

Aluminium Production



Extraction of Non-Ferrous Metals

Details about of Al

Atomic Number: 13

Details about of Al:

Atomic Weight: 27 amu

Density: 2.702 gm/cm³

Melting Point: 660.37 °C

Boiling Point: 2467 °C

Common Minerals

Bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)

Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$)

Cyanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)

Sillimanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)

Corundum (Al_2O_3)

Cryolite (Na_3AlF_6)

Aluminate ($\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$)

Problems of conventional pyro-metallurgy processing

Carbothermic reduction of aluminium oxide is **not** commercially feasible because of:

- High temperature requirement ($\sim 2000^{\circ}\text{C}$).
- Formation of undesirable aluminium carbide at this temperature.
- Refractory required for such high temperature are expensive and also not readily available.

Problems of electrolysis of aqueous salt

Extraction of aluminium by *electrolysis of aluminium salt* in aqueous medium is *not feasible*. This is because:

- Hydrogen evolution, due to the decomposition of aqueous solution occurs at a much lower voltage than that needed for the electrodeposition of aluminium ions.
- The hydrogen overvoltage is insufficient to overcome the 1.67-volt difference in potential between aluminium deposition and hydrogen evolution.

Primary Aluminum Production

The primary ore of aluminum is bauxite, a mixture of hydrated aluminum oxides:

- Gibbsite - $\text{Al}(\text{OH})_3$ (most extractable form)
- Boehmite – $\gamma\text{-AlO}\cdot\text{OH}$ (less extractable than Gibbsite)
- Diaspore – $\alpha\text{-AlO}\cdot\text{OH}$ (difficult to extract)

It is formed by weathering of aluminum-bearing rocks by rainwater, and so bauxite deposits tend to be found in areas that are now, or were in the past, tropical high-rainfall areas.

Aluminum is contained in many minerals, but bauxite is the preferred ore because it has the highest aluminum oxide content and is therefore the cheapest to process.

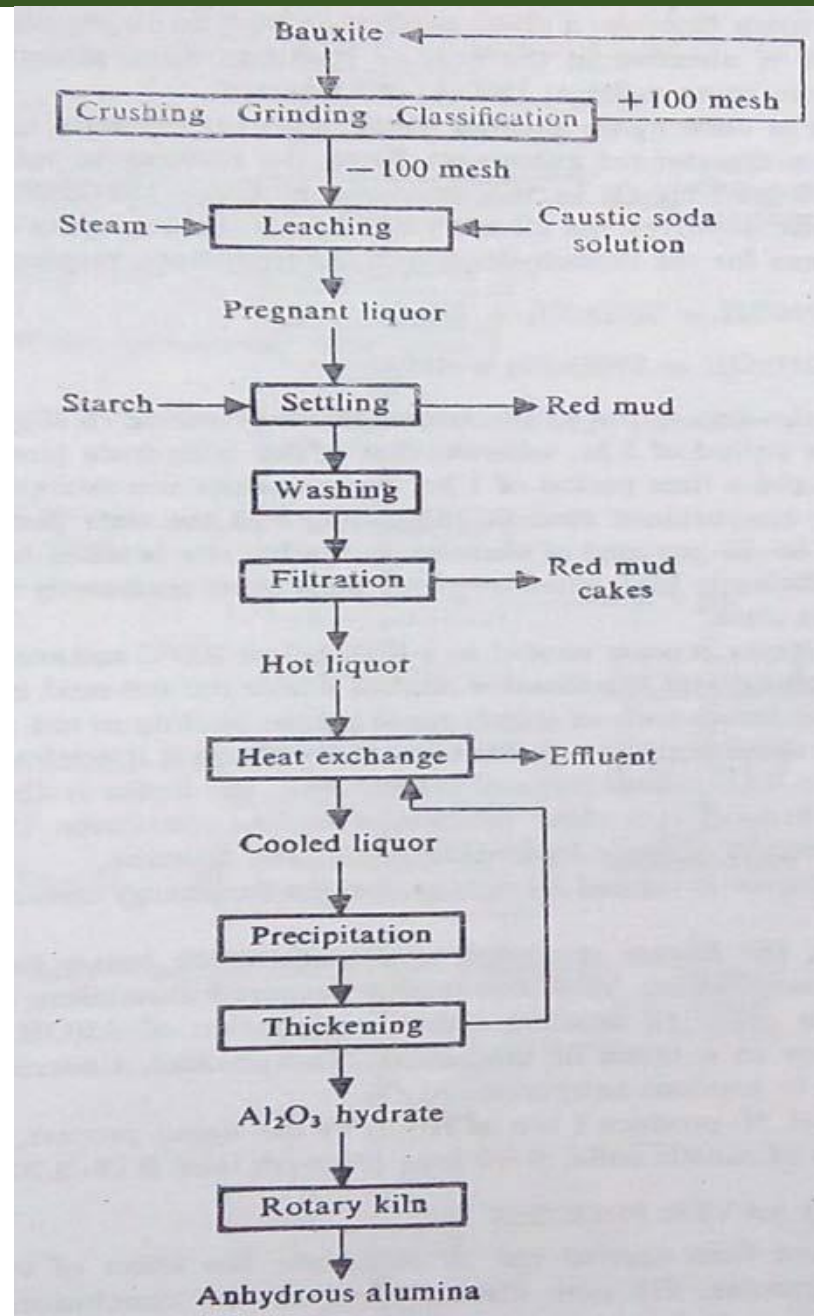
Although aluminum is an extremely common element on earth, it was not practical to produce aluminum metal at a reasonable cost until two breakthroughs had been made: a method for producing purified aluminum oxide from bauxite (*the Bayer process*), and a method for converting aluminum oxide to metallic aluminum (*the Hall-Heroult process*).

General method of extraction:

Step 1: Production of Alumina (Al_2O_3) from Bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) \rightarrow *Bayer Process*.

Step 2: Electrolytical decomposition of Alumina (Al_2O_3) dissolved in cryolite ($\text{AlF}_3 \cdot 3\text{NaF}$) bath \rightarrow *Hall-Heroult Process*.

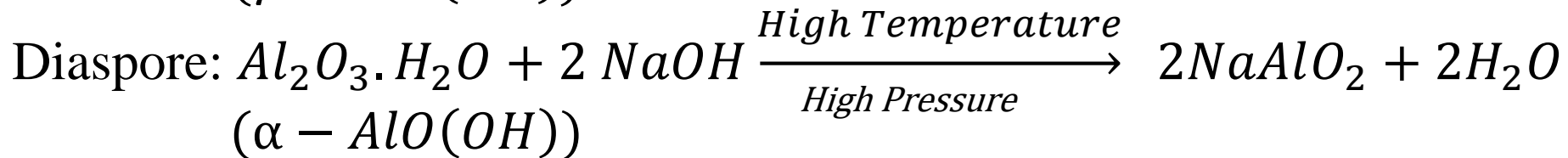
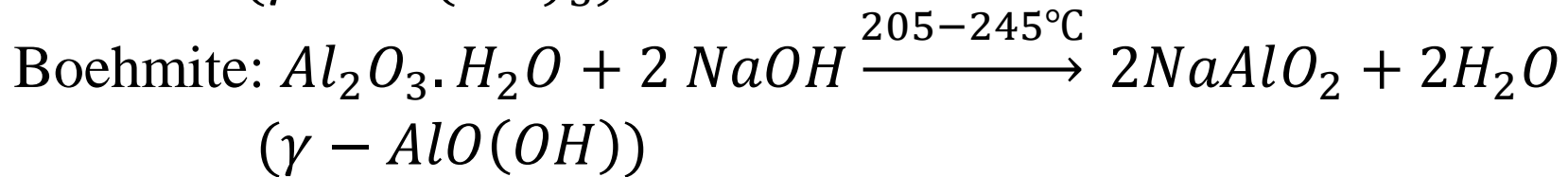
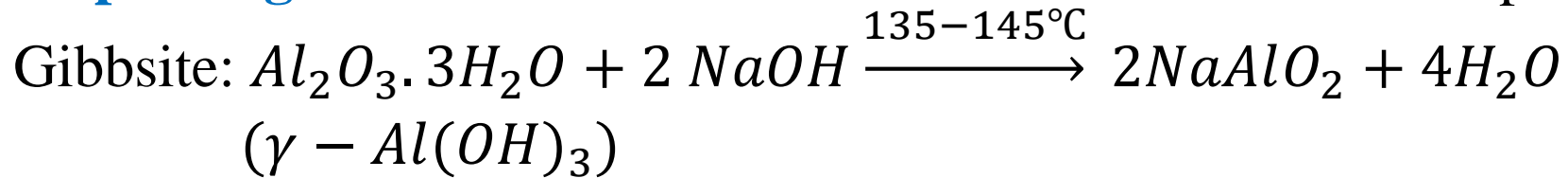
The Bayer process (continue..)



The Bayer process

Steps involved in Bayer Process are:

Step 1. Digestion: Dissolution of the alumina at elevated temperatures.



Step 2. Clarification: Addition of flocculants then separation and washing of the insoluble impurities of bauxite (red mud) to recover the soluble aluminate and caustic soda.

The Bayer process (continue..)

Step 3. Precipitation: Precipitation of pure Gibbsite by seeding the cooled, clarified solution with previously precipitated crystals.



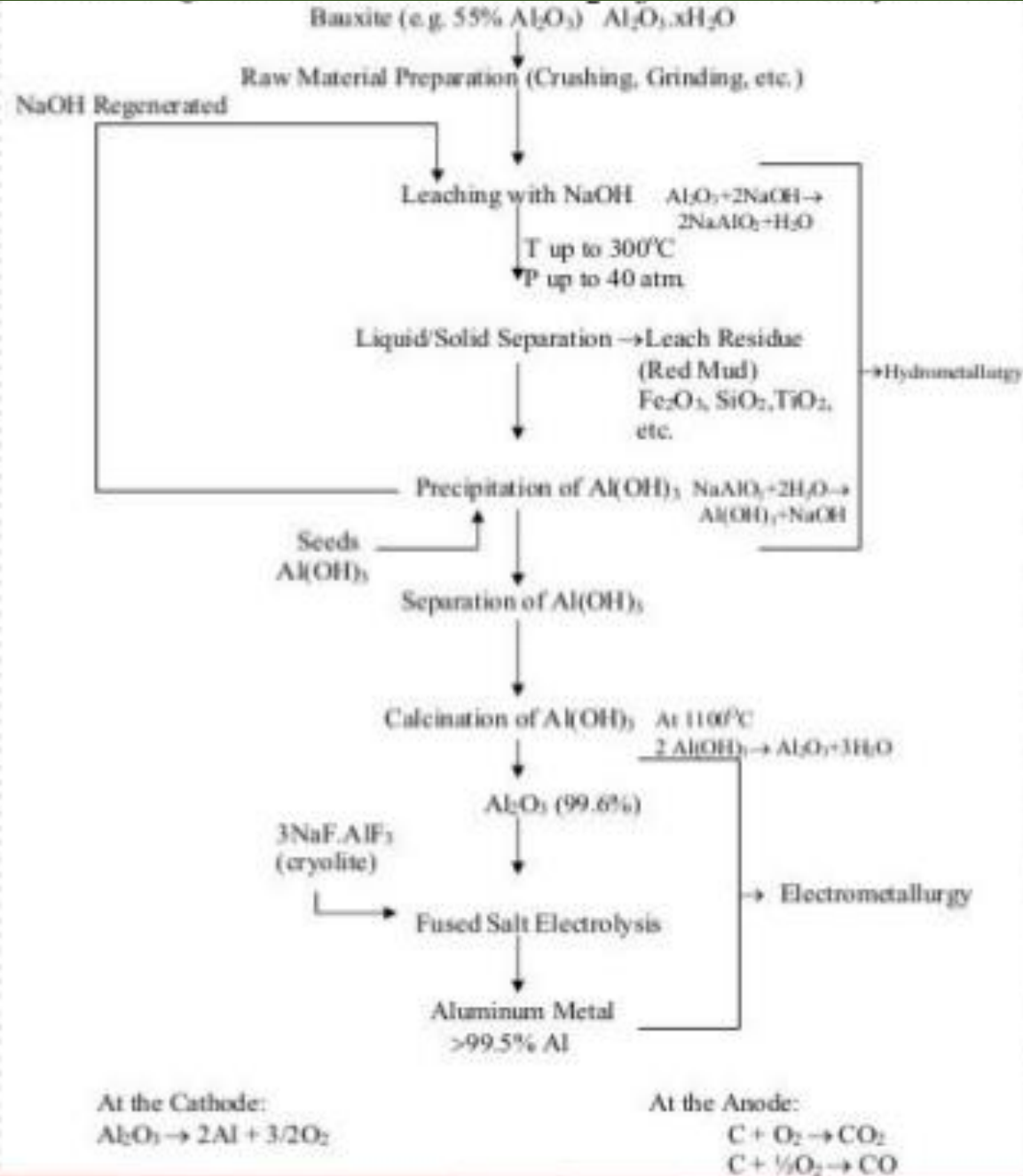
Step 4. Regeneration: Regeneration of the solutions for recycling to step 1 by evaporation of the water introduced by the washings.

Step 5. Calcination: Heating the precipitated Gibbsite, to 1100 °C (calcination), to remove the chemically combined water, hence producing alumina.



The Bayer process (continue..)

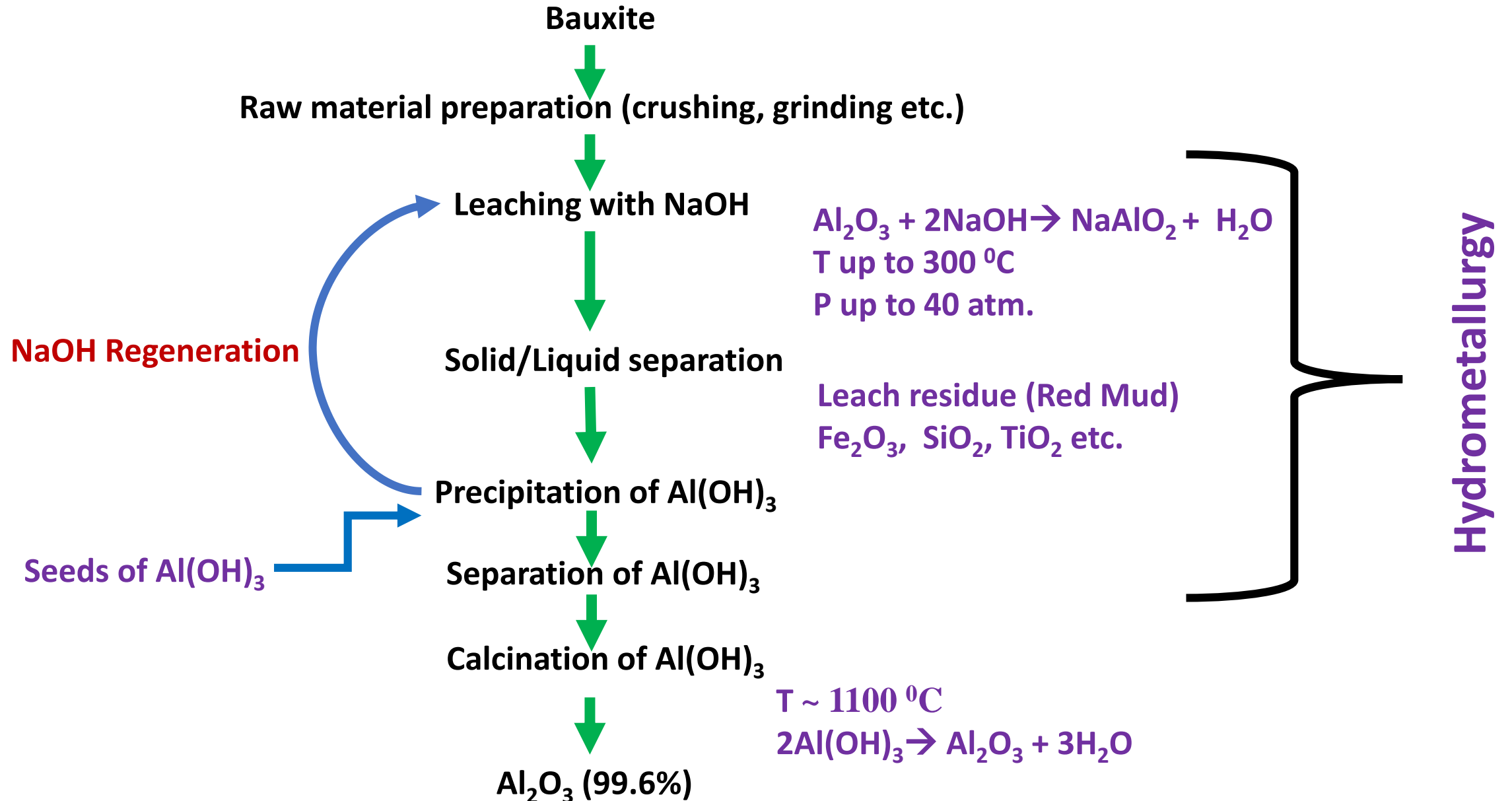
Complete Al-
Extraction flow
chart



Factors affecting Bayer Process:

- Finer bauxite gives better digestion of alumina in liquid liquor.
- Wet grinding is more efficient than dry grinding.
- Digestion accelerates at high temperature. To prevent evaporation of water at high temp. (say 220 °C) a high pressure (say 25 atm.) is applied.
- There is a lower limit of temp. at which digestion and its subsequent processing can be carried out. Below this temp. aluminum hydroxide may precipitate out during clarification and/or filtration. This may lead to alumina loss and deterioration of filter cloth due to clogging.
- Sensible heat of hot pregnant liquor after filtration is recovered by heat exchangers.
- In precipitation stage, entire precipitates of alumina not allowed because it may cause precipitation of silica along with alumina.
- For efficient calcinations of alumina in rotary kiln, required temp. is 1400°C. Decomposition of $\text{Al}(\text{OH})_3$ produces $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Required dehydration temp. is 1200°C and 800°C respectively. The addition of small amount of CaF_2 sometimes helps in dehydration.

Bayer Process(continue..)



Hall-Heroult Process

In 1886, Hall (in the U. S.) and Heroult (in France) independently developed this. processes using cryolite (Na_3AlF_6) as a molten salt electrolyte for producing aluminum. Cryolite is electrically conductive, and dissolves alumina.

Both the anodes and the cathode are made of carbon. The anodes are gradually consumed by the oxygen that migrates to the anodes, and so the overall electrolysis reaction is



The theoretical voltage for this reaction to occur is 1.15 volts, but due to anode overvoltages the potential in actual practice is 1.5-1.7 volts. In order to overcome the electrical resistance of the electrodes, conductors, and containers, the typical operating voltage is 4 -5 volts.

Operating conditions for an aluminum electrolysis cell are:

- Temperature: 935-975°C
- Alumina content of electrolyte: 2-6%
- Cell voltage: 4-5 volts
- Faraday efficiency: 85-90%

Hall-Heroult Process(continue..)

Additives to cryolite bath:

- AlF_3 (improves Faraday efficiency)
- CaF_2 , LiF , MgF_2 (reduce freezing point of electrolyte)

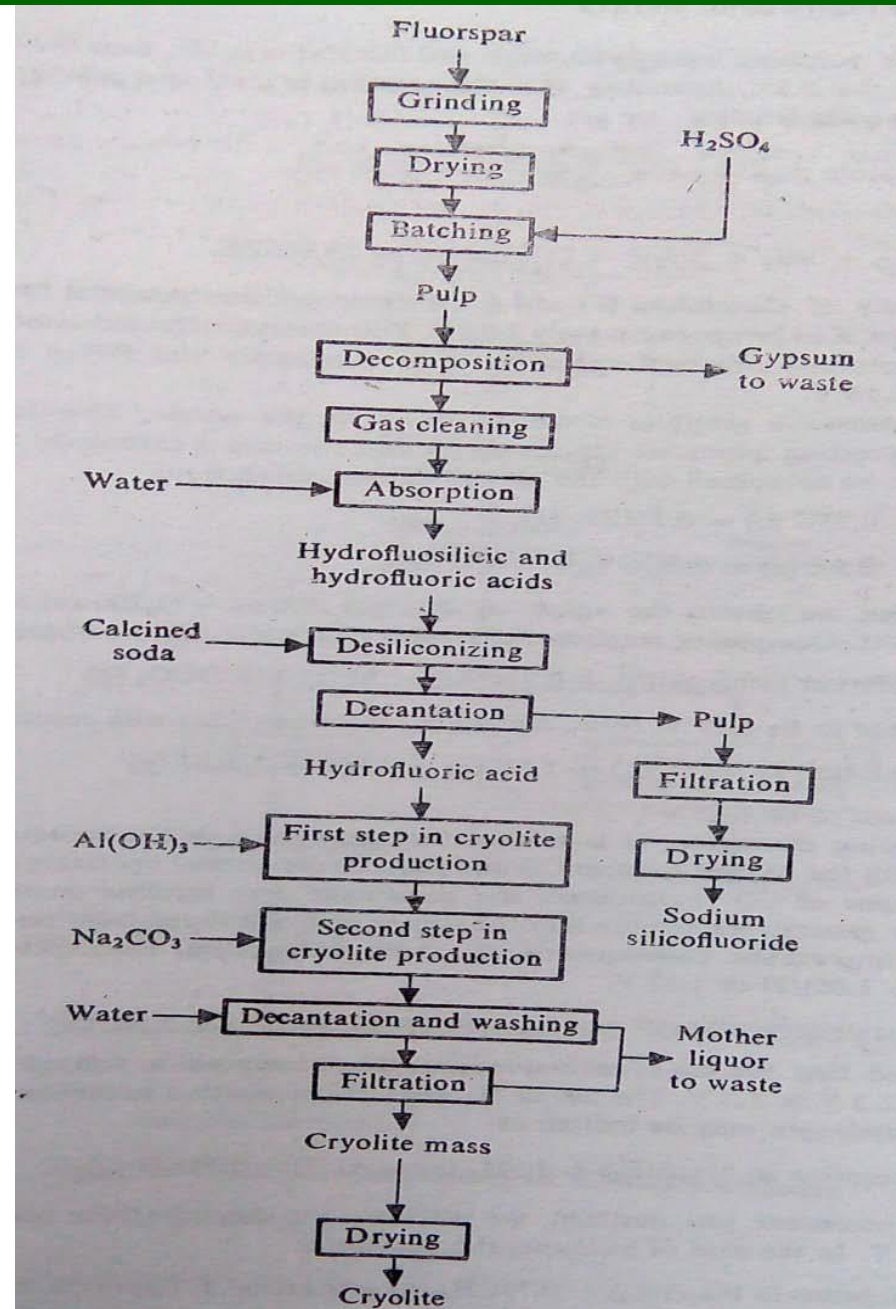
Raw material and power usage per ton of Al produced:

- Al_2O_3 : 1.90-1.95
- Electrolyte: 0.04-0.06
- Anode carbon: 0.43-0.50
- Power, Kw-hr: 13,000-16,000

Wastes produced in aluminum electrolysis:

- HF , CF_4 , and other fluorocarbons (from anode reactions)
- CO_2
- “Salt cake” (spent electrolyte, metal oxides, and entrained metallic aluminum droplets)

Synthesise of Cryolite



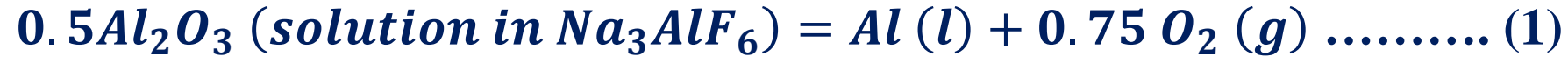
Hall-Heroult Process(continue..)

- Note the tremendous power consumption of aluminum production.
- The electrolysis must supply three electrons for every atom of metallic aluminum, and so very high currents are needed to produce aluminum at a reasonable rate.
- Because of this, electric power is the single largest cost in aluminum production, and so aluminum smelters are typically located in areas where electric power is inexpensive, generally near major hydropower sites.
- The high power consumption of primary aluminum production also encourages aluminum recycling, which requires much less electric power

At 1000°C density of molten cryolite is 2.1 gm/cm³ and Al₂O₃ is 3.96 gm/cm³. Al liberated heavier than bath and sinks at bottom. Higher the amount of Al₂O₃ in bath, the higher its density and consequently the sinking of Al is rendered more difficult.

Hall-Heroult Process: Decomposition Potential of Al_2O_3 in dissolved in Cryolite

For Al cathode and oxygen anode the decomposition reaction given as:



In practice consumable graphite electrode serves as anode. Therefore, decomposition potential for Al (l) cathode and carbon (c) anode has to be incorporated i.e. Eq.(1) has to be combined with carbon oxidation reactions:



Combining Eq.(1) and Eq.(2):



Combining Eq.(1) and Eq.(3):



Where E is the decomposition potential. It is to be noted that Eq.(4) and Eq.(5) are of equal importance. Therefore, the theoretical decomposition potential can be taken as $\{(1.19+1.05)/2\}$ or 1.12V.

Hall-Heroult Process: Influence of H₂ or CH₄ injection at Anode

Carbon reduces decomposition voltage of alumina in cryolite bath from 2.2 V to 1.2 V.

Effect of H₂ addition:



Effect of CH₄ addition:



Injection of hydrogen or methane is *not much effective* in reducing decomposition potential of Al₂O₃. Such injection may effective in cut down the graphite consumption.

Hall-Heroult Process: Anode Effect

When the alumina concentration of the [electrolyte](#) falls too low (between 1 and 2%), a phenomenon called [anode](#) effect occurs.

As alumina is depleted from the electrolyte anodic [overvoltage](#) increases. The increase in surface tension of the bath with decreasing alumina concentration coupled with the electrocapillary effect resulting from the higher anode overvoltage reduces wetting of the anode and the bubble contact angle decreases, forming large bubbles. Gas bubble shielding causes the current density on unshielded areas to increase. At 1.2V anode overvoltage, sufficient [fluorine](#) activity is produced to cause fluorine to bond to the carbon. [Fluorocarbon](#) compounds have low surface energy and further decrease wetting of the anode by electrolyte. Soon a continuous film of gas lies between the bath and the anode. Since the cells are operated at essentially constant current, the voltage rises and current flows across the gas film by sparking or arcing. This phenomenon is called the anode effect. During anode effect the gas from the anode changes from CO_2 to a mixture of 2–10% CO_2 , 10–20% CF_4 , 1–3% C_2F_6 and the balance CO.

Hall-Heroult Process: Factors Influencing Electrolysis

Bath Temperature: Increase in temperature, current efficiency decrease. For every 4°C rise in bath temp. (above the normal 970°C) current efficiency decreases by 1% due the increase in No. of side reactions and greater dissolution of metal in the bath. More number of side reaction and hence dissociation of metal in bath.

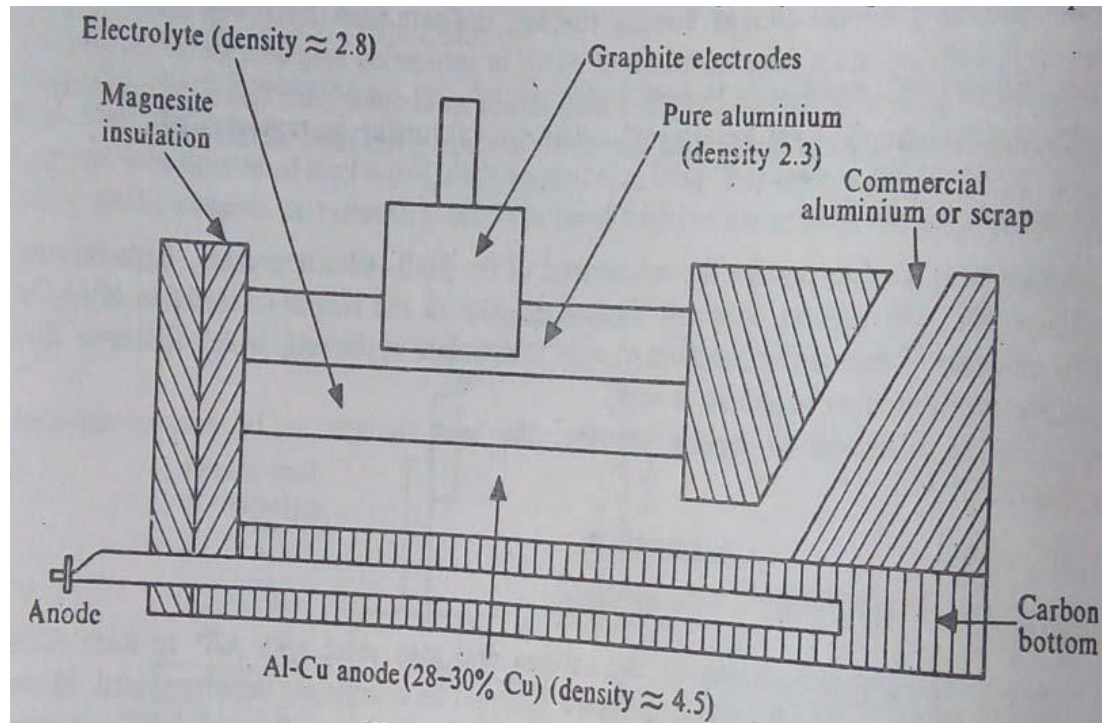
Current Density: Current efficiency increase with increase in current density, therefore, the current density is maintained at a very high value.

Inter polar Distance (distance from the bottom of the anode to the top the top of the bath): As the inter-polar distance, current efficiency increases to a maximum ($\sim 90\%$) when the distance is ~ 65 cm.

Addition of Al_2O_3 : At Al_2O_3 content of bath is 4%, the current efficiency is minimum. At value, higher or lower than 4% current efficiency increases. To maintain high current efficiency cell should be operated with high Al_2O_3 content.

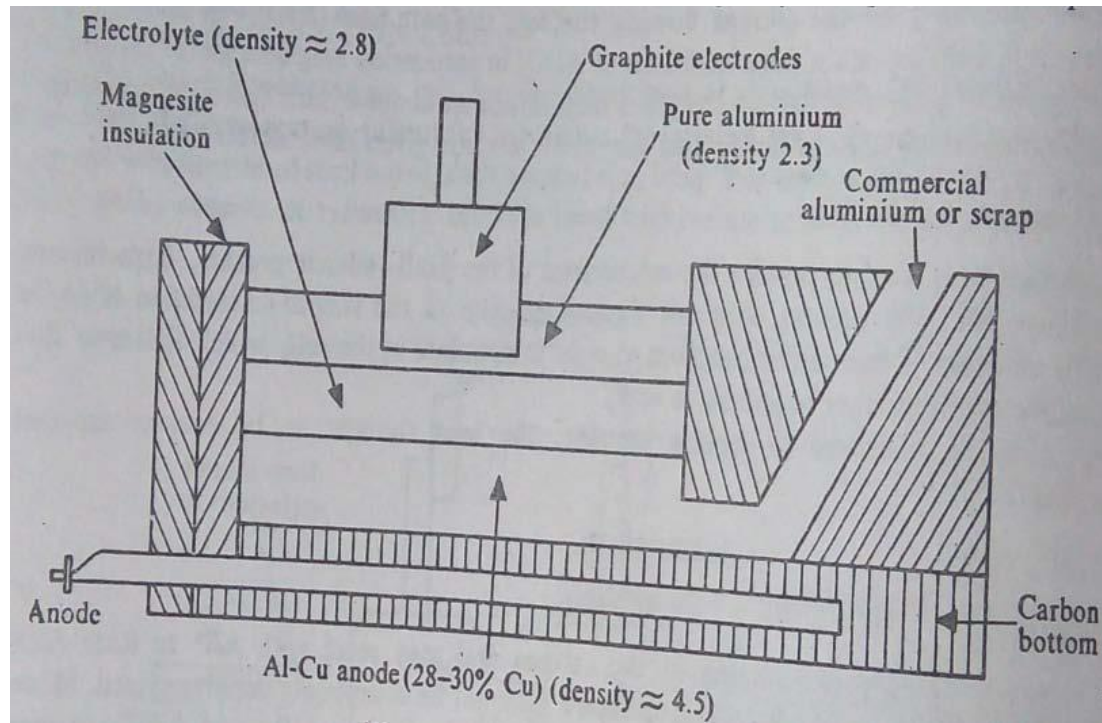
Bath Density: Lower bath density yields higher rate of separation of liberated metal. Bath density lowered by high AlF_3/NaF ratio. But, for large $\text{AlF}_3\%$ lowers bath conductivity, solubility of alumina and large volume of fluorine produced. A high NaF content decreases current efficiency due to an increase in concentration of Na ions and Na deposition on the cathode. An NaF/AlF_3 ratio slightly less than 3 is optimum.

Electrolytic Refining of Aluminum: Three-Layer Process



- Electrical applications and canning requires Al of more than 99.5% purity, which can no be obtained by Hall-Heroult process.
- Three-layer process is an electrolytic method, employed to attain such high degree of purity.
- A *dense electrolyte* of approximate composition: aluminum fluoride 36%, cryolite 30%, barium fluoride 18% and calcium fluoride 16% forms the *middle layer*.
- Density of the electrolyte enables the Al purified during electrolysis to float upward and form the *top layer*.
- The impure metal is alloyed with Cu, sand this heavy alloy forms the *bottom layer*.
- Temp. of operation about 950°C .

Electrolytic Refining of Aluminum: Three-Layer Process (continue..)



- Average purity of the metal 99.99%.
- Productivity: about 100 kg per cell per day.
- Consumption of electrolyte and graphite each about 6% of the metal produced.
- The process is ineffective if the impure aluminum contains magnesium say Al-Mg scrap, because Mg reacts with electrolyte and renders it unsuitable.

Hall-Heroult Process: Environmental Problems

The main environmental concern of the industry is related to primary aluminum production, where GHGs including CO₂, fluorinated compounds, SO₂, etc., are generated as a result of the anode effects during the process of aluminum production.

CO₂: A major GHG in the environment, which may lead to various health impacts within the context of global warming.

SO₂: Conifers, lichens, and mosses are among the plants, which are most sensitive to SO₂, a principal pollutant contributing to acid rain. Thus, SO₂ emission in atmosphere is the one of the major causes of atmospheric acidification, thereby affecting living beings on the earth.

Fluorinated compounds: 99% of these emissions are produced by electrolytic cells. Fluorine is a highly reactive and toxic halogen readily absorbed by plants (particularly conifers). Animals, including livestock that feed on contaminated plants can develop osteoporosis or even osteosclerosis. Also, it may cause dental fluorosis during the critical tooth development period in children less than 6 years of age. The permissible limit for fluorine in forage is usually in the order of 40 ppm. Continuous exposure to fluorine compounds for 8 h/day may lead to eye and skin irritations (>900 µg/m³), of the respiratory tract irritations (>2100 µg/m³), dental fluorosis, and osteoporosis (>1780 µg/m³). Aluminum plant workers are the most exposed, because ambient concentrations in pot lines can sometimes reach 1500 µg/m³. Chlorofluorocarbon compounds emission into atmosphere may cause ozone layer depletion.

Hall-Heroult Process: Environmental Problems (continue..)

Polycyclic aromatic hydrocarbons: Several polycyclic aromatic hydrocarbons (PAHs) are considered potential carcinogens. Workers are most at risk, and bladder cancer has been associated with PAH exposure. Benzo{a}pyrene is a typical PAH, and its ambient air concentration should not exceed 0.9 ng/m^3 .

Spent pot lining: The refractory materials in the electrolytic cells are commonly referred as spent pot lining. Because of mainly carbon, cyanide, and fluoride contents, spent pot lining is considered hazardous waste and must be stored safely, when exposed to water, acids, or alkaline substances, pot lining can emit toxic, flammable, and potentially explosive gases (fluorides, ammonia, hydrogen cyanide, sulfur oxides, hydrogen, and acetylene).

Coal tar pitch: Volatiles from coal tar pitch in the workroom atmosphere of aluminum smelters contain PAHs. Atherosclerosis is a characteristic lesion in ischemic heart disease and peripheral arteriosclerosis.

Other human health problems associated with toxic emissions from aluminum production are cancer, senile psychoses, hypertensive disease, Ischemic heart disease, cerebrovascular disease, peripheral arteriosclerosis, pneumonia, chronic bronchitis, emphysema, asthma, peptic ulcer, liver cirrhosis, chronic nephritis, and in extreme cases may cause sudden death.

Newer Processes for Aluminium Production: ALCOA Process

ALCOA Process: The chloride process was developed by Aluminum Company of America (ALCOA) is much more energy efficient.

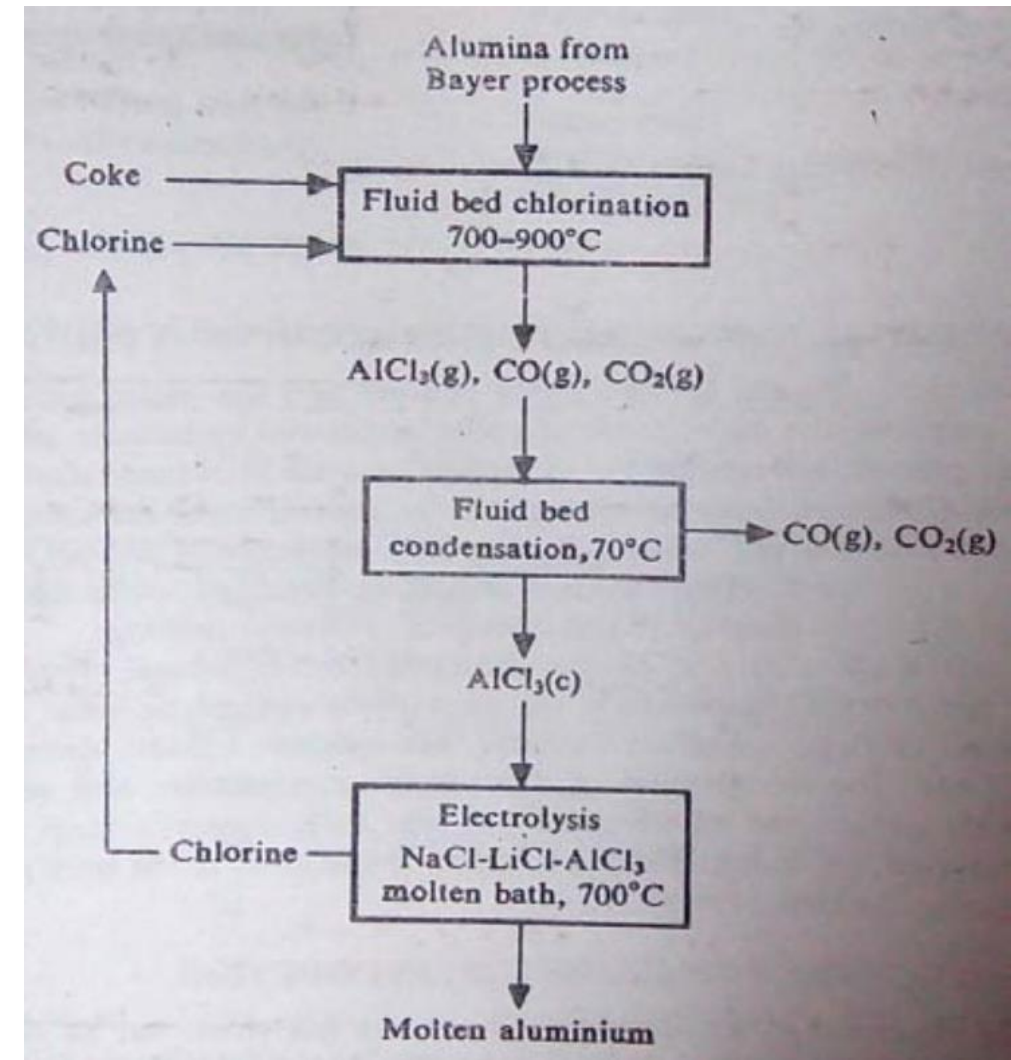
➤ The alumina produced by Bayer process is chlorinated under reducing condition in presence of carbon at 700-900°C to produce a mixture containing AlCl_3 , CO and CO_2 .



➤ The AlCl_3 vapor is separated by condensation at about 70°C in a fluidized bed containing AlCl_3 particles.

➤ The solid AlCl_3 particles thus formed are continuously fed into an electrolytic cell containing a fused chloride electrolyte made of 5% AlCl_3 , 50% NaCl and 45% LiCl; maintained at 700°C.

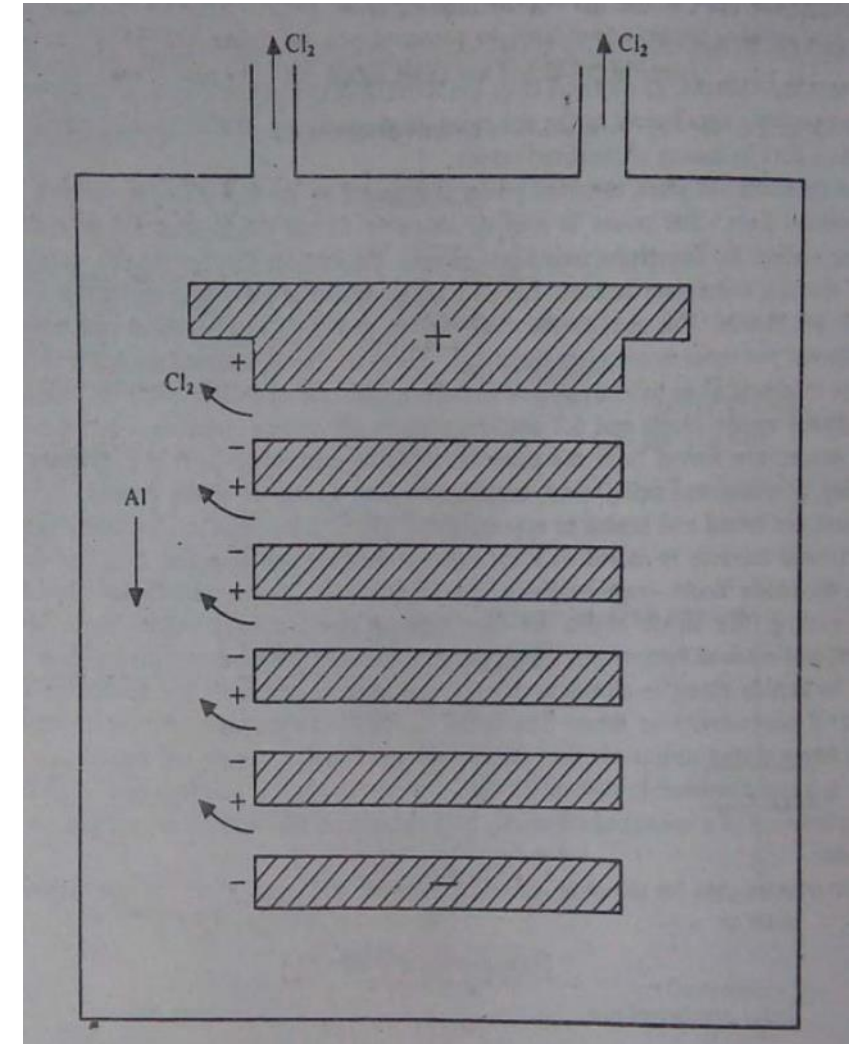
➤ Upon electrolysis by direct current, liquid aluminum formed at cathode and gaseous chlorine liberated at anode (recycled to chlorinate fresh alumina).



Flow Sheet of ALCOA Process

Newer Processes for Aluminium Production: ALCOA Process (continue..)

- The *ALCOA bipolar cell* consists of several bipolar electrodes, which behaves like as cathode at the top surface and like an anode at the bottom surface.
- A continuous flow of electrolyte must be maintained across the cell to prevent formation of molten aluminum pool on the electrodes.
- Arrangements are made to collect molten aluminum at the bottom and chlorine at the top.
- One bipolar cell is equivalent to five (5) conventional monopolar cells in series. The productivity and cell voltage are also 5 times than those monopolar cell. (Claimed operational current density up to $23,000 \text{ A/m}^2$ with electrode gap less than 1.3 cm).
- The conductivity of the Chloride electrolyte (4.0 mho/cm) is much higher than Hall-Heroult cell (2.8 mho/cm). Also the distance between the electrodes are lower → this two (2) factors lowers energy wasted in form of heat. Further, the chloride electrolyte leads to higher current efficiency and decreases overall energy consumption by over 30%.



ALCOA Bipolar Cell

Thank you