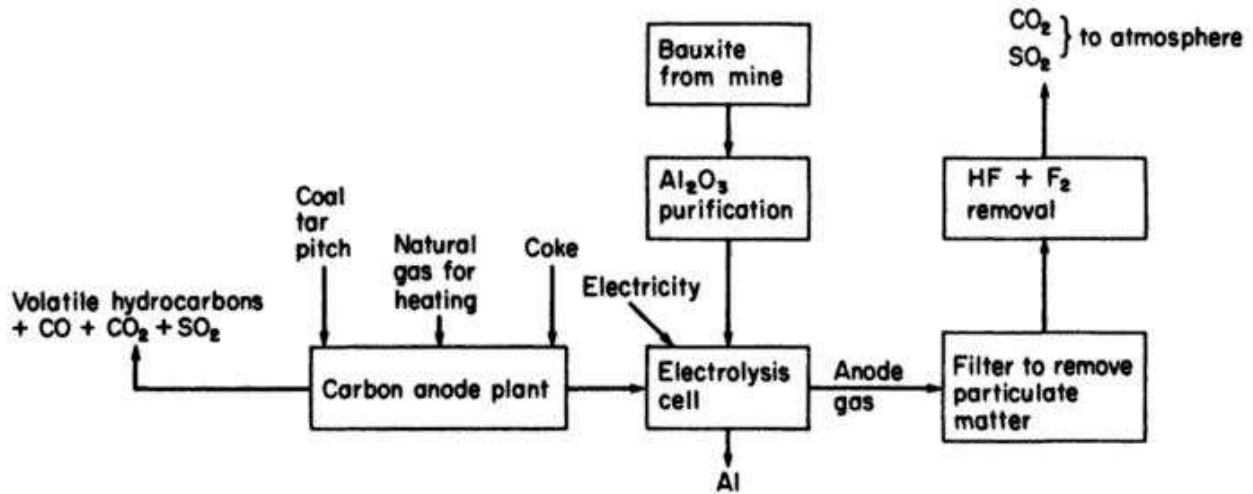


Fig. 4.2 Steps in the Hall-Heroult process for aluminium extraction.

(4–6%) and calcium fluoride (4–6%). These additives increase the conductivity of the medium and lower the melting point of the cryolite to 960–980°C. A reduction in the operating temperature has the advantages of decreasing energy consumption and lowering the extent of the back reaction (4.4) (by about 1%/10°C). On the other hand, by both decreasing the operating temperature and diluting the cryolite, the additives cause a decrease in the solubility of the alumina and this limits their total concentration.

Alumina must be added to the cell periodically and this is done through a hopper which breaks through the surface crust. In the normal electrolysis conditions, i.e. cryolite with calcium fluoride and excess aluminium fluoride and an operating temperature of 970°C, the alumina is only soluble to 6 wt %. During electrolysis its concentration drops, and if it is allowed to fall below about 2%, the electrolysis cell undergoes a sudden and major operational failure known as an ‘anode effect’. The cell voltage increases rapidly from –4.5 V to a value in the range –40 to –60 V, and this is thought to be due to an insulating gas film, fluorine or carbon tetrafluoride, across the anode surface. To return the cell to its normal operating conditions, alumina must be added and the bath stirred to remove the gas film. The anode effect is, however, not regarded as totally unhelpful since sparking across the gas film burns off macroscale surface roughness to produce a better anode and provides a simple, if unusual, *in situ* analysis of alumina concentration in the electrolyte. Overfeeding of the cell causes problems by precipitation of alumina on the molten aluminium cathode. Hence, it is common to permit an anode effect to occur at regular intervals.

A typical cell house will contain about 200 cells arranged in series on two lines, each 3 × 8 m cell having a total anode area of 15 m². The optimum current density is around 1 A cm⁻², giving a total cell current of 150 kA and this requires a cell voltage in the range from –4.0 to –4.5 V. The cell voltage, of course, depends on alumina concentration since this determines the concentration of electroactive species at both electrodes. It drops to just below –4 V

after addition of alumina to 6% and rises to about -4.5 V before the onset of an anode effect. All cell houses have a strong magnetic field due to the large currents used and it is particularly important to take this into account in the design of aluminium electrolyzers because of the turbulence the magnetic field can produce at the aluminium/electrolyte interface due to the small difference in their densities. Hence, the cells are arranged in the cell house to produce the minimum magnetic field.

Reaction (4.4) always leads to some loss in current efficiency and in most cells the aluminium current efficiency is only 85–90%. From these data the energy requirement may be estimated to be 14 000–16 000 kWh per ton of aluminium and we can also calculate that the cell house described would produce 70 000 ton year⁻¹.

It can be seen that the energy consumption of the aluminium electrolyser is very high (cf. 3000 kWh per ton of Cl₂). This is partly because the production of aluminium requires 3 F, partly because of its low atomic mass and finally because of very substantial inefficiencies in the cell. Table 4.1 shows how the cell voltage is made up. The reversible potential is calculated from thermodynamic data and it can be seen that it represents only a small fraction of the observed cell voltage. Similar calculations for a cell where the reaction (4.3) occurs, i.e. where the anode reaction is oxygen evolution and the electrode is inert, show that the reversible potential would be -2.21 V. An anode which is stable in the molten salt and able to evolve oxygen at low overpotentials would, however, be advantageous since it would remove the need to manufacture carbon anodes and, hence, remove considerable environmental problems. Moreover, the penalty of a higher reversible potential may be more than outweighed if the anode overpotential and resistance were less than those shown in Table 4.1.

In view of the high temperature, it is to be expected that the kinetics of the electrode reactions will be rapid and this is certainly the case at the cathode. A

Table 4.1 Estimate of voltage distribution in the Hall-Héroult cell

	– Voltage/V
Reversible cell potential	1.2
Overvoltages	
anode	0.5
cathode	0.0
<i>iR</i> drop in electrodes	
anode	0.5
cathode	0.6
<i>iR</i> drop in the electrolyte	1.5
Total cell voltage	4.3

substantial overpotential has been found at the anode but it must be remembered that the oxidation of an oxyanion at carbon to give carbon dioxide is probably an unknown reaction at room temperature.

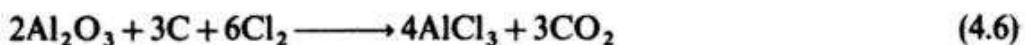
The iR drops in the cell are large. Those in the electrodes arise because of their size and the relatively low conductivity of carbon, particularly the form used in this electrolysis; the carbon cathode has inlaid steel bars to decrease its resistance. The substantial electrolyte iR drop is due to the need for a large (≈ 5 cm) interelectrode gap. This overpotential is, however, used to some extent since it gives rise to heat which maintains the electrolyte in a molten state.

If the energy required to maintain the cell at 970°C is taken into account, the energy efficiency of the process is only 33%. Even this relatively poor performance has only been achieved as a result of a careful examination of the physical chemistry of the electrolyte and electrodes and of the cell technology. Moreover, the process has several environmental problems associated with both the curing of the carbon anodes and the anode gases, which must be treated to remove both fluoride and particulate matter. Hence, it is not surprising that considerable effort has gone into developing an alternative technology.

While some of this effort has gone into inert anodes, the major emphasis has been to develop a process in a chloride medium. Much of the work has been unsuccessful, but Alcoa in the USA have recently operated a small plant based on a chloride electrolyte. The cell reaction is:



and the electrolysis is carried out at C electrodes in a 3:2 mixture of sodium and lithium chloride containing 2–15% aluminium trichloride. The temperature is 700°C , almost 300°C below that of the Hall-Hérout process but above the melting point of aluminium (this greatly simplifies the process). The process requires the prior conversion of alumina to aluminium trichloride by the chemical reaction:



The cell for the electrolysis consists of a bipolar stack of horizontal carbon anodes with an interelectrode gap of 1.5 cm. The electrodes and electrolyte flow is designed to ensure the minimum contact between the electrolysis products, since the molten aluminium and gaseous chlorine would otherwise react rapidly. The aluminium falls to a pool below the electrodes while the chlorine is pumped out the top of the cell to be used in the reaction with alumina. A simplified cell is shown in Fig. 4.3. It may be noted that the overall process again uses carbon in at least stoichiometric quantities although now in a chemical step. Overall the process run at 1 A cm^{-2} has an energy efficiency which is currently claimed to be about 10% better than that for the Hall-Hérout process.

Aluminium is regarded as a strategic material, i.e. it is essential for military applications. Bauxite is, however, not found in large quantities in the developed Western world; rather it comes from Africa, South America, Australia and Asia

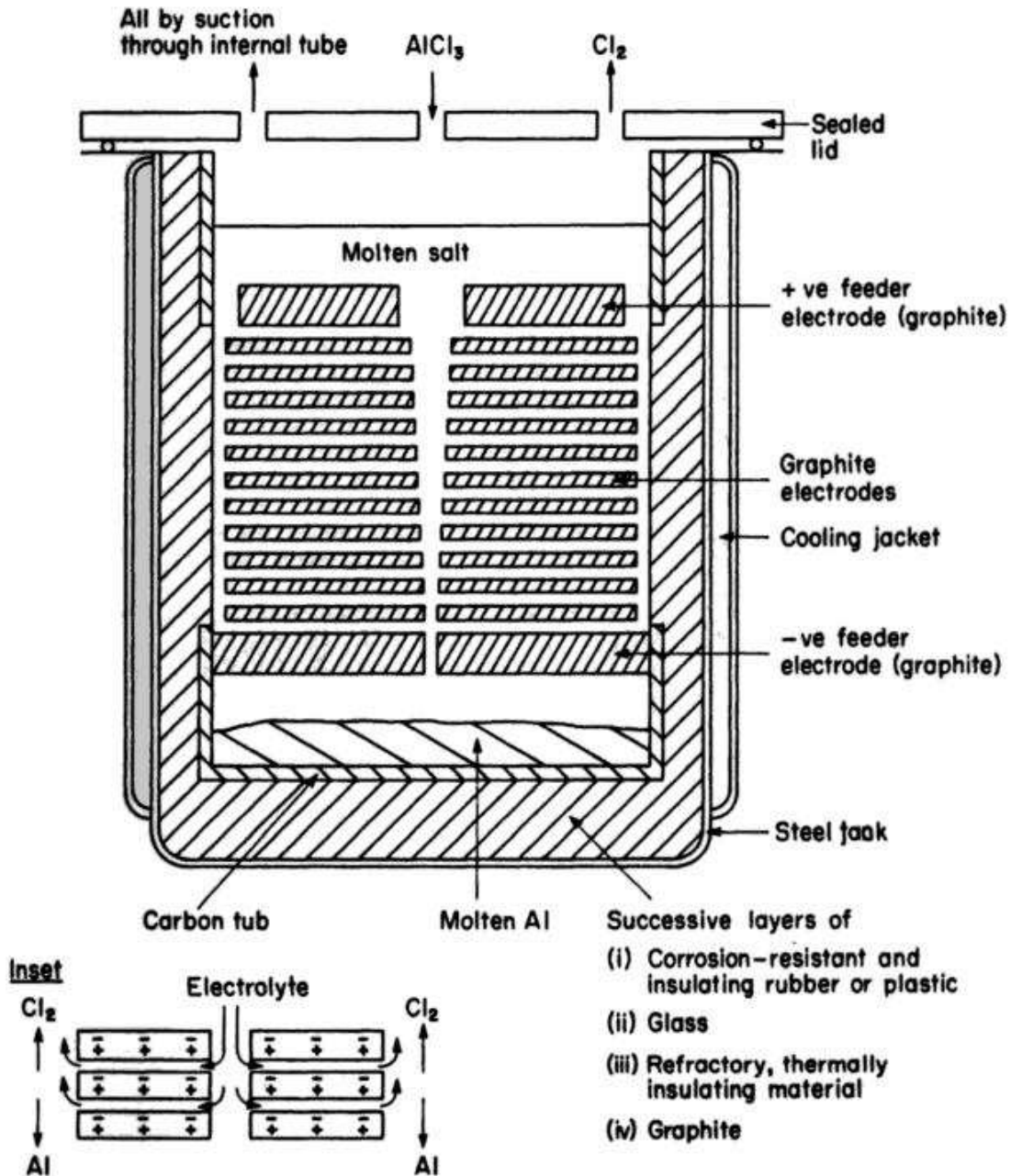


Fig. 4.3 Cell for aluminium extraction by the Alcoa process.

and is transported in the form of purified alumina. On the other hand, aluminium is the most abundant metal in the Earth's crust and is found everywhere, although in a less concentrated form than in bauxite, in common clays. Hence, a further objective of R and D activity is to develop processes for the extraction of aluminium metal from clay.

Aluminium production will always be a highly energy-intensive industry. Table 4.2 shows a breakdown of the costs in a typical Hall-Héroult plant and it can be seen that electrical power is the second largest item; hence, the importance of energy conservation cannot be overemphasized.

Table 4.2 Cost breakdown for aluminium metal production

	% of total cost
Alumina	30
Anodes	7
Other materials	7
Electricity	23
Labour	16
Capital cost	17

4.1.2 Sodium, magnesium and lithium manufacture

These metals are all produced by electrolysis of a mixture of molten metal chlorides; the electrolyte composition is selected to minimize the process temperature and to ensure that it is the desired metal that is discharged at the cathode. The estimated annual world production of sodium and magnesium is a few hundred thousand tons while that for lithium is only a few thousand tons. The major uses are: (a) sodium—manufacture of lead alkyls, isolation of titanium metal, production of several organic and inorganic substances; (b) magnesium—organic synthesis, metal alloys; (c) lithium—polymer initiation, organic synthesis and batteries.

The general technology may be illustrated by the example of sodium production in the Down's cell. The electrolyte is a molten mixture of sodium chloride (40%) and calcium chloride (60 wt % requiring a process temperature of about 600° C. The principle of cell design is shown in Fig. 4.4, although more modern cells have four anodes and cathodes in each cell. The design and materials of construction are again determined by the electrolysis medium. The electrode reactions are simple; at the cylindrical graphite anode:



and at the steel cathode surrounding the anode:



Some separation of the products is necessary to prevent the back-reaction and a steel gauze diaphragm ensures that the chlorine gas and the liquid sodium are guided to different collection reservoirs. The sodium is much less dense than the melt and readily rises up a pipe into a reservoir; indeed, this is the basis of its separation from the small quantity of calcium which also forms at the cathode. The calcium is more dense and sinks back into the electrolyte where the equilibrium:



ensures that its concentration remains constant and low. The operation of the