Aluminium Production

• **Introduction**
• **The aluminium production process**
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  – Prebake Cell
  – Pechiney technology
  – Inert anode
Aluminium Production: intro

Aluminium can be produced by using anodes and cathodes in the aluminium smelter.

The main components of anodes are petroleum coke, a product from the distillation of oil, and coal tar pitch, a distillation product extracted from the tar that is obtained in coking plants. A part of the anode material, the so-called anode butts, is returned by the aluminium smelters to be reused as raw material. Petroleum coke and anode butts are crushed, dried if necessary, graded, ground, heated and mixed with an exact amount of pitch and finally kneaded. An optimal composition is yet another prerequisite for good anode quality. Depending on the anode format the compound will be moulded to a 'green anode' either in a press or in a vibrating machine. After forming, the anodes are baked at approx. 1150°C to carbonize the pitch binder and eliminate the volatile parts of the pitch. After cleaning, inspecting and packaging, the anodes are ready for delivery. Anodes can be produced in all shapes and sizes. Click here for a picture of the Anode production process steps. Click here for a short overview of the aluminium production process.
the Hall-Héroult-Electrolysis
Anode production process steps

1) Petroleum coke storage
2) Butt storage
3) Liquid pitch storage
4) Sampling
5) Drying
6) Grading
7) Crushing
8) Grinding
9) Sifting
10) Intermediate storage
11) Metering
12) Preheating
13) Mixing and kneading
14) Homogenizing/cooling
15) Pressing
16) Vibrating
17) Baking
18) Inspecting
19) Packaging, storage
20) Dispatch
Cathode blocks

Cathodes made from carbon and graphite are applied for the production of primary aluminium.

- Cathodes in aluminum electrolysis - content
- Production of primary aluminium
- Aluminium electrolysis
- Electrolysis cell lining
- Aluminium electrolysis cell
- Electrolysis cell - General data
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Cathodes in aluminum electrolysis - content

- Electrolysis cell
- Cathode blocks
- Graphitized blocks
Aluminium electrolysis

General chemical reaction

\[2 \text{Al}_2\text{O}_3 \text{(dissolved)} + 3 \text{C} \text{(s)} \rightarrow 4 \text{Al} \text{(liquid)} + 3 \text{CO}_2 \text{(gas)}\]

Cathode reaction:

\[4 \text{Al}^3+ \text{(bath)} + 12 \text{e}^- \rightarrow 4 \text{Al} \text{(liquid)}\]

or

\[4 \text{AlF}_4^- \text{(bath)} + 3 \text{e}^- \rightarrow \text{Al} \text{(liquid)} + 4\text{F}^-\]

Anode reaction:

\[3 \text{C} \text{(solid anode)} + 6 \text{O}^2- \rightarrow 3 \text{CO}_2 \text{(gas)} + 12 \text{e}^-\]
Electrolysis cell bottom lining

Requirements to the cell lining
• electrically conductive
• resistant against high temperature
• low chemical reaction with bath components
• no alloy-formation with liquid aluminium
⇒ Single candidate: CARBON/GRAPHITE

Technological challenge
Tremendous increase over past century in
• Cell size
• Efficiency
• Productivity
Demand for substantial cathode carbon developments

Main targets
Reduction in power consumption
Increase in potlife
Aluminium electrolysis cell

6 Carbon Anode
7 Molten Cryolite
8 Liquid Aluminium
Electrolysis cell - General data

- **Cathode Block**: 10 - 20 blocks/pot = 8 - 26 t/pot
- **Sidewall Blocks**: 2 - 7 t/pot
- **Ramming Paste**: 2 - 10 t/pot

- **Steel Shell**: 8 - 15 m long; 3 - 4 m wide

- **Pot Amperage**: 100 – 330+ kA
- **Pot Voltage**: 4 - 5 V

- **Potline**: 100 - 300 cells connected in series

- **Potlife**: 1500 - 3000 days
Western world cathode demand
(*cathode = bottom blocks and sidewall blocks)

37 kt
23 kt
10 kt
12 kt
8 kt
11 kt

Total world: 101 kt
Cathode block production

- Binder pitch
- Anthracite
- Graphite
- Petrolcoke
- binder pitch
- Anthracite
- Graphite
- Petrolcoke
- Extrusion
- Baking
- Graphitization
- Machining
Classification of cathode blocks

**Anthracitic / Semi-graphitic**

- based on anthracite (gas or electrically calcined)
- with or without additions of graphite; baked at ~1200 °C

**Graphitic**

- based on 100% graphite aggregate; baked at ~1200 °C

**Graphitized**

- based on petroleum/pitch coke; baked at ~800 °C
- followed by graphitization at over 2500 °C
Cathode blocks - selection criteria

- Low sodium expansion
- Low electrical resistivity
- High thermal conductivity
Graphite layer structure
Chemical / structural changes during heat treatment

Marsh and Griffiths, Int. Symp. on Carbon, Japan 1982
Advantages of graphite

1) Low electrical resistivity
   - Lower cathode voltage drop
   - Less energy consumption

2) High thermal conductivity
   - Uniform temperature distribution
   - Less sludge deposition on cathode surface

3) High thermal shock resistance
   - No rodding cracks

4) Low sodium uptake
   - No cathode laminations

Result: Higher pot amperage / pot metal productivity
Rapport expansion curves

- Amorphous
- Graphitic
- Graphite
Disadvantages of graphite

- Mechanical data lower than anthracite
  Mechanical wear

- High thermal conductivity
  Longer electrical preheating time
  Dissipation of more heat into ramming paste

- Change in current distribution
  Increased horizontal currents in the metal pad

- Larger differential expansion
  Collector bars can move in the slot after cooling
# Graphitized cathodes

**Pot results vs semi-graphitic blocks**

<table>
<thead>
<tr>
<th></th>
<th>Plant A (180 kA)</th>
<th>Plant B (280 kA)</th>
<th>Plant C (300 kA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production increase (%)</td>
<td>+ 2.3</td>
<td>+ 3.2</td>
<td>+ 4.8</td>
</tr>
<tr>
<td>Cathode drop (µΩ)</td>
<td>- 0.25</td>
<td>- 0.25</td>
<td>- 0.26</td>
</tr>
<tr>
<td>Energy from cath. drop (kWh/t)</td>
<td>- 142</td>
<td>- 221</td>
<td>- 246</td>
</tr>
<tr>
<td>Energy from red. ACD (kWh/t)</td>
<td>+ 48</td>
<td>-</td>
<td>- 154</td>
</tr>
<tr>
<td>Total energy (except C.E.)</td>
<td>- 94</td>
<td>-</td>
<td>- 400</td>
</tr>
<tr>
<td>Instability (n.ohm)</td>
<td>+ 1</td>
<td>+ 4</td>
<td>- 11</td>
</tr>
</tbody>
</table>

(P. Homsi; 6th Australasian Aluminium Smelting Technology Conference & Workshop)
Graphitized cathodes
Positive impact on technical results

• Enhanced production output
  - higher current efficiency
  - increased pot amperage

• Lower cathode drop

• Constant or improved specific energy consumption

• Improved pot stability,
  allowing a reduction of the anode-to-cathode distance (ACD)
Graphitized cathodes
Achieved potlife (published data)

- 130 kA pot (low amperage pot)  114 months
- 180 kA pots                   up to 84 months
- 300 kA pots                   65 months
Wear Reduction of graphitized cathodes

Approach
Create a 'harder' cathode by e.g.

- Improved raw materials
- Optimized composition / formulation
- Densification
- Use of Refractory Hard Material (RHM)
- Reduced degree of graphitization
The aluminium production process

The raw material for the extraction of aluminium is aluminium oxide, also called alumina, produced from bauxite. Direct current of a very high intensity is passed through the anodes in the process. The anodes are part of the chemical reaction. For the production of 1 ton of aluminium, approximately 400 kg anodes ton of Aluminium metal is required. The aluminium production process is also called the Hall-Héroult-Electrolysis.

Picture of the general process

Overview of the aluminium production
The Hall-Héroult-Electrolysis

Bauxite $\rightarrow$ $\text{Al}_2\text{O}_3$ + $\text{C}$ + $\text{13,800 KWh}$ = $\text{1t Al}$

4 t

2 t

1/2 t
Prebake Cell:

Pre-bake technology uses multiple anodes in each cell which are pre-baked in a separate facility and attached to "rods" that suspend the anodes in the cell. New anodes are exchanged for spent anodes - "anode butts" - being recycled into new anodes.
Söderberg technology

Söderberg technology uses a continuous anode which is delivered to the cell (pot) in the form of a paste, and which bakes in the cell itself.

An electrolytic cell or pot is an electro-chemical reactor with anodes arranged horizontally or vertically. In case Söderberg anodes are used, the anode is delivered to the cell as a paste that is baked in-situ. In Söderberg cells the power supply is either horizontal, as with HSS (horizontal stud Söderberg) cells or vertical, as is the case with VSS (vertical stud Söderberg) cells.
Pechiney technology

The Pechiney anode technology covers all steps of anode manufacturing:
- Raw materials selection and anode characterization
- Green process
- Baking process
- Anode handling and rodding
- Recycling

The anodes are baked in open type bake ovens, using the following technology:
- low gas consumption (2300 to 2600MJ/t)
- low packing coke consumption
- consistent level of baking
- low tar and fluoride emissions
- long fluewall life (130 to 160 cycles)

For the brickwork maintenance, the fluewalls can continuously be replaced without reducing the production of the furnace.

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Inert anode/wettable cathode

The aluminium industry has employed the Hall-Heroult process for more than 100 years to produce aluminium. The new inert anode technology is believed to reduce the anode, labor, maintenance and environmental costs associated with running a smelter. The wettable cathodes also holds potential for reduced costs and increased operating efficiencies. Due to the fact that inert anodes would not use carbon, the smelting process would not create carbon dioxide, carbon monoxide or other greenhouse gases.

(from “An Aluminium Revolution” Thomas Van Leeuwen, CFA)
Inert anode/wettable cathode

Technology:

The inert anode/wettable cathode invention relates to production of a metal by electrolytic reduction of a metal oxide to a metal and oxygen. A preferred embodiment relates to production of aluminum by electrolytic reduction of alumina dissolved in a molten salt bath. An electric current is passed between an inert anode and a cathode through the salt bath, thereby producing aluminum at the cathode and oxygen at the anode. The inert anode preferably contains at least one metal oxide and copper, more preferably the oxides of at least two different metals and a mixture or alloy of copper and silver.

(from “An Aluminium Revolution” Thomas Van Leeuwen, CFA)
Inert anode/wettable cathode

Technology (2):

The cermet materials used in anodes are deemed inert because, unlike carbon, they do not react with oxygen generated by electrolysis of alumina. The cermet materials also have relatively low solubility in the electrolyte. However, inert electrodes are subject to corrosion through several different mechanisms. Aluminum droplets floating or suspended in the molten salt bath may rapidly attack all components of the anodes. This problem is more likely to occur at temperatures below 900°C than at higher temperatures because lower operating temperatures are generally associated with higher electrolyte densities that can cause aluminum droplets to float. Secondly, aluminum and sodium dissolved in the molten salt bath may also attack the ceramic or dissolve the metallic components of the anode. The solubility of aluminum and sodium in cryolite drops rapidly from 960°C to 910°C, probably by about a factor of five. Further reduction in temperature below 910°C will reduce the solubility even more, but the benefit is small compared with other mechanisms such as electrochemical corrosion of the anode metal phase.

(from “An Aluminium Revolution” Thomas Van Leeuwen, CFA)
Inert anode/wettable cathode

Technology (3):

The electrolytic cell operates at a temperature in the range of about 700°-940°C, preferably about 900°-940°C, more preferably about 900°-930°C, and most preferably about 900°-920°C. An electric current is passed between the inert anode and a cathode through a molten salt bath comprising an electrolyte and alumina. In a preferred cell, the electrolyte comprises aluminum fluoride and sodium fluoride, and the electrolyte may also contain calcium fluoride, magnesium fluoride and/or lithium fluoride. The weight ratio of sodium fluoride to aluminum fluoride is preferably about 0.7 to 1.1. At an operating temperature of 920°C, the bath ratio is preferably about 0.8 to 1.0 and more preferably about 0.96. A preferred molten salt bath suitable for use at 920°C contains about 45.9 wt. % NaF, 47.85 wt. % AlF₃, 6.0 wt. % Cap, and 0.25 wt. % MgF.

(from “An Aluminium Revolution” Thomas Van Leeuwen, CFA)