

LECTURE 35

165] Hydrometallurgy → Leaching Methods

1. In-situ leaching
2. Dump
3. Heap
4. Vat (Percolation)
5. Agitation - [Mechanical Air]

} we have also covered a comparative study of these

166] There are also some more recent methods:

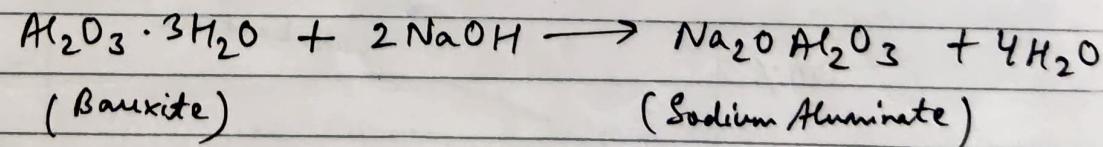
6. Pressure leaching

↓
Autoclaves are used as they are closed vessels

↓
inside which pulp is present

↓
& since it is pressurized
so it can be heated to a higher temperature
without boiling etc.

Leaching of Bauxite ← one example
↓ (Bayer Process)



Another case where pressure leaching is used

↓
when conc. of
 O_2 & NH_3 gases needs to be increased

167]

7. Bacterial Leaching

Effective for Sulphide ores \rightarrow since usually they are not soluble in water

On investigation of sulphides present in river water which was later found to be in sulphate form

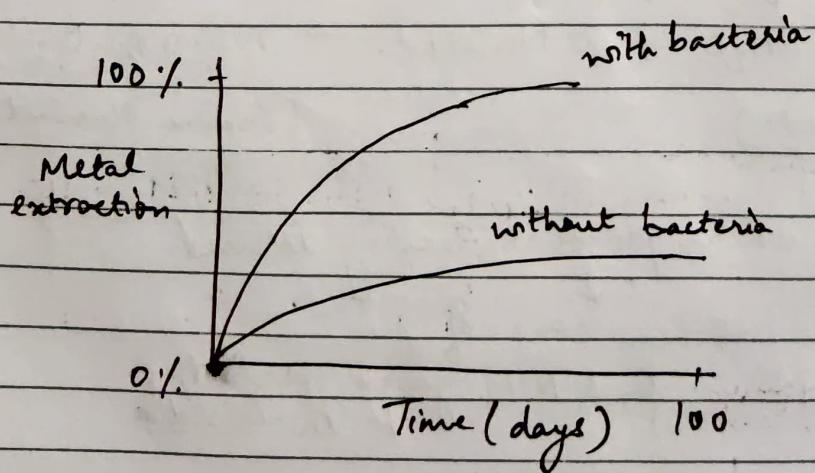
(& can't even be attacked by most acids)

Was it discovered that bacterial action oxidized the sulphides to sulphates

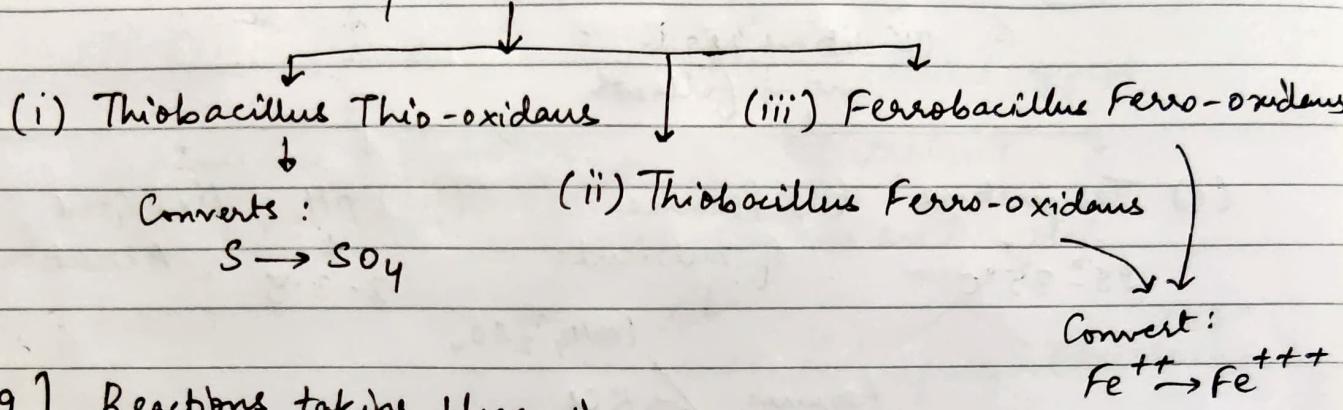
Sulphide minerals :

{ Chalcopyrite, Pyrite, Galena, Sphalerite
 $(CuFeS_2)$ (FeS_2) (PbS) (ZnS)

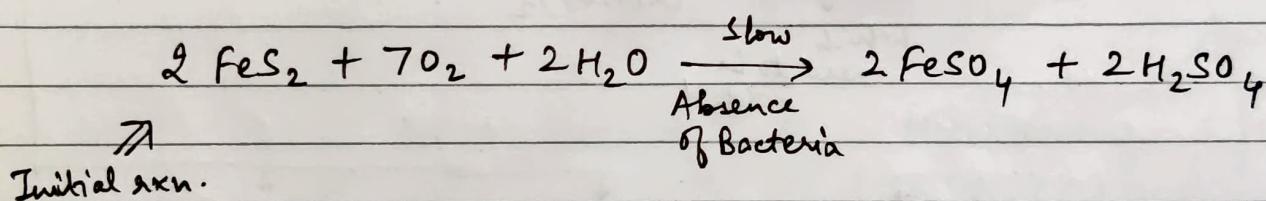
These all can get converted (oxidized) to sulphates by bacterial action.



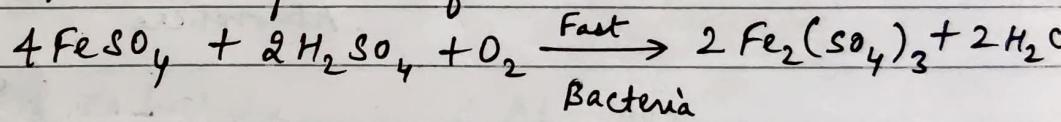
168] Three important bacteria
in sulphide dissolution :



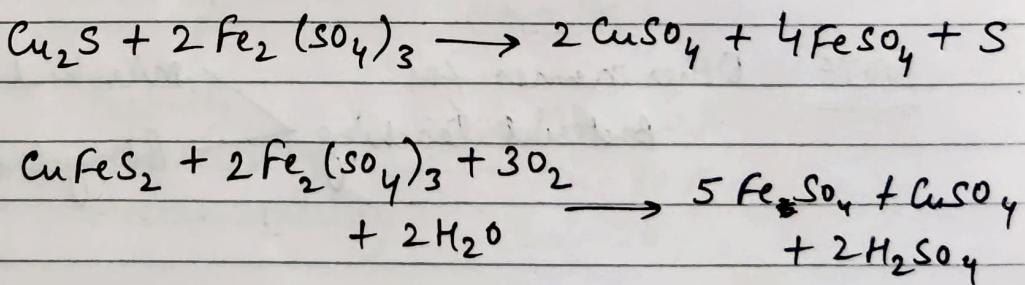
169] Reactions taking place in
Oxidation of Sulphide by Bacteria



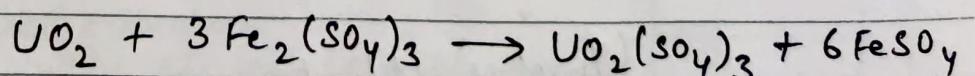
Then, under the presence of bacteria:



After this
there rxns.
takes place
depending on
what is present



These were Cu ores, but it
can also similarly occur for other metals :



(Uranium
dioxide)

from Uranium
ore

170] Growth of Bacteria

Conditions reqd.
are as follows

- (i) Temperature (ii) Presence of nutrients (iii) pH (iv) Good Aeration

$25^{\circ} - 35^{\circ}\text{C}$ ↓
 \downarrow $(\text{NH}_4)_2\text{SO}_4$

Requires
nutrients such as
 KCl
 MgSO_4
 $\text{Ca}(\text{NO}_3)_2$

- (vi) Humid Atmosphere (v) Absence of Sunlight

{ since too much
sunlight can kill }
bacteria

171] ELECTROMETALLURGY

Definition : (Involves) Utilization
of electrical energy in metallurgical
process

Types of Electrometallurgy

(i) Electrothermics

resistance
induction
arc furnace

(ii) Electrochemical effect

electrolysis

There are two main methods

(a) Electro-refining

(b) Electro-winning

Apart from this there are also

(c) Electro-deposition methods

Metal coating
(Cu, Ni, Cr)

Corrosion
Electropolishing

Anodizing

172] Note: Metals exclusively produced by E.W. { Al - 100%.
Na - 100%.

Partially produced by
electrometallurgy

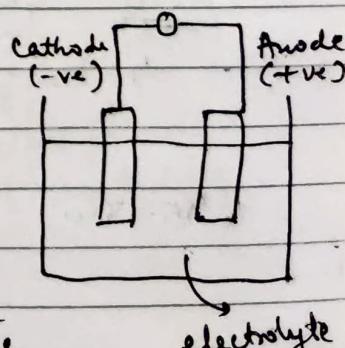
Mg - 80%.
Zn - 80%.
Cu - 20%

173] Electrolytic Cell

Box-like structure in which electrolyte is kept

along with two metal plates

Connected by external circuit



174] The rate of deposition
is controlled based
on Faraday's Law of Electrolysis *

$$W = \frac{ItA}{ZF} \quad \begin{cases} F = \text{Faraday} \\ \text{Constant} \end{cases}$$

↓
weight
deposited 96500 C)

175] Properties of Electrolyte

- (i) Should have sufficient Ionic conductivity
 - (ii) Should be chemically inert towards electrodes
 - (iii) Should be stable
Should not decompose or vapourise
 - (iv) Should not dissociate by itself when current is passed
- For example:
- Mall works but sugar does not
- (has good ionic cond.)

NOTE: Generally the kinds
of electrolytes are

Aqueous
(Cu, Zn, Sn, Au, Ag)
these can be produced from aqueous salt

Molten Salt
(Al, Na, Mg)

they CANNOT be produced from aqueous salt

176] Current Efficiency

↓
Using Faraday's law

we can calculate amt. of metal deposited which can also be measured experimentally

↓
Now, the current efficiency is defined as:

$$\text{Current Efficiency} = \frac{\text{Actual amount of metal deposited}}{\text{Theoretical amt. of metal deposited}} \times 100\%$$

177] Theoretically it should be 100%.

but in reality it is lower than that

↓
Reasons for lower efficiency are:

(i) Mechanical losses

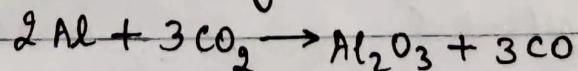
e.g.: metal that is deposited slightly falls down & isn't recovered

(ii) Chemical dissolution

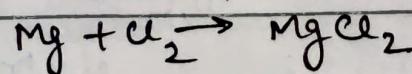
(iii) Recombination of anodic & cathodic product

(iv) Side Reaction
e.g.: $\text{Fe}^{+++} \rightarrow \text{Fe}^{++} \rightarrow \text{Fe}^{+++}$
(reoxidized)

this can occur especially if distance b/w Anode & Cathode is not kept large



(In this process it may occur)



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178] Electrometallurgy

$$V_T = V_{E^\circ} + V_R + V_o + V_{E_x}$$

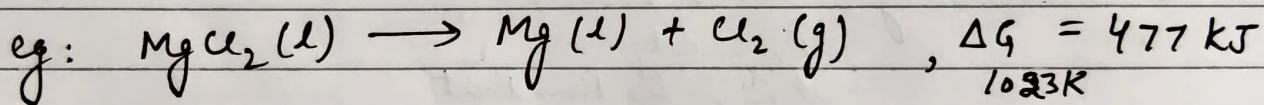
V_T = Total Voltage of cell

V_{E° = Theoretical (Thermodynamic) Voltage

V_R = Voltage drop due to resistance of electrolyte

V_{E_x} = Voltage drop due to fitting of external current

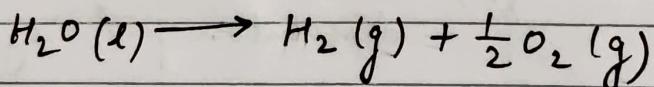
Now, $V_{E^\circ} \Rightarrow \underline{\Delta G = -nFE^\circ}$



$1023K$
 $(750^\circ C)$ ↓

$$E^\circ = -2.47 \text{ V}$$

(not spontaneous
& not feasible)



$$\Delta G_{298}^\circ = 236 \text{ kJ}, E^\circ = \underline{-1.23 \text{ V}}$$

but in reality

the voltage requirement
is much greater

based on
Kinetic factors * (due to overpotential)

actual voltage reqd.
is about 2 V.

Reasons for this: (i) Change in conc. of

ions near the electrodes

179] V_o — overpotential

(ii) Accumulation of products of electrolysis at the electrodes

this happens when
at cathode some product
is deposited

which hinders further electrolytic process

(& thus greater voltage
is reqd. than
theoretical value)

NOTE: This effect of increase
of voltage required

is called Polarization

180] H_2 evolution during electrodeposition of metals

H_2 overpotential

$$\text{Discharge potential} = E^\circ + V_0$$

i.e. both
theoretical &

[81] Emf series

overpotential have
to be overcome

* However
in reality
due to
overpotential
metals
upto Zn
can be
deposited
as well

Al

Mn

Zn

Fe

Cd

6

H

11

A9

10

Since these
are more
reactive

Then H
thus, theoretically their deposition is NOT possible on cathode

metals below H are more electropositive than H

* \downarrow & are preferentially deposited over cathode instead of H_2 .

-1.66	Al
-1.18	Mn
-0.76	Zn
-0.44	Fe
	Cd
	Ni
0	H
+0.34	Cu
+0.7	Ag
+1.5 V	Au

eg: For Zn

theoretical
value is -0.76

but practically
we can measure
a value of
-2.35 V

(due to overpotential)

whereas, H \rightarrow -2.4 V

(due to overpotential)

\Downarrow
thus Zn is more
preferable than H
for deposition
on cathode.

182]

* NOTE: Sometimes, some impurities
may reduce the H overpotential
slightly (eg: it may make it
around -2.3 or so)

\Downarrow
& then Zn will NOT
deposit

\therefore Purification of electrolyte
is important

183] Energy requirement for Hall-Heroult Process

\Downarrow
we need to find
quantity of current reqd.
to deposit one gram eq.
of any metal

1 gram equivalent of any metal — 26.8 Ahr
is required \downarrow explanation

$$\left(\frac{96500}{60 \times 60} = 26.8 \text{ Ahr} \right)$$

$\therefore 1 \text{ g Al (8.994 g)} = 26.8 \text{ Ahr}$

$$\Rightarrow 1 \text{ gram of Al metal} = \frac{26.8}{8.994} = 2.98 \text{ Ahr}$$

$$\text{Energy} = \frac{I \times V}{C.E.}; \text{ For 1 gram Al} = \frac{2.98 \times V}{C.E.} \text{ Wh/gm}$$

$$1 \text{ kg Al} = \frac{2.98 \times V}{C.E.} \text{ kWh/kg}$$

of Al

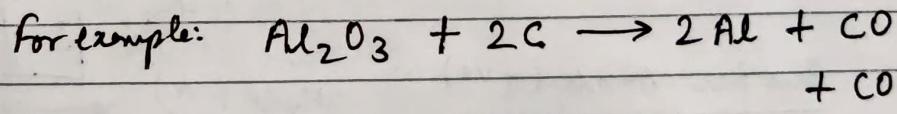
C.E. is current efficiency

$$\text{eg: } \Delta G = \Delta G^\circ + RT \ln K$$

calculate this

put this

find this from reaction



$$K = \frac{a_{\text{Al}}^2 \times p_{\text{CO}} \times p_{\text{CO}_2}}{a_{\text{Al}_2\text{O}_3} \times a_{\text{C}}^2}$$

$$= \frac{1}{a_{\text{Al}_2\text{O}_3}}$$

(and using this we can solve further)

184] Arrangement of Electrodes in Electrolytic cell

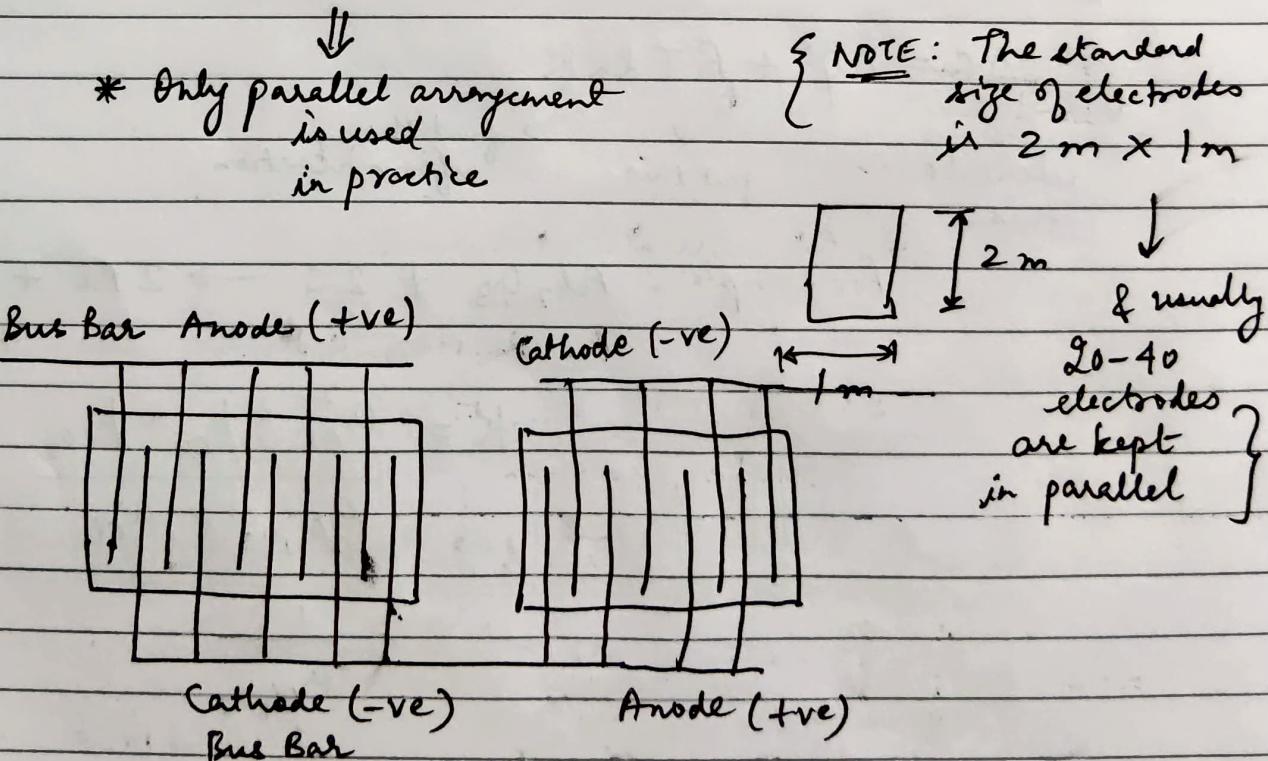
Current Density at which deposition is done is kept fixed

but increasing beyond some point leads to uneven deposition
reducing it will reduce deposition



∴ In practice we keep multiple electrodes in parallel (generally)

- (i) Parallel (multiple) arrangement of electrodes
- (ii) Series arrangement of electrodes



* NOTE: Cells are in series but electrodes are in parallel

Assignment

1. Iron Blast Furnace
2. LD Converter
3. Hall-Heroult Electrolytic cell
4. Outokumpu Flash Furnace
5. Copper Converter

Draw these 5 figures
on A4 size sheets

185] Extraction of Aluminium

Most important
Non-Ferrous
metal

steel - 1950 mT

Al - 69 mT

Cu - 22 mT

Zn

:

Produced first
in 1825

by $\text{AlCl}_3 + \text{K}$

(but K was difficult
to handle)

In 1854 commercial
production started

(using
 $\text{AlCl}_3 + \text{Na}$)

186] Properties : low density (2.7)

(i) $\frac{1}{3}$ rd of Fe or steel
(7.86)

(ii) High thermal conductivity

(iii) Plastic material

(i.e. can easily deform)

(iv) Chemically resistant to most acids

(v) Can be anodized

which is used
to produce bright surface finish

Uses : (i) Structural material — weight saving

(ii) Corrosion resistance — thus, increasing
use in Building Construction

(also, hinges of doors
nowadays made more of
Al than Brass)

(iii) Electrical Conductor

↓
More than 30% Al
is used to make
electrical conductor

187] Ores of Aluminium

Earth's Crust — 8% Al

(3rd most abundant
element
after O & Si)

↓
& it is the
most abundant
metal

{ 8% — Al }
5% — Fe }

The most important
ore of Al is Bauxite

↓ it is the hydrated
oxide of Al & Fe

188] Three different mineralogical forms

1. Diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
 2. Boehmite, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
 3. Gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- } diff. crystal
structures
→ easily
soluble

189] Process steps

1. Extraction of Pure Alumina (Al_2O_3)
for Bauxite → Bayer
Process
2. Electrolytic reduction of Al_2O_3
+ Al metal → Hall-Heroult
Process

{ Hall — USA
Heroult — France
they both
came up with
this independently
(around the age of
about 23 yrs)

190] Extraction of Pure Alumina (Al_2O_3) from Bauxite
 {Bayer Process}

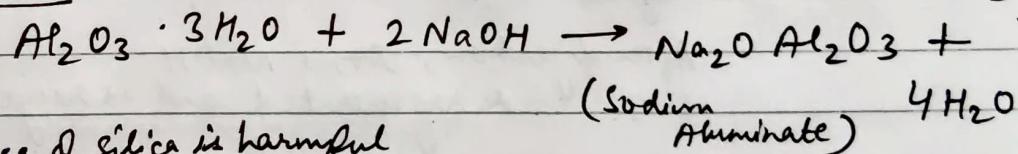
Open cast mines $\xrightarrow{\text{then}}$ subjected to:
 Crushing, Grinding, Digestion, Leaching
 takes place using NaOH
 (high temp. - 250°C
 pressure - 25 atm)

* { NOTE: Commercial Bauxite:
 $30-60\%$ Al_2O_3 + Fe-oxide, TiO_2 + SiO_2

\downarrow
 this should be $< 5\%$.

(otherwise process may become uneconomical)}

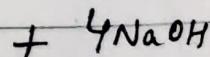
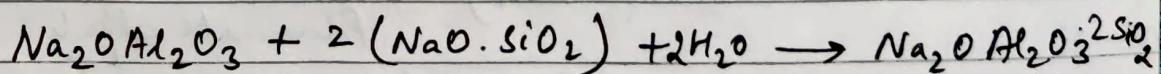
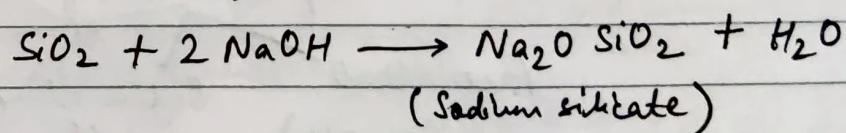
191] During Digestion:



Presence of Silica is harmful

to the process, since part

of the silica reacts with NaOH :



(Desilication Production)

$\therefore *$ for 1 kg SiO_2 \rightarrow loss of 0.85 kg of Al_2O_3
 \rightarrow loss of 0.67 kg of NaOH

{ That is why we want $< 5\% \text{ SiO}_2$ to reduce losses }

NOTE: V_2O_5 , Ga_2O_3 , Cr_2O_3 → these are soluble & can be recovered

192] Dissolution of Bauxite

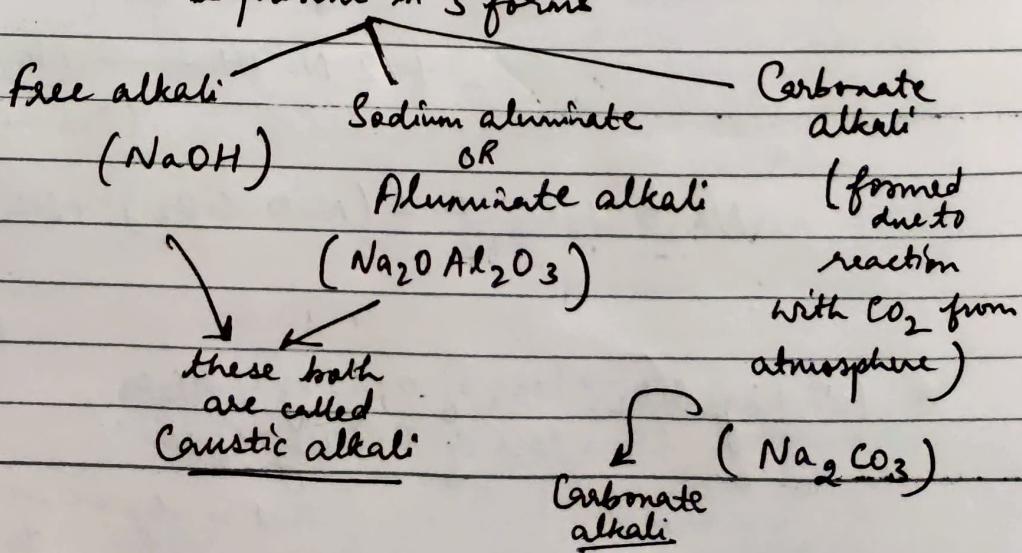
Depends on multiple factors:
 ↓ ↓ ↓
 NaOH Temp ... etc.

<u>Variable</u>	<u>Gibbsite</u>	<u>Diaspore & Boehmite</u>
Temp (°C)	105 - 145	200 - 300
Pressure (atm)	1-4	15-35
Duration (hrs)	1	2-2.5
Concentration of NaOH	200	200-300
Caustic Ratio	3.4-3.8	3.4-3.8

193] Caustic Ratio

After digestion, some NaOH is regenerated and is recycled back

In leach liquor, the alkali (Na_2O) is present in 3 forms



\therefore Total alkali, $[Na_2O_{Alkali}] = Na_2O_{Caustic} + Na_2O_{Carbonate}$

∴ We define Caustic ratio as:

Definition: Molar ratio of caustic alkali to alumina in leach liquor

$$\text{Caustic Ratio} = \frac{\text{Moles of Na}_2\text{O}_{\text{Caustic}}}{\text{Moles of Al}_2\text{O}_3}$$

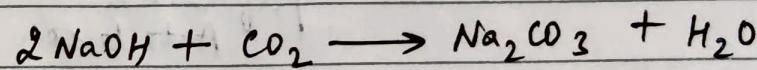
Ques Leach liquor from Bayer process contains 300 g/L of caustic alkali, & 145 g/L of alumina. Find the caustic ratio.

$$[\text{M.W. of } \text{Al}_2\text{O}_3 = 102 \text{ g} \\ \text{M.W. of } \text{Na}_2\text{O} = 62 \text{ g }]$$

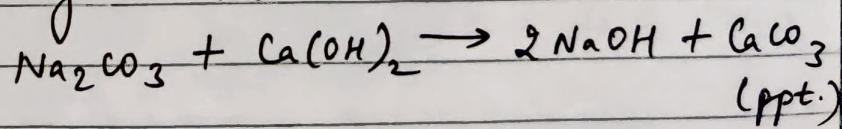
$$\text{Sol. Caustic ratio} = \frac{300}{62} / \frac{145}{102}$$

194] Role of Lime

(i) Causticization of Na_2CO_3



Thus we regenerate NaOH: (this bad carbonate is useless)



(ii) Grinding process

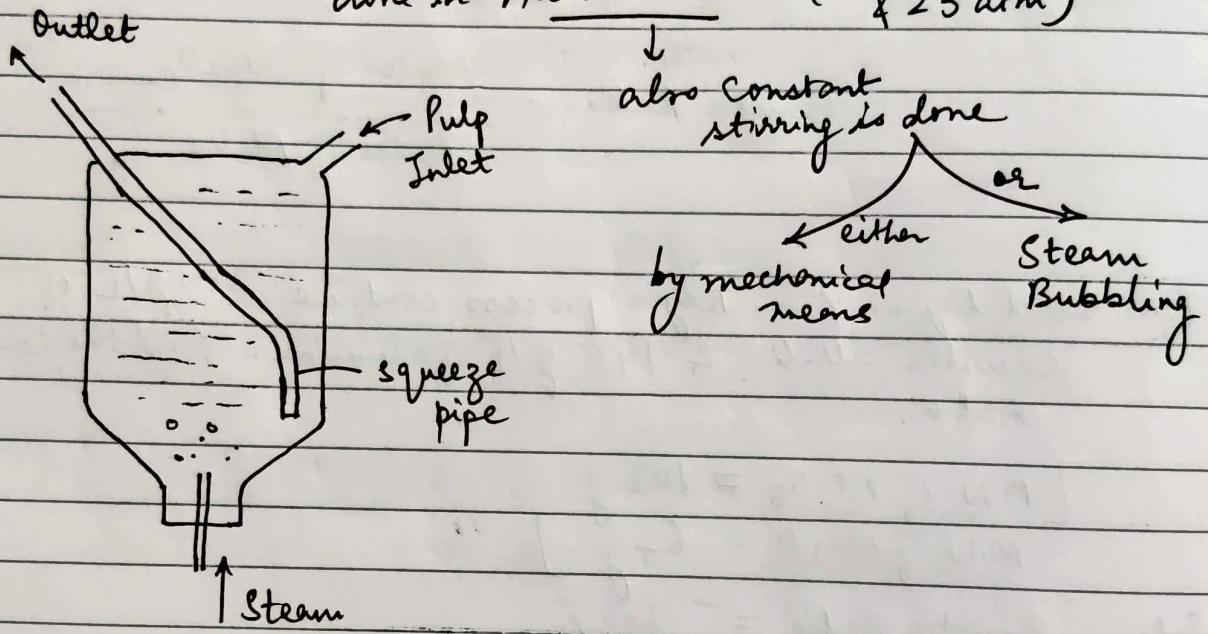
(iii) Dissolution of diaspora

(iv) $\text{Ca}_2\text{TiO}_4 \cdot n\text{H}_2\text{O}$

195] Dissolution Process

Since it is performed
at high. T & P

done in Autoclaves (250°C
& 25 atm)



also constant stirring is done
either by mechanical means or
Steam Bubbling

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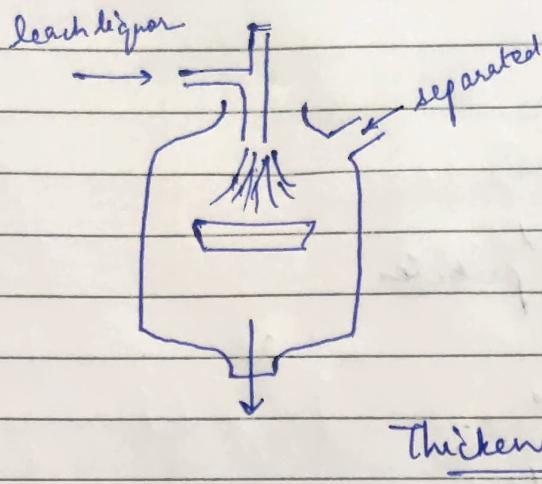
196] Extraction of Alumina → Bayer Process

performed in
Autoclaves

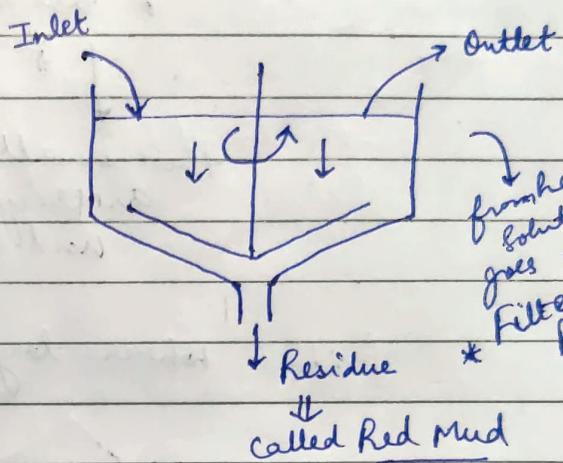
done using
mechanical stirrers
OR
steam bubbling

7-8 autoclaves
put in series

After this, from final outlet sent to Steam Separators



Steam separators Autoclaves 7-8 atm 1-2 atm
25 atm



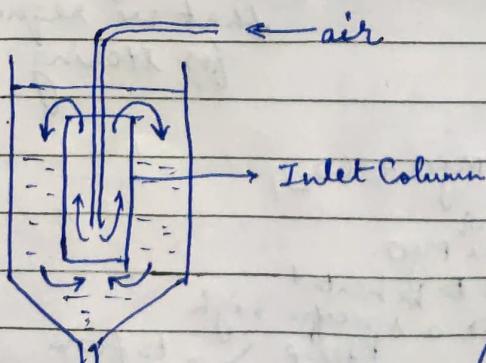
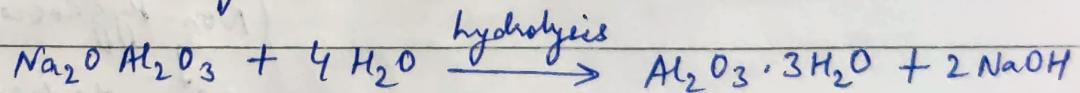
for every 1 ton Al
2 ton of Red mud produced

(it is red in colour due to presence of Iron oxides)

(this has v. high pH value, &
this is harmful for environment)

197] Precipitation

Sodium aluminate in clear solution is subjected to hydrolysis:



* Seeds are added $\rightarrow \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

since they provide ready crystallization sites

(otherwise precipitation from homogeneous soln is thermodynamically difficult)

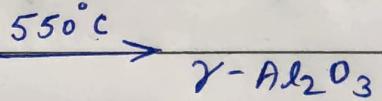
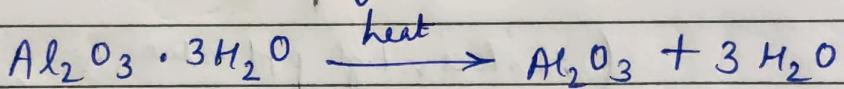
198] Hydrolytic Classification
is performed
↓

i.e. small particles
are separated
↓ from large particles

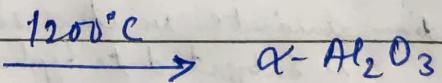
these small particles
are recycled &
used as seeds
↓

whereas large particles
are subjected
to washing, thickening, drying
& calcination.

199] Calcination of Al-Hydroxide



(Hygroscopic)



(Non-Hygroscopic)

↓
this is the form
that we require
for steering Al_2O_3

NOTE: { Similarly in: $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2$

Here MgO
needs to be heated
to a specific high
temp. to form
Periclase

only then does it become
stable } }

200] Calcination of Al-hydroxide

(i) Rotary Kiln → earlier this was used (obsolete now)

(ii) Fluidized Bed Calciners

→ nowadays this is used

201] Flow Sheet of Bayer Process

