202] **Hall-Heroult Process**

this is NOT practically feasible
$$Al_2O_3 + 3C \longrightarrow 2Al + 3CO$$
$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$

C can't reduce Al
(it requires v. high temp., > 2000°C & that is v. hard to maintain)

* { Al emf is −1.66 which is so high that even H overpotential is not sufficient to overcome it }
↓
if this were possible, then Al would become much cheaper

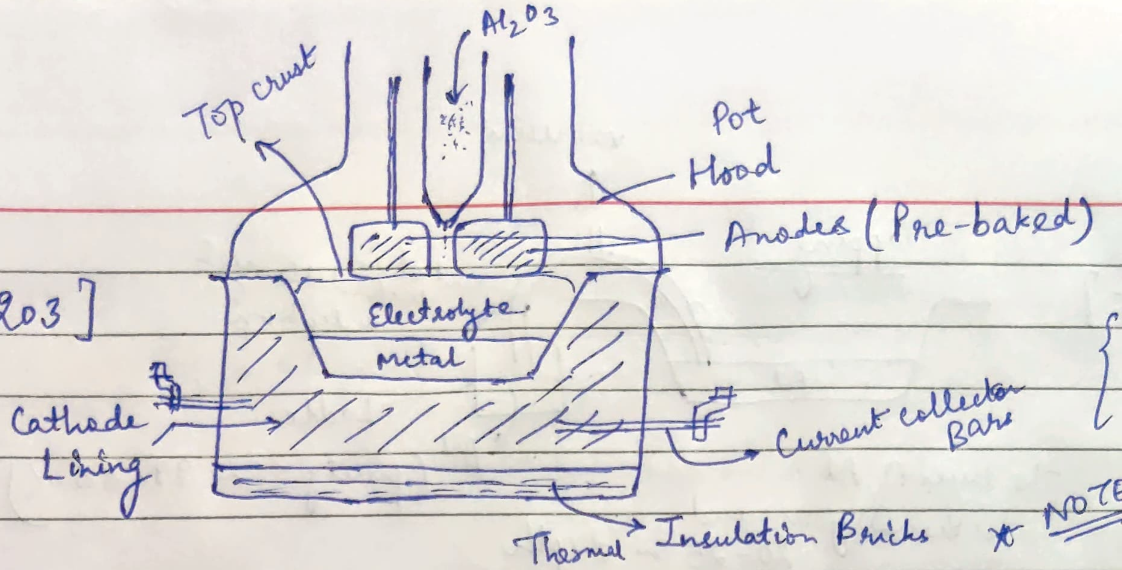
Further, there are two other problems

- Al_4C_3 forms on rxn. with Carbon
- Al has low melting point & thus ~40 % Al would simply evaporate

Thus, Hall-Heroult Process is used
↓
involves use of
Cryolite (Na_3AlF_6) → in the process of Molten Salt Electrolysis
↓
this is a v. rare salt
↓
only found in one place in the world → in Greenland
↓
Process was developed in 1886 independently by → till date no better process has been found

- Charles Martin Hall (in USA)
- Paul Heroult (in France)

203]



$\left\{ \begin{array}{ll} 9-12\,m & L \\ 3-4\,m & W \\ 1-1.5\,m & H \end{array} \right\}$

* NOTE: { Part of the bottom portion is under the ground

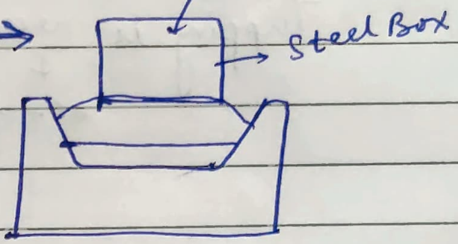
Cathode — Prebaked Carbon Bricks

(i) Soderborg Anode

(ii) Pre-baked Anode

↓

nowadays only these are used



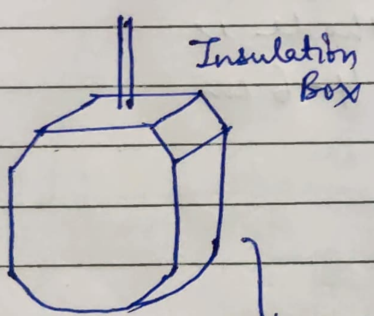
they are a single anode (in the form of a steel box)

↓

it is pushed from the top & gradually gets consumed

↓

NOT used now since too quick consumption & replacement occurs



this is baked to get Pre-baked Anode

(needs to be replaced once after every day)

LECTURE 39 (21/04/2023)

204] ~~The top crust~~

↓

~~prevents Anode~~ from getting oxidized

At bottom

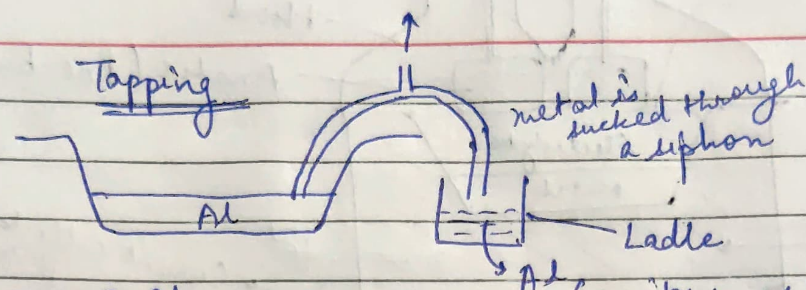
↓

Iron collector bars are present that carry current

the bars help carry these currents to the next cell ("Pot")

Current comes from Anode, & leaves through Collector bars

205] **Tapping**



(purity : ~ 99.85%)

The layer of Al is usually around 20–25 cm depth

(but may vary from 15–40 cm)

Tapping is necessary
↓
bcz if metal accumulates too much
↓
the distance b/w Anode & Cathode would reduce
↓
The ideal distance maintained b/w Anode & Cathode is 4–6 cm

206] In reality there is not just one pot
↓
there are several pots connected in series
(125–175 pots)
↓
called "Pot Line"

{* Thus, production can be increased simply by increasing the Pot lines (i.e. length of pot lines)}

207] Capacity → given in terms of current passed per pot
(for Al pots)
↓
Earlier : 50–60 kA (per pot)
Nowadays : > 300 kA (per pot)

208] <u>Advantages of increasing size of pot</u>
↓
(i) Capital & Labour cost per unit weight of metal is decreased

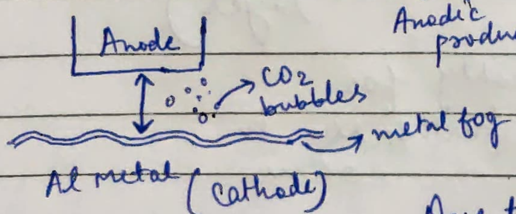
(ii) Energy consumption decreases
(since heat loss is proportional only to the size of the cell)
↳ eg: 300 kA is not losing ~~more~~ heat than 50 kA one

(iii) Cell life increases
(i.e. life of cathode lining)

209] <u>Cell Performance</u>
↓
measured in two terms

I] <u>Current Efficiency</u>   II] <u>Voltage (Energy) Efficiency</u>

(a) Re-combination of Al & CO_2
Al → cathodic product
CO_2 → Anodic product



Due to Electromagnetic flux disturbances, the Anode may come into contact with metal :

$$2\,Al + 3\,CO_2 \longrightarrow Al_2O_3 + 3\,CO$$

(b) Short Circuiting

↓

which may occur due to turbulence

↓

due to electromagnetic flux

(c) Presence of impurities

↓

which come from carbon cathode

↓

Contain impurities like Fe, Si, Ti, etc.

(eg: $Fe^{+++} \xrightarrow[\text{at cathode}]{\text{reduced}} Fe^{++} \xrightarrow[\text{oxidised}]{\text{again gets}} Fe^{+++}$ ...... (so on))

Iron present in ferric form

⇓

this process leads to losses

(d) formation of Al_4C_3

↓

wherever Al comes into contact with cathode, it forms Al_4C_3

↓

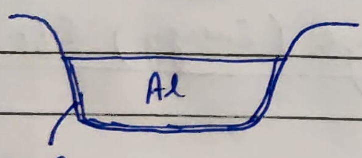
This layer protects against further rxn.

↓

However, when tapping is performed, it causes this layer to get slightly removed due to electrolyte coming in contact with it (which dissolves the layer)

↓

opening it freshly for further rxn. to occur



Al_4C_3

210] Voltage (Energy) Efficiency

$E^\circ \rightarrow 1.2\,V$

V_o (overpotential) → 0.5 V

$\therefore 1.7\,V$ ⇐ Total Voltage (Sum of E° and V_o)

Resistance of Bath — 1.76 V

Anode — 0.32 V
Cathode — 0.47 V
Other (Bus Bar) — 0.3 V
0.77 V

Total : 2.85 V

Hence, the total voltage of the electrolytic cell is:

Total voltage = 1.7 + 2.85
= $\boxed{4.55\ V}$

* We want to minimize this voltage (in order to reduce power consumption)

The Power consumption for the cell is : 14 – 15 kWh/kg Al

{ Even for the best plant in the World ⇒ 13.5 kWh/kg Al }

2.11] Simplified reaction in Electrolytic Baths

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

Al Anode — $\frac{3}{2} O^{2-} \rightarrow \frac{3}{4} O_2 + 2e^-$

$C + O_2 \rightarrow CO_2$

The major electrolyte is:

Na_3AlF_6 (cryolite) dissolved in 7 – 8 % Al_2O_3

* AlF_3 must be added constantly

since it gets consumed by vaporization

But to improve performance, (properties of the bath) we also add → CaF_2, MgF_2, $LiF + AlF_3$

LECTURE 40 (25/04/2023)

212] Hall-Heroult Process
↓
Anode Effect : Sudden rise in cell voltage from 4.5 V to about 30-40 V

Leads to following problems:

(i) Increase in power consumption
(ii) Increase in temp. of bath
(iii) Bath gets decomposed
↓
Chloride gets preferentially evaporated

This generally happens when Alumina conc. in electrolytic bath
↓
decreases from 7-8 % to about 1 %

{This problem is Controlled by adding Alumina}

213] Importance of Anode Effect

(i) It indicates whenever fresh charge of Alumina needs to be added

(ii) Also indicates whenever cell is working normally
↓
eg: if voltage doesn't increase after certain time
↓
this indicates a problem bcz it means Alumina is not getting consumed

214] **Reasons for Anode Effect**

↓

when there is decrease in Alumina conc.

↓

Critical current density will also decrease

Critical Current Density depends upon:

(i) Character & type of molten salt
(ii) Amount of oxide (solute) dissolved in bath
(iii) Material of Anode
(iv) Temp. of bath

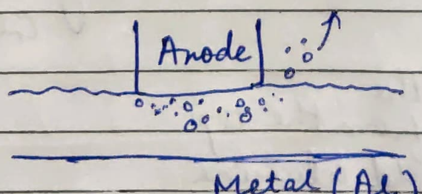
For Hall-Heroult Electrolytic Cell → Critical current density depends on conc. of Alumina in bath

* In any bath

↓

Anode Effect occurs when actual current density <u>becomes lower than critical current density</u>

215] **Mechanism of Anode Effect**



If Alumina conc. is more

↓

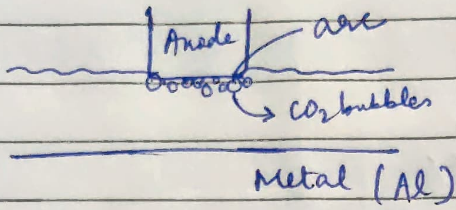
Surface tension is low

↓

& wettability is high

↓

CO_2 bubbles get easily detached from Anode, & move to atmosphere



If conc. of Alumina is low
↓
Surface Tension is high
↓
∴ CO_2 bubbles don't get detached from surface of Anode
↓
thus a gas layer comes in b/w Anode & electrolyte
↓
leading to increase in resistance
↓
which leads to sharp rise in voltage

Bubbles also get popped due to high voltage
↓
leads to formation of arcs
↓
Causes v. high temperatures leading reaction with Carbon
↓
forming : Perfluorinated Carbon

$(CF_4,\ C_2F_6)$
↓
these are bad for environment since they lead to Global Warming

this is the ultimate solution which would need to be done

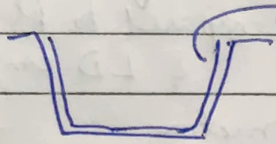
Thus, the only remedy for this is to break the crust from the top & Add alumina & allow it to mix
↓
however even this will take 5–10 mins which can lead to large power losses
↓
this is immediate solution

so what is generally done alternatively, is to lower down the Anode, which can pop the bubbles as well

216] Some more disadvantages of Anode Effect

1. Bath gets overheated
   ↓
   leading to formation of AlF_3
2. Also there is formation of perfluorinated carbons (PFCs)
3. Current efficiency decreases
4. There is melting of side walls due to excessive temp.

NOTE:



Ledge ("leádge")
↓
solidified electrolyte on surface of side walls

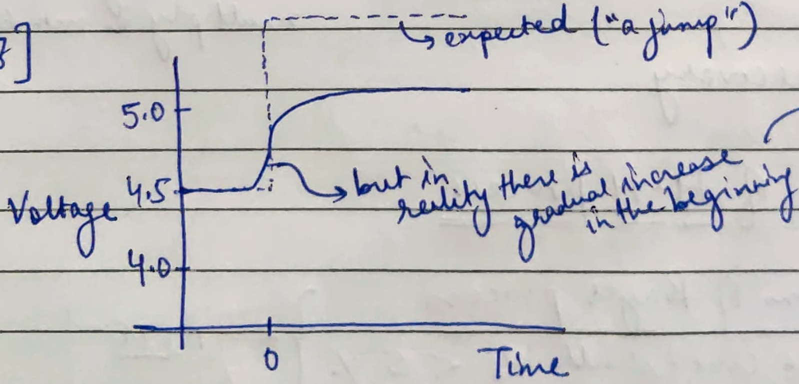
217] Advantages of Anode Effect

1. Indicates normal function of cell.
2. Due to turbulence, Carbon dust floats to surface, gets burned on contact with air, & thus gets removed

produced from Anode Carbon

{ **NOTE:** Carbon dust is formed due to graphite particles in Anode }

218]



Nowadays everything is Computer Controlled
↓
& as soon as this is seen
↓
Alumina is added to prevent Anode effect

219] Advantages & Limitations of Hall-Heroult Process

Advantages:

(i) Easy control of process

(ii) High Purity Al produced directly → 99.8 %
(without any refining needed)

(iii) Simple Construction of electrolytic cell
{as compared to Blast furnace & LD converter}

(iv) Has multiplicity of construction
(i.e. once one cell is made, you can easily go on increasing no. of cells in the chain)
↓
thus there is ease in mass-production
{For other processes this is not true : for example – Blast furnace is too big to constantly multiply in numbers}

(v) High recovery

220] Limitations of H-H process

{Limitations of Bayer process
(i) Silica conc. should be < 5 %} ← NOTE:

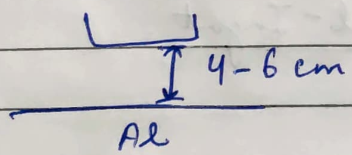
H-H Limitations
(i) Requires high purity Al_2O_3
(ii) High power consumption → 14-16 kWh/kg
(iii) High specific capital investment
(iv) Low production rate (i.e. Low Productivity)
→ 0.07 ton/cubic-m/day
(whereas: Blast furnace is 3.0 ton/cu.m/day)

(v) Large consumption of high purity electrode carbon
(vi) Harmful fluoride evolution ← Bad for health of workers
Causes Global Warming
(vii) Spent Pot lining
(after electrolytic cell is used
↓
lining has to be replaced
↓
the spent lining is dumped, where it can react with substances to form Potassium cyanides, etc. which are dangerous)

221] Improvement of H-H Process

(i) Optimisation of H-H Bath
↓
since a v. ~~simple~~ specific composition is known for optimization

(ii) Anode cathode distance is well-defined & should be optimized



(iii) Bath temp. ~ controlled within 955-960°C
(iv) Current distribution
(v) Size of cell → can be kept > 300 kV (which is better)

{NOTE: Mathematical modelling results have also now allowed reduction in turbulence in the cell}

(vi) Collection & cleaning of gases
(vii) Automation in Alumina feeding (Al_2O_3)
(viii) Control of Anode effect.

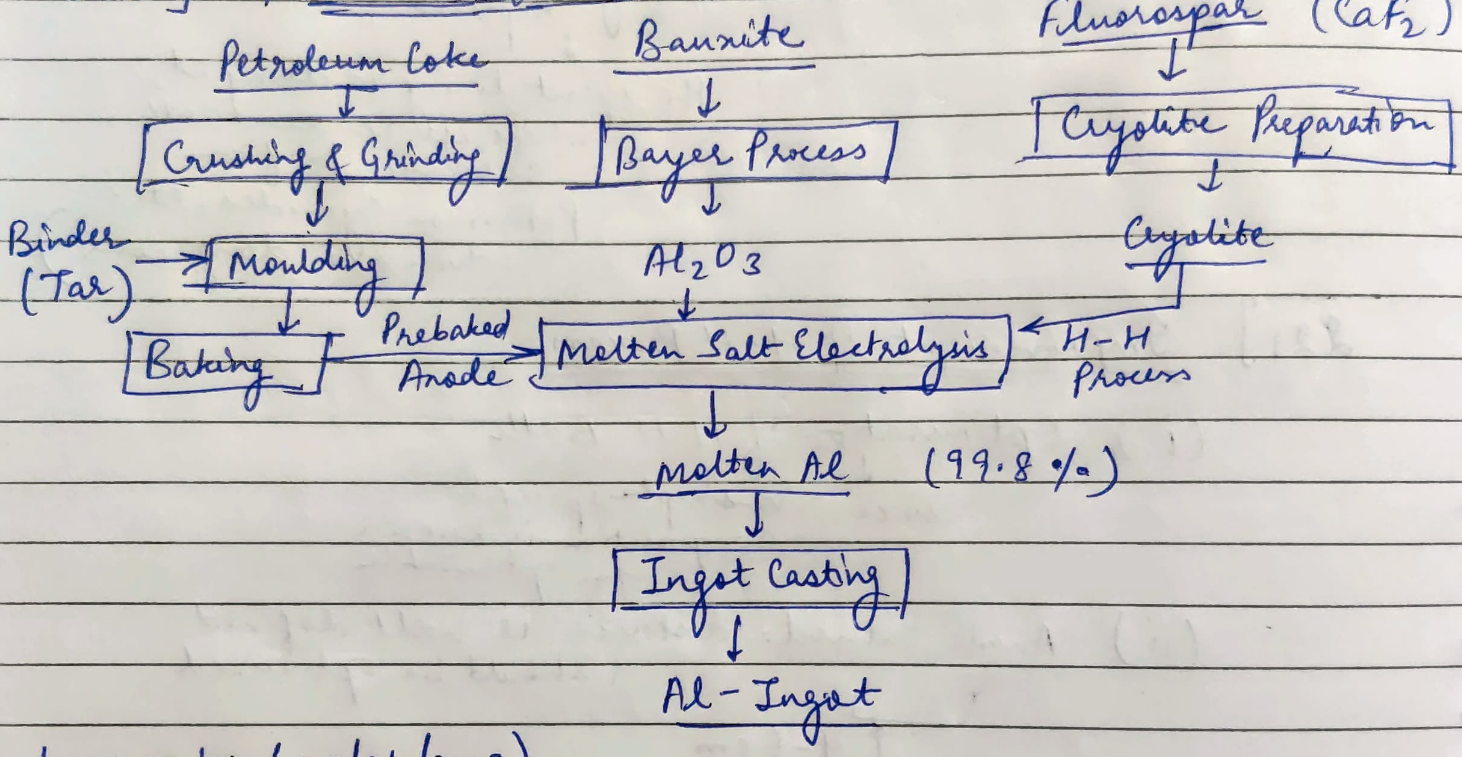
which leads to significant power & cost saving

NOTE: Due to these improvements ~ Current Efficiency has been improved from 93% to 95%.

NOTE: Power consumption is reduced from 17 kWh to 13.5 kWh

(Theoretically, it should be 6.5 kWh)

222] Flow Sheet for H-H Process



LECTURE 41 (27/04/2023)

223] Aluminium Production Plants in India

3 companies & 8 Al plants

* (NOTE: India has one of the largest Bauxite reserves in the World)
↳ ~3 billion tons

{ > 75% Indian Bauxite Reserve situated in the East Coast of Odisha & A.P. }

(5th largest in the world after: Australia, Guyana, Jamaica, Brazil)

224] World Production [Aluminium]
(2022) (million tons)

World	69
China	40
India	4.0 (2nd in the world)
Russia	3.7
Canada	3.0
UAE	2.7
⋮	
USA	0.86

225] Aluminium Production Plants in India

Company	Plant Location	Year of Establishment	Production Capacity (tons) per year
1. Hindalco Industries Ltd. {This is a Private Company}	1. Hirakud, Sambalpur, Odisha (earlier was owned by INDAL)	1956	1,35,000
	2. Renukoot, U.P.	1962	4,10,000
	3. Mahan Aluminium, Bargawan, Siddi, M.P.	2013	3,60,000
	4. Aditya Aluminium, Lapanga, Sambhalpur, Odisha	2014	3,60,000
2. National Aluminium Company (Nalco) {Government owned (i.e. Public sector) Company} → this is the ONLY Govt. owned plant	5. Angul, Odisha	1981	4,60,000