

Inorganic Chemical Technology
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Lecture - 24
Chlor-Alkali Industry - Chlorine and Caustic Soda

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Chlor Alkali Industry, Chlorine and Caustic Soda. In the previous lecture we started discussing about Chlor alkali industries; where we found that you know sodium carbonate, sodium hydroxide and chlorine are the primary component which are forming basis for the chlor alkali industries.

We have also discussed production of sodium carbonate or soda ash by two different methods. One is the Solvay process; another one is the modified Solvay process which is also known as the dual process right. In the Solvay process we only get sodium carbonate as the product.

Whereas, in the modified Solvay process or dual process we get a ammonium chloride also as a product along with the sodium carbonate product ok. In this lecture we will be discussing about the remaining two major components of chlor alkali industry. They are nothing but chlorine and caustic soda.

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Chlorine (Cl₂) - Caustic Soda (NaOH)

- Cl₂ and NaOH are produced as co-products in electrolysis of brine; thus, being discussed in combination
- Start of Cl₂ industry in 1920's was results of successful development of electrolytic brine decomposition process
- NaOH formed in the ratio of 1.1 tons per ton of chlorine in the electrolytic process
- This process accounts for 80% of caustic soda and >95% of chlorine production in India *
- Previously Cl₂ had been solely manufactured by a lime-soda ash process which is gradually being replaced by electrolysis process
- The required inventory for diaphragm and mercury cell processes for the brine electrolysis were made during 1883 - 1893
- With the development of Solvay process for making Na₂CO₃, the NaOH became relatively common chemical
- Even though electrolytic NaOH was produced in 1890's, lime-soda process remained dominant until late 1940's
- NaOH is no longer produced for sale by lime-soda process; however, small amounts continue to be made by the method (largely for captive consumption)

This chlorine and caustic soda are produced as co-products in electrolysis of a sodium chloride brine solution. That is the reason we are discussing about the production of this chlorine and caustic soda together simultaneously in combination. Actually, start of chlorine industry in 1920s was result of successful development of electrolytic brine decomposition process. Until then the chlorine etcetera caustic soda was produced by you know lime and soda ash process right.

Once these electrolytic decomposition process have been developed then production of this caustic soda as well as chlorine has been produced by this electrolytic decomposition process. Once this electrolytic brine decomposition process has been established then mostly chlorine and then caustic soda are produced by electrolytic brine decomposition process only.

Electrolytic brine decomposition process is so much established by this point. NaOH formed in the ratio of 1.1 tons per ton of a chlorine in the electrolytic process ok. So, let us say you get a 1 ton chlorine in a process, then it is possible that you may be getting 1.1 or 1.15 tons of a sodium hydroxide in general in a given electrolytic process. Moreover, whatever the caustic soda that is available or produced in India out of that 80 percent is produced by electrolytic process.

Similarly, whatever the chlorine is being produced in India or more than 95 percent is produced by this electrolytic process ok. Previously chlorine had been solely manufactured by a lime soda ash process which is gradually being replaced by the electrolysis process; because of the several advantages of electrolytic processes as we are going to discuss.

However, once these electrolytic processes have been established and then found that very much beneficial economical this lime soda ash process has become incompetent. So, mostly it is not being used nowadays whatever it is being used or you know whatever the sodium hydroxide etcetera is produced by lime soda process that is produced in-house and then for the captive uses purpose only.

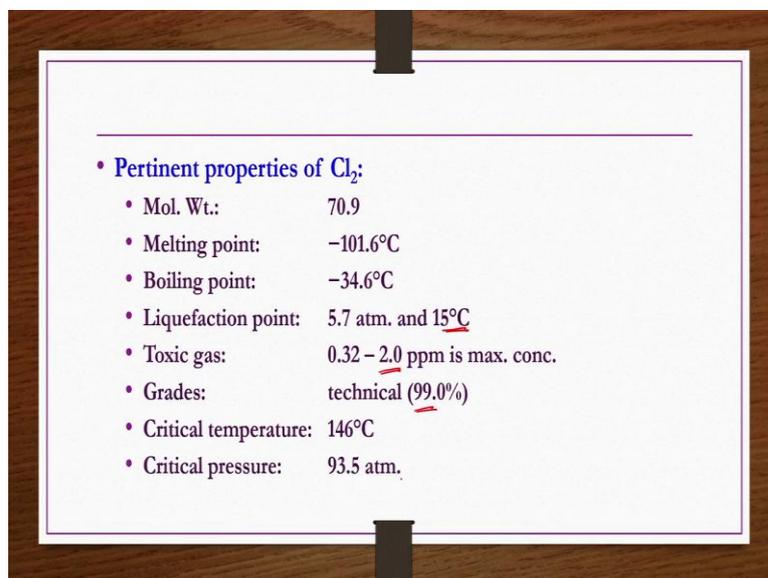
The required inventory for diaphragm and then mercury cell processes actually electrolytic process is having different types of you know cell processes. Electrolytic brine decomposition can be done by diaphragm cell as well as the mercury cell process right.

So, there are some requirements of you know asbestos cells etcetera mercury cells etcetera all those things are required for these processes. Those inventory for the these diaphragm and mercury cell processes which are nothing but electrolytic processes they were developed well before chlorine production started by the electrolytic process.

Actually, chlorine production started in approximately 1920s onwards it was produced before also, but you know dominant production started from the 1920s only. With the development of Solvay process for making sodium carbonate the sodium hydroxide production has become relatively common chemical.

Even though electrolytic sodium hydroxide was produced in 1890s lime soda process remained dominant until late 1940s, but; however, nowadays mostly these chemicals are produced by the electrolytic processes as mentioned here ok. But; however, sodium hydroxide is no longer produced for sale by lime soda processes; however, small amounts continue to be made by this method largely for captive consumption only not for the marketing purpose.

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• Pertinent properties of Cl ₂ :	
• Mol. Wt.:	70.9
• Melting point:	-101.6°C
• Boiling point:	-34.6°C
• Liquefaction point:	5.7 atm. and 15°C
• Toxic gas:	0.32 – 2.0 ppm is max. conc.
• Grades:	technical (99.0%)
• Critical temperature:	146°C
• Critical pressure:	93.5 atm.

Pertinent properties of a chlorine molecular weight is 70.9 melting point is minus 101.6 degree centigrade boiling point is minus 34.6 degree centigrades, liquefaction point is at 15 degree centigrade 5.7 atmospheres it is very toxic gas. So, it is not allowed to have more than 2 ppm maximum concentration. Grades technical grades are available 99

percent critical temperature 146 degree centigrades and in critical pressure 93.5 atmospheres.

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• **Pertinent properties of NaOH:**

- Mol. Wt.: 40.00
- Boiling point: 1390°C
- Melting point: 318°C
- Solubility: very soluble in water with high exothermic heat of solution
- Grades: available in solid form of flakes, granules, sticks, lumps, pellets and aqueous solutions
- Purity of aqueous form: 50 and 73% NaOH
- Purity of solid forms: 60% Na₂O (77.4% NaOH) to 76% Na₂O (98% NaOH) ✓

Handwritten chemical structure: NaOH

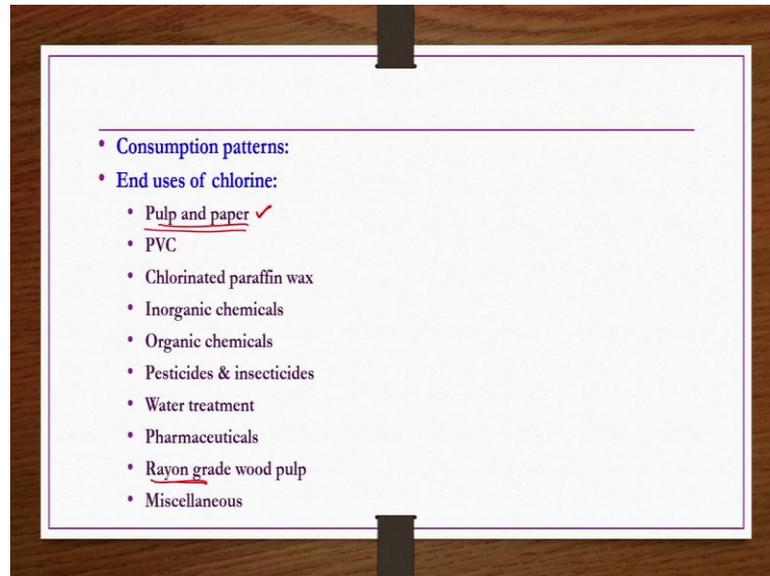
Similarly, pertinent properties of sodium hydroxide if you see molecular weight is 40 boiling point is 1390 degree centigrades melting point is 318 degree centigrades. Solubility very much soluble in water with high exothermic heat of solution; you know when you dissolve NaOH crystals in a beaker of water then what happens usually you do not add kilos or you know gram several grams of sodium hydroxide and then mix it because it is very exothermic lot of heat is being evolved.

So, then you know one by one crystals you drop into the water and then mix it and then by the time this one crystal itself is mix the beaker becomes very warm. So, you wait for this beaker to become cooled down on normal temperature and then only you add additional crystals of sodium hydroxide or additional pellets of sodium hydroxide that is how it is been done in the laboratory.

Because when the sodium hydroxide crystals or pellets are dissolved in water, they liberate huge amount of heat. Grades available in solid forms of flakes granules, sticks, lumps, pellets and aqueous solutions also for example if you are having or if you wanted to have a aqueous form a sodium hydroxide purity is available in 50 and 73 percent NaOH.

If you wanted to have the same thing in solid form then 60 percent Na_2O that is 77.4 percent NaOH to 98 percent NaOH crystals are available if you wanted to have a you know these NaOH in solid forms.

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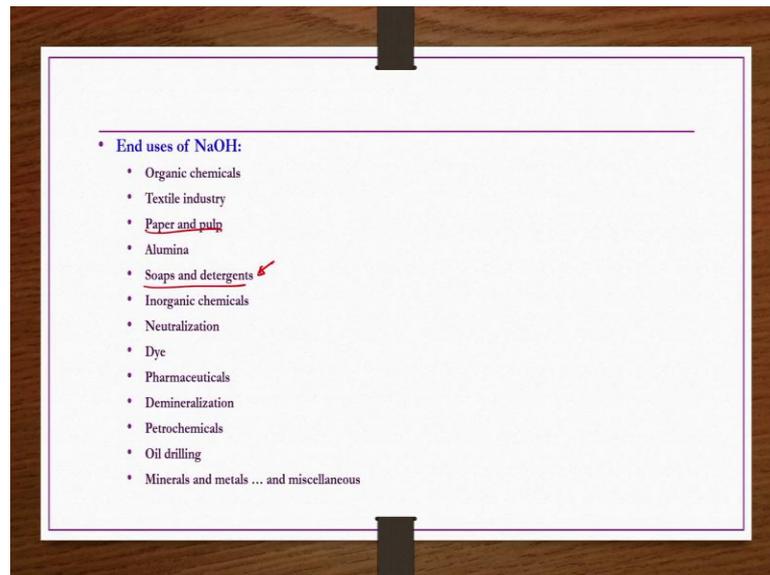


Consumption pattern we see for both the components chlorine and then sodium hydroxide. If you see the end uses of chlorine it is used in pulp and paper industries PVC, poly vinyl chloride manufacturing also it is used. Chlorinated paraffin vaccine inorganic chemicals, organic chemicals, chlorinated organic chemicals, pesticides, insecticides, water treatment purpose also this chlorine is used pharmaceuticals also some chemicals you know chlorine requirements are there.

Rayon grade wood pulp for example, you know some of these chlorine and then sodium hydroxide productions by electrolytic processes are installed near or within the industrial complex of such industries like pulp and paper industries are Rayon grade wood pulp etcetera ok.

So, what I mean to say that these are you know required for these industries in large quantities. So, rather procuring them from other places industrial prefer to have these electrolytic processes in their industrial complex itself. So, that they can produce the required Cl_2 and NaOH and then use there itself.

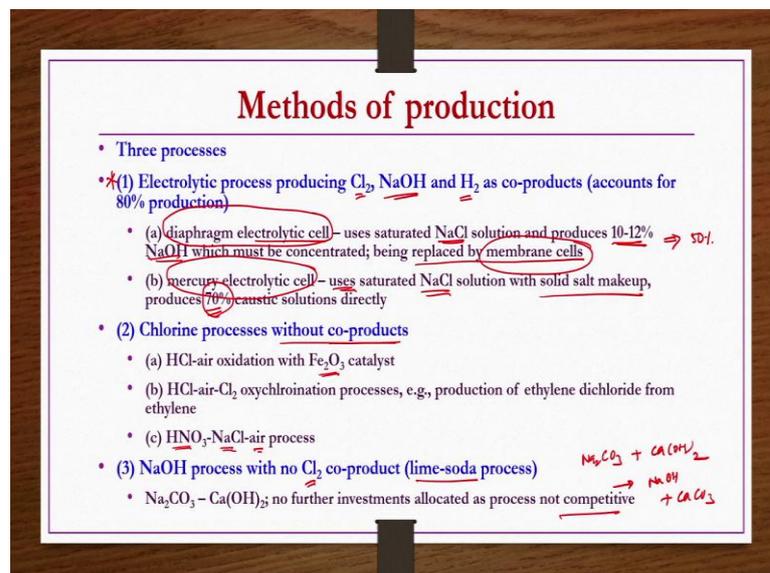
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Similarly, end uses of NaOH if you see organic chemicals several organic chemicals, textile industries, paper and pulp, alumina, soaps and detergents manufacturing this NaOH is being used. Several inorganic chemicals neutralization purpose it is used in dye industries also it is used pharmaceuticals also it is used.

Demineralization purpose also it is used petrochemicals oil drilling minerals and metals extraction and so many if you keep on listing. So, many applications of NaOH are existing and that is the reason NaOH has become a common chemical.

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Methods of production; there are three different types of methods of productions are there we are going to discuss about electrolytic process only because we are discussing the production of a Cl_2 and NaOH together. So, out of three processes first process is electrolytic process producing chlorine, sodium hydroxide and then hydrogen as co-product which accounts for 80 percent of the production of these chemicals.

This electrolytic process can be done by using different cells. So, one is the diaphragm electrolytic cell another one is the mercury cell another one is the membrane cell ok. See diaphragm electrolyte cells uses saturated sodium chloride solution and produces 10 to 12 percent of NaOH which will be concentrated by using evaporation processes.

However, this process is being replaced by membrane cells why what there are some merits and demerits of each of these three cell processes are there that we are going to discuss anyway. Second one is the mercury electrolytic cell this is also within the electrolytic process this mercury electrolytic cell uses saturated NaCl solution with solid salt makeup ok and it produces 70 percent caustic solutions directly.

Here you get 10 to 12 percent only then you do the evaporation process to increase up to maximum 50 percent only whereas, here you can produce NaOH up to 70 percent purity ok. So, we are going to see these details anyway. So, second process is the chlorine processes without co-products without any co-products.

For example, HCl air oxidation with iron oxide catalyst then HCl air Cl_2 oxychlorination process example production of ethylene dichloride from ethylene etcetera then nitric acid sodium chloride air process. Then third one is nothing but the lime soda process where NaOH is being produced without chlorine production. Here soda whatever Na_2CO_3 is there that reacts with the lime CaOH twice to give NaOH and CaCO_3 products ok.

However, this process found to be not competitive. So, people are not using this process nowadays. So, we will be discussing primarily this process. In fact, only this process within this process we are going to see how diaphragm electrolytic cell and then mercury electrolytic cell and then membrane cells are being used to produce or being used to do the electrolytic decomposition of the NaCl brine.

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Electrolytic process

- Electrolysis reactions:
- (a) diaphragm cell type
- Cell notation
 - $(\uparrow \text{Cl}_2) \text{ C} | \text{NaCl(aq)} || \text{NaOH(aq)} | \text{Fe, H}_2 \uparrow$
- Cell reaction
 - Anode: $\text{Cl}^- - e \rightarrow \frac{1}{2} \text{Cl}_2$
 - Cathode: $\text{Na}^+ + \text{H}_2\text{O} + e \rightarrow \text{Na}^+ + \text{OH}^- + \frac{1}{2} \text{H}_2$
 - Overall: $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2; \Delta H = +53.4 \text{ kcal}$

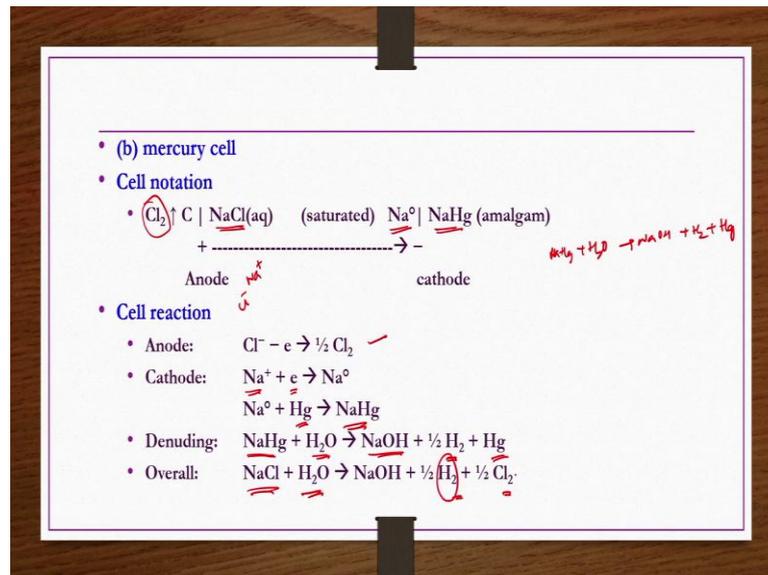
Electrolytic process first we start with electrolysis reactions we see for the diaphragm cell type cell notations first we have a anode and then we have a cathode right. So, in the compartment NaCl solution is introduced and then electromagnetic field has been supplied. So, that decomposition of this NaCl takes place. So, that you get Na plus and Cl minus; this Cl minus releases an electron at the anode and then produces the chlorine gas.

Whereas, this Na plus passes towards the cathode right here it reacts with the OH minus of water whatever water is there that also being decomposed into OH minus and then H plus that Na plus of NaCl that is reacting with NaOH and informing NaOH solution aqueous solution which is 10 to 12 percent only right. Whatever the proton is there that receives the electron released by the chlorine ion and then forms hydrogen gas ok.

So, this is the common representation of the reaction, but specifically if you write at anode chloride ions release electron to form chlorine gas at cathode sodium ions react with water and then electrons. So, that you know this water decomposes into the H plus and OH minus.

So, you have Na plus and then OH minus forming NaOH and then whatever the proton H plus of water is there that receives the electron from here and then produces the hydrogen gas. So, the overall reaction if you see NaCl plus H 2 O giving rise to NaOH plus chlorine plus hydrogen ok.

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Mercury cell, cell notation we see similarly here also we have a anode and cathode, but here we are using NaCl aqueous saturated solution. Here what happened whatever the NaCl is there that forms Na plus and then Cl minus this Cl minus move towards the anode and then release the electron to produce chlorine same as the previous one.

Whereas, the Na plus here that receives the electron released by the chlorine and then it takes and then forms a 0 valence sodium Na naught at the cathode and then it reacts with mercury to form sodium amalgam that is NaHg right.

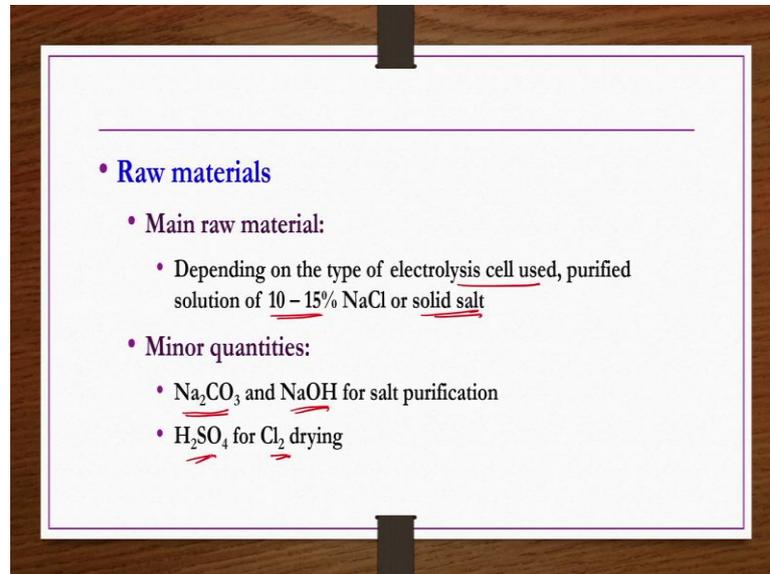
This NaHg further denuding of this sodium amalgam takes place where this NaHg reacts with water to form NaOH plus H 2 and then releasing the mercury ok. So, it is a general representation reactions if you see at the anode it is same reaction as in the diaphragm cell.

But at cathode Na plus plus electron forming Na naught this Na naught reacting with mercury to form sodium amalgam this sodium amalgam undergo denuding reaction where NaHg reacts with water to form NaOH and then hydrogen gas and then releasing the mercury ok.

So, overall reaction is same NaCl plus H 2 O giving rise to NaOH plus H 2 and then Cl 2 gases ok. So, here in both the process H2 is also being produced, but you know amount

of H_2 is very small compared to the $NaOH$ and Cl_2 ok. That we are going to see anyway.

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Now, what are the raw materials? Whether are you using the diaphragm cell electrolysis process or mercury cell electrolysis process or membrane cell electrolysis process the raw material is same ok $NaCl$ brand ok. Main raw material is depending on the type of electrolysis cell used purified solution of 10 to 15 percent $NaCl$ or solid salt is required.

Here in the case of diaphragm cell you can use 10 to 15 percent sodium chloride solution in the mercury cell process you need solid salt ok. Minor quantities because some kind of purification drying kind of things are required here for example, chlorine that is produce it is in wet condition. So, it has to be dried. So, for that purpose you need H_2SO_4 ok. And then similarly the solution brand solution whatever you have taken there may be impurities.

So, you need sodium carbonate soda ash kind of components. So, that to remove those impurities like you know in the form of calcium salts or magnesium salts etcetera. So, for those purpose some amount of sodium carbonate or a sodium hydroxide are required for the salt purification. And then similarly for the chlorine drying you need some amount of H_2SO_4 how much it is that we are going to see in the next slide.

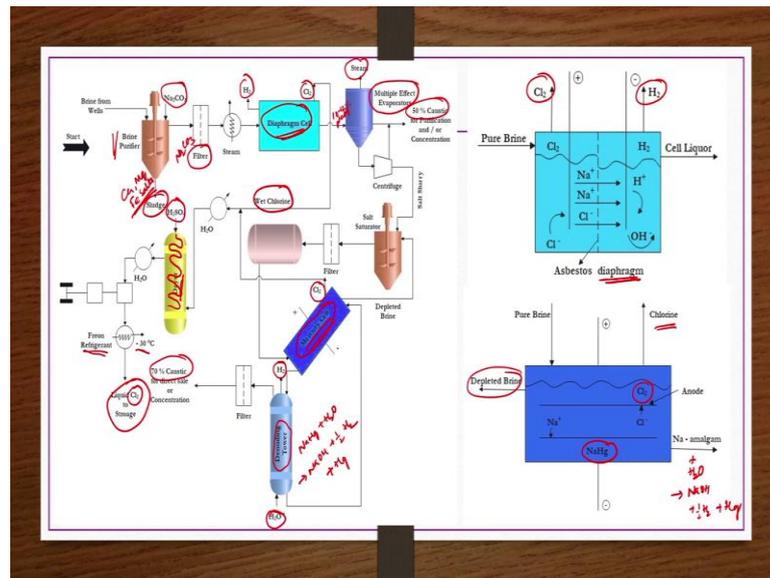
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- Quantitative requirements:
- (a) Basis: 1 ton of Cl₂; 1.15 tons of NaOH (98%); 283 Nm³ of H₂ (26 kg)
 - Salt: 1.3 tons
 - Soda ash (58% Na₂O): 26 kg
 - Sulfuric acid (98%): 5 - 6 kg
 - Sodium hydroxide: 10 - 15 kg
 - Graphite and mercury
 - Steam: 11 tons (diaphragm cell process)
 - Electricity: 2,900 kWh
- (b) Plant capacities: 100 - 1000 tons/day of Cl₂ in a series of electrolysis units, each producing 0.5 - 2 tons Cl₂ per day

Quantitative requirements basis is 1 ton of Cl₂ that is we are taking basis and doing the calculations. So, if you are taking 1 ton of Cl₂ production as a target. So, then you will get 1.15 tons of sodium hydroxide 98 percent purity and then 283 normal meter cubes of H₂ only that is only 26 kgs small amount is being produced.

Salt 1.3 tons required soda ash 26 kgs sulfuric acid 5 to 6 kgs sodium hydroxide 10 to 15 kgs graphite and mercury required as per the cell depletion steam 11 tons for diaphragm cell process and electricity 2,900 kilowatt hours. Plant capacity usually 100 to 1000 tons per day of chlorine in a series of electrolysis units how many units may be there may be units like 500 or something as possible 200 to 500 it is possible in general because each one is producing 0.5 to 2 tons of Cl₂ per day.

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Now, this is the flow sheet for the production of a chlorine as well as the sodium hydroxide. But here we are studying this process in a combined approach actually in industry you may not be having combined approach you may be having individual approaches as well, but; however, there are some industries combined approaches are all there. So, then that is what we are discussing ok. So, one is the diaphragm cell another one is the mercury cell here.

So, for the diaphragm cell we have a brine from the wells and then that has to be purified in brine purifier using sodium carbonate or sodium hydroxide depending on what kind of impurities that is there in the brine solution. So, whatever the calcium, magnesium, iron, salt, etcetera are there they will be removed as sludge in this brine purifier chamber.

Then almost purified brine is passed through a filter to check if any Na_2CO_3 or any of these calcium, magnesium, iron, salt, steel are there. So, then they will be filtered ok. So, pure brine is passed through a steam chamber and then dry one is sent to the diaphragm cell.

Here the reactions diaphragm cell reactions whatever the reactions are reactions are the anode and then cathode and overall reaction that we have seen they are taking place here ok. So, those reactions separately shown because here we are not able to discuss in the flow sheet ok. So, here H_2 is produced.

So, that is being taken out for the as a fuel for the boilers etcetera or for R₂ use as synthetic chemical within the industrial complex ok. Whatever the Cl₂ is formed that is in wet condition so, that wet chlorine you know you try to remove water and then dry it in a dryer where H₂SO₄ is supplied.

These H₂SO₄ and Cl₂ they are not contacting actually they are passing through in a different shells like let us say if it is having some helical shapes like this right. So, in the helical shapes this H₂SO₄ may be passing and then in the surroundings you know this chlorine wet chlorine is go passing through.

So, when it can indirectly there is no direct contact indirect contact between Cl₂ and then H₂SO₄ takes place and then H₂SO₄ is if it is 98 percent pure. So, it fumes actually. So, then because of that hot condition the Cl₂ get dries ok. If at all still moisture is there that is removed and then Cl₂ is refrigerated at minus 30 degree centigrade and then stored as a liquid Cl₂ right.

Whereas the solution here whatever you get here usually 10 to 12 percent of NaOH only it is having. So, that solution is passed through multiple effective operators not one we have shown only one there may be 4 or 5 effective operators are possible to increase its concentration to 50 percent ok.

How we do it we use the steam for the evaporation of the 10 to 12 percent NaOH solution and then when it pass through multiple effective operators its concentration increases by releasing the water vapours from the solution ok. Whatever the salt precipitates are there they will be centrifuged and then they will be sent to salt saturators right. Brine solution is also supplied.

So, whatever the brine solution is there that will be passed through a filter to check if any impurities are there to remove then it will be passed through a mercury cell right. Here now this is the mercury cell here again the reactions whatever the reaction we have discussed under mercury cell those reactions takes place.

Let us say at the anode the Cl₂ formation is taking place and then that Cl₂ is being dried in a similar way as we have done for the diaphragm cell ok. Whereas the sodium amalgam that is forming that has been sent to denuding tower to which in a counter current direction water is supplied.

So, that this sodium amalgam reacts with water to give sodium hydroxide and then hydrogen gas and then this mercury right. So, hydrogen is taken from the top to collect as a synthetic fuel or it will be sent to the boilers for the burning purpose etcetera ok. Whatever the solution is there that will be passed through a filter to check you know if at all a mercury is present or not and then you get a 70 percent caustic soda from the top as a product whereas, the depleted brine is there that will be recirculated to mercury cell as well ok.

So, this is the process where we have discussed both diaphragm cell process as well as mercury cell process in a combination individually also you can do ok. The pictorial representation of the reaction that are occurring in diaphragm cells if you see we have a diaphragm separating two compartments towards the anode compartment a pure brine is passed.

And then Na plus Cl minus ions are forming by applying the electromagnetic field then this Cl minus releases electron towards the anode and then forms chlorine. And then taken from the top through the diaphragm Na plus ions passes through towards the cathode and then Cl minus also passes, but less amount it passes.

So, towards the anode this water is being separate. So, then H plus and then OH minus are forming that Na plus and OH minus react together to give NaOH plus solution and then H plus receives the electron from the that is released by the chlorine and then whatever the H₂ is from that is taken from the top.

Cell liquor is taken from the top and then concentration minimum NaCl concentration has to be maintained how you do it either you add water to the cathode side or you add a NaOH solution or you know not add or you recirculate the NaOH solution towards the anode side. So, that to maintain minimum NaCl concentration because it acts as a barrier and then there should be a concentration gradient to transfer of the ions.

Similarly, mercury cell process reactions are shown schematically here again whatever the pure brine is there that is taken towards the anode and then Cl minus Na plus are formed by applying the electromagnetic field this Cl minus releases electron towards the anode and forms chlorine and then gets as a product from the top ok.

Na plus reacts with the mercury to form NaHg this NaHg taken and then denuding of the sodium amalgam has been done by reacting with water to form NaOH and then hydrogen gas and then mercury released. Depleted brine is taken from the top ok. Now, these are the processes or the reactions that are occurring in the electrolytic process whether it is diaphragm cell or a mercury cell right. The same thing we are going to see as a description here in the next slide.

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• **Process description**

- A combination of the diaphragm and mercury cell processes shown in flowchart and same discussed here
- Brine solution flows through pipelines to a storage reservoir and then through a brine treatment system
- Caustic soda, soda ash and/or barium carbonate removes calcium, magnesium and iron salts which would clog up diaphragms
- This purified, saturated brine (25 – 28% NaCl) is heated and electrolyzed in a diaphragm cell
- The cell, operating at (45 – 55%) decomposition efficiency, discharges a 10 – 12% solution of NaOH with about an equal concentration of NaCl
- Multiple effect evaporation concentrates the cell liquor to 50% NaOH ✓ solution

Process description a combination of the diaphragm and mercury cell processes shown in the flowchart and then we are discussing here. Brine solution flows through pipelines to a storage reservoir and then through a brine treatment system. Actually, all those steps have not been shown in the flowchart we have just shown a brine purification chamber like that. In that one there may be several steps before getting a purified brine ok.

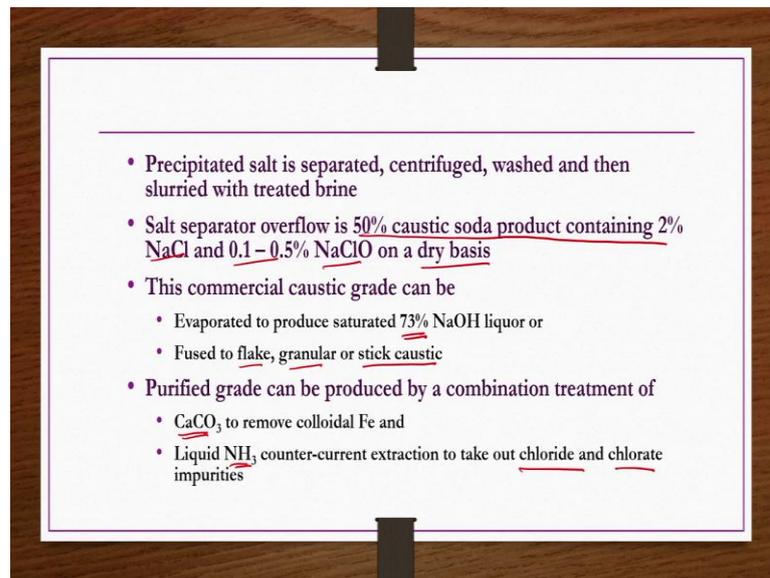
So, caustic soda, soda ash and or barium carbonate are being used in the purification treatment system or brine purification system to remove calcium, magnesium and then iron salts. If you do not remove it is possible that they may be clogging up the diaphragms and then efficient electrolytic decomposition of NaCl may not take this.

This purified saturated brine which is having 25 to 28 percent NaCl is heated and electrolyzed in a diaphragm cell. The cell which is operating at 45 to 55 percent decomposition efficiency discharges 10 to 12 percent of NaOH solution. Actually, you

know if efficiency is more then it is possible that higher concentration NaOH solution may be produced.

And then it is produced with an amount and equal concentration of NaCl. Then multiple effective operators are used to concentrate this 10 to 12 percent NaOH solution to increase its concentration to 50 percent NaOH solution. This may be taken as a product or further subsequent concentrating processes can be done.

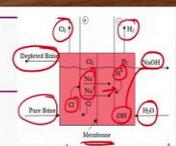
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Precipitated salt is separated, centrifuged washed and then slurried with the treated brine. Salt separator overflow is 50 percent caustic soda product containing only 2 percent NaCl and then 0.1 to 0.5 percent sodium hypochlorite on dry basis. This commercial caustic grade can be evaporated to produce saturated 73 percent NaOH liquor or fused to flakes granular or stick caustics different forms as per the requirement.

Purified grade can be produced by a combination of a treatment of calcium carbonate to remove colloidal iron and then liquid ammonia counter current extraction to take out chloride and chloride impurities if at all present. Depending on the impurities present one has to choose the purification process as well as the depending on the requirement of purification also one has to choose the concentrating process or purification process.

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- **Membrane process:**
- In a membrane cell, a cation exchange membrane separates the anolyte and catholyte
- Brine is fed into the anode compartment where
 - Chlorine gas is created and
 - Sodium ion and associated water of hydration migrate through the membrane into the catholyte
- Unlike the diaphragm cell process, cation exchange membrane prevents the migration of chloride ions into the catholyte
- Depleted brine is discharged from the anolyte to maintain a minimum NaCl concentration

Now, we see the third process membrane process. In a membrane cell a cation exchange membrane separates the anolyte and catholyte. Brine is fed into the anode compartment where chlorine gas is created and sodium ion and associated water of hydration migrate through the membrane into the catholyte. Actually, the membrane has to be very selective it should allow only sodium ions ok. So, here pictorially it is shown. So, we have a membrane and then it's a ion exchange membrane ok.

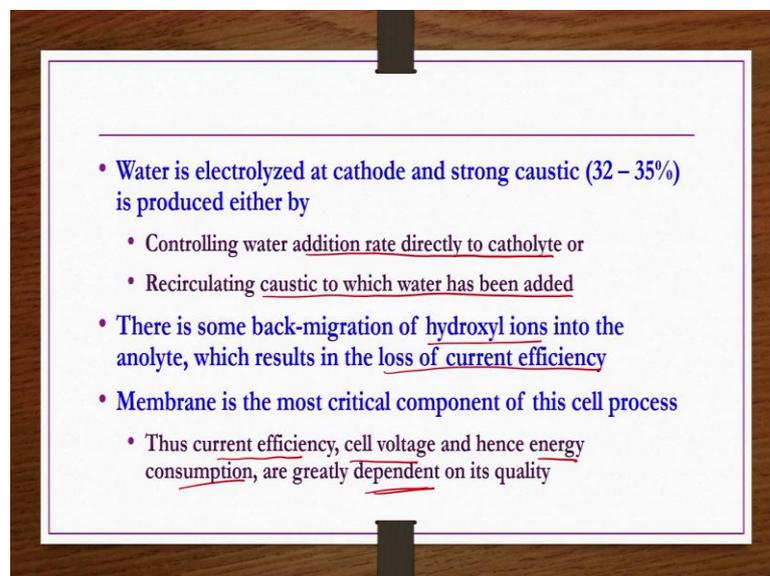
So, one side of this one is anode another side is the cathode size. So, towards the anode compartment pure brine is being supplied. So, that Na plus and then Cl minus ions are forming by decomposing or by electrolytic decomposition of a NaCl on application of a electromagnetic field ok. The Cl minus ions whatever are there they release the electrons and then form chlorine gas that is taken from the top whereas, the membrane is selective to Na plus ions only.

So, these Na plus ions will move towards the cathode where it reacts with the OH minus which is already being present towards the cathode size because towards the cathode side you are supplying water and then that is being decomposed into H plus and OH minus. So, this Na plus and then OH minus are forming together as NaOH. This H plus is receiving the electron released by the chlorine ion and then forming the hydrogen gas. Depleted brine is taken from the top of the anode compartment ok.

So, this is the process actually pictorially that is what it is happening. Unlike the diaphragm cell process cation exchange membrane prevents the migration of chloride ions into the catholyte. Diaphragm cells also you know chlorine ion transport from the anode side to the cathode side is very less.

But; however, it is completely prevents the transport of chloride ions you know from anode compartment to the cathode compartment such kind of selective cationic exchange membrane one has to choose. Depleted brine is discharged from the anolyte to maintain a minimum NaCl concentration.

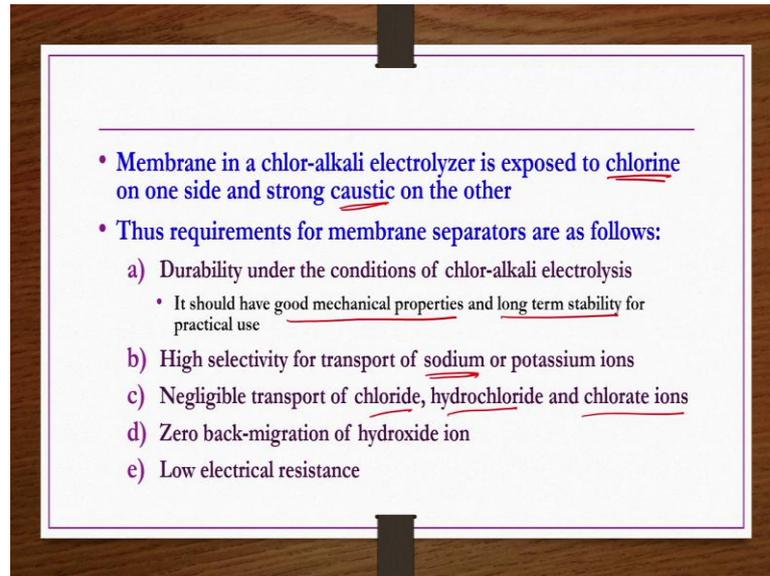
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Water is electrolyzed at cathode and strong caustic 32 to 35 percent is produced either by controlling water addition rate directly to cathode side or cathode compartment size which is known as the catholyte or recirculating caustic to which water has been added ok. There is some back migration of hydroxyl ions we should not be occurring, but; however, it occurs.

So, because of that one there is a loss of current efficiency. Membrane is the most critical component of this cell. So, because of this one current efficiency cell voltage and energy consumption are greatly affected by the quality of the membrane that you are using for the membrane cell electrolytic process to produce chlorine and sodium hydroxide.

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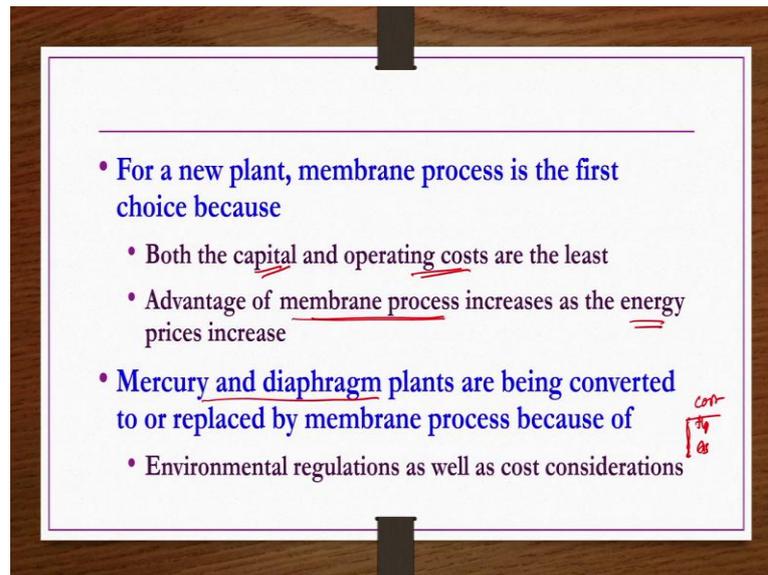
So, we know the importance of the membrane. So, other important factor about consideration or selection of membrane in chlor-alkali industry is that it is being exposed to the chlorine and then caustic soda on either side. So, one side it is being exposed to the chlorine, other side of the membrane it is exposed to the strong caustic that is NaOH. Both of them are very corrosive.

So, then membrane should have a certain characteristics to sustain longer ok. So, thus requirements for membrane separators are as follows. Durability under the conditions of chlor-alkali electrolysis it should have good mechanical properties and long term stability for practical use.

Then it should be highly selective for transport of sodium ion only or potassium ions only. It should not allow the chloride ions to pass through membranes. Negligible transport of chloride, hydrochloride and chlorate ions that should be the other characteristic of the membrane.

Zero back migration of hydroxide ions it is unavoidable. There may be something, but it one should make sure that it should be zero back migration of hydroxide ions and then low electrical resistance. It should not have electrical resistance because this process taking place you know electrolysis. Electrolytic decomposition is taking place. Then only processes movement of charges etcetera is taking place.

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For a new plant membrane process is the first choice because both capital and operating costs are the least. You know membrane cells you need if the membrane is not expensive then you know membrane process is the best one because it is capital as well as the operating costs are very less. Also advantages of the membrane process further increases if the energy prices increasing.

Energy prices usually increase gradually right. Under such conditions membrane processes are found to be very attractive. Mercury and diaphragm plants are being converted to or replaced by membrane processes because of two reasons. One is the cost. Another one is the you know environmental consideration.

As best as mercury impurities you know losses you have to make sure that that is almost zero. So, because of these two reasons these mercury and diaphragm plants are being replaced or should be replaced by membrane processes.

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• Merits and demerits of mercury process

Advantages	Disadvantages
<ul style="list-style-type: none">• Pure 50% NaOH solution (without evaporation)	<ul style="list-style-type: none">• Higher voltage than with the diaphragm process• Thus 10 – 15% higher electrical energy consumption
<ul style="list-style-type: none">• Pure chlorine gas	<ul style="list-style-type: none">• More stringent brine purification requirements• Stringent mercury contamination avoidance measures required

Handwritten notes on the right side of the slide:
High voltage
↓
river & fish

So, now we see merits and demerits of each of the process three processes. We start with the merits and demerits of mercury process. Advantages pure 50 percent NaOH solution is produced without requirement of any evaporations. Chlorine gas whatever produced is pure. Disadvantages higher voltage requirement than the diaphragm cells thus energy consumption would be 10 to 15 percent higher compared to the diaphragm cell process.

And then more stringent brine purification requirements you need highly pure brine solution for the mercury process and then mercury contamination should be avoided. Stringent mercury contaminants avoidance measure should be required because you know whatever the liquor discharges to express if at all there is a mercury that releases into the or that goes into the rivers.

And then rivers and the fishes may be consuming them because of the might bacterial activity taking place between bacteria and then mercury you know methyl mercury formation is taking place. This is very dangerous if these are being consumed by the fishes both the fishes as well as the human being consuming those fishes.

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• **Merits and demerits of diaphragm process**

Advantages	Disadvantages
• Utilization of <u>less pure brine</u>	• NaOH produced is both dilute and chloride-contaminated
• Lower <u>voltage</u> than in the mercury process	• Thus <u>evaporation</u> required
	• Chlorine gas contains <u>oxygen</u>
	• Rigorous measures required to avoid <u>asbestos</u> emission

Now, merits and demerits of diaphragm process advantages utilization of less pure brine is a is one advantage and then; obviously, as discussed previous slide voltage requirement is lower compared to the mercury process. Disadvantage is that NaOH produced is both dilute and chloride contaminated.

So, its purification is required and then that purification is done in multi effective operators. Chlorine gas also it is not pure it contains oxygen rigorous measures required to avoid asbestos emissions same like mercury emissions or mercury losses.

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• **Merits and demerits of membrane process**

Advantages	Disadvantages
• Pure <u>NaOH</u> solution	• NaOH content only <u>~33%</u> by weight
• Electrical energy consumption only about <u>77%</u> of that of the mercury process	• Chlorine gas contains <u>oxygen</u>
• No <u>mercury</u> or <u>asbestos</u> used	• Very high purity <u>brine</u> required *
	• High cost and short lifetime of the <u>membranes</u>

Merits and demerits of membrane process advantages of a membrane process you get pure NaOH solution and then electrical energy consumption is only about 77 percent of that of the mercury process much lesser than the mercury process ok and since there is no mercury or asbestos being used their loss is not there. So, then this environmental problems may not be there.

Disadvantages NaOH content only 33 percent by weight whereas, the chlorine gas here also contains oxygen and then very high purity brine is required for this process that is a major important thing and then high cost and short lifetime of membranes. Membranes are expensive and then their replacement has to be done very often ok because of their short lifetime.

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Comparisons of three processes

- Catholyte from diaphragm cells typically analyzes as 10 – 12% NaOH and 15 – 17% NaCl
- This cell liquor is concentrated to 50% NaOH in a series of steps primarily involving three or four evaporators
- Whereas membrane cells produce 30 – 33% NaOH which is evaporated in a single stage to produce 50% NaOH
- 70% of caustic containing very little salt is made directly in mercury cell production by reaction of sodium amalgam from the electrolytic cells with water in denuders
- Electrical energy consumed during the electrolysis of brine to produce chlorine gas and sodium amalgam is
 - Greater than that used to generate Cl_2 and H_2 in the diaphragm or membrane cell
 - But latter processes also use energy in the form of steam for evaporation of cell liquor
- Minimum energy required to convert salt to Cl_2 , H_2 and 50% NaOH (6.05 GJ/ton of Cl_2) is almost same in all three processes

Handwritten annotations:
 - Left margin: "No impurities in NaOH"
 - Top left: "Membrane is 33% NaOH"
 - Right margin: "4-5 times higher capacity cost"
 - Middle right: "H₂O"
 - Bottom right: "φ"

Now, we see comparisons of three process what we have seen is a kind of a merits and demerits of individual process now we compare one with the other in terms of the purity and then other kind of things. So, catholyte from diaphragm cells typically analyzes 10 to 12 percent NaOH and then 15 to 17 percent NaCl.

This cell liquor is concentrated to 50 percent NaOH in a series of steps primarily involving 3 or 4 evaporators multi effect evaporators are used to increase its concentration that is the big problem, but such kind of problem is not there in the case of membrane cell whereas, membrane cells produce 30 to 33 percent NaOH which is evaporated in a single stage to produce 50 percent NaOH.

Now, you see here in order to get 50 percent NaOH you need the series of evaporators multi stage evaporators are there. Here you need only single stage evaporator to get the same 50 percent NaOH right. So, now you see the capital cost you know capital cost here would be 4 to 5 times higher. Higher capital cost because you need 4 to 5 evaporators whereas, here you need only one single stage evaporator is sufficient ok.

So, if you have more equipment their maintenance their operation cost would also be increased. So, that means, operating cost would also be higher in the case of a diaphragm cell compared to the membrane cell and then 70 percent of caustic containing very little salt only 2 percent is made directly in mercury cell production by reaction of sodium amalgam from the electrolytic cells with the water.

Here good thing about this mercury process is that you get the 70 percent pure sodium hydroxide solution which you do not get by even by the membrane cells or the diaphragm cells also ok. So, but only problem with this is that you know how are you handling the mercury losses.

There should not be any mercury losses because if there is a loss of mercury's and that will be going into the plant wastewater and then that is having strong environmental constraints. Electrical energy consumed during the electrolysis of brine produce chlorine gas and sodium amalgam is greater than that used to generate chlorine and hydrogen in the diaphragm or membrane cell right.

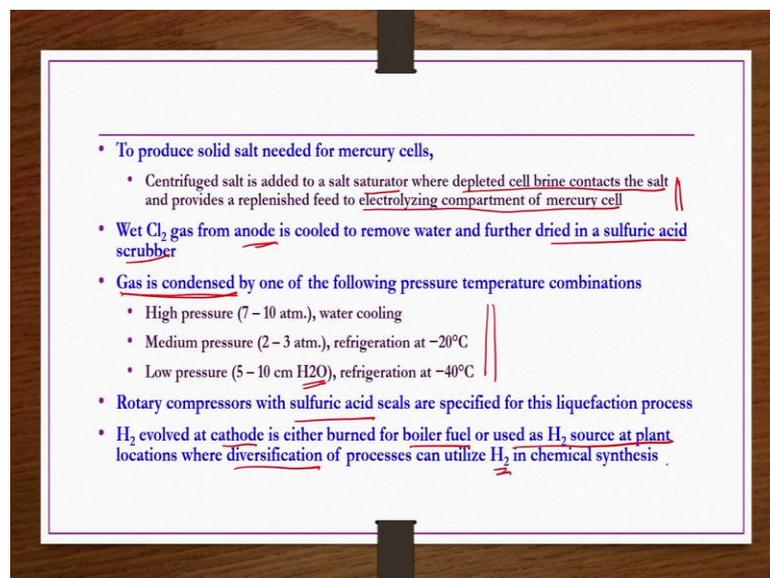
In the mercury cell this is another problem the electricity and electrical energy requirement is much higher compared to the remaining 2 processes. However, other side of the coin if you see when you produce these things using membrane or diaphragm cells they also use energy in the form of steam for evaporation of cell liquor. Now, you see here diaphragm 4 to 5 effective evaporators are required to get 50 percent NaOH solution. In the membrane cells you need a single stage evaporator right.

Whereas in mercury cell no evaporator required directly you are getting 70 percent NaOH solution by mercury cell process whereas, in these 2 process by using different evaporators then you are getting 50 percent NaOH. So, but energy consumption is slightly higher in the mercury cell, but energy if you see only electrical energy then it is higher in the mercury cell.

But energy consumed in the form of steam for evaporation purposes in the other 2 processes of diaphragm and membrane cell processes then almost energy is same that is minimum energy required to convert salt to Cl_2 , H_2 , and 50 percent NaOH is almost same in all 3 process how much it is approximately 6.05 gigajoules per ton of chlorine produced ok.

So, that way energy is not a factor to consider to select a process ok. Mercury process is the best one from the product point of view, but only thing that if you can handle mercury losses without releasing them into the wastewater of the process then mercury process is the best one.

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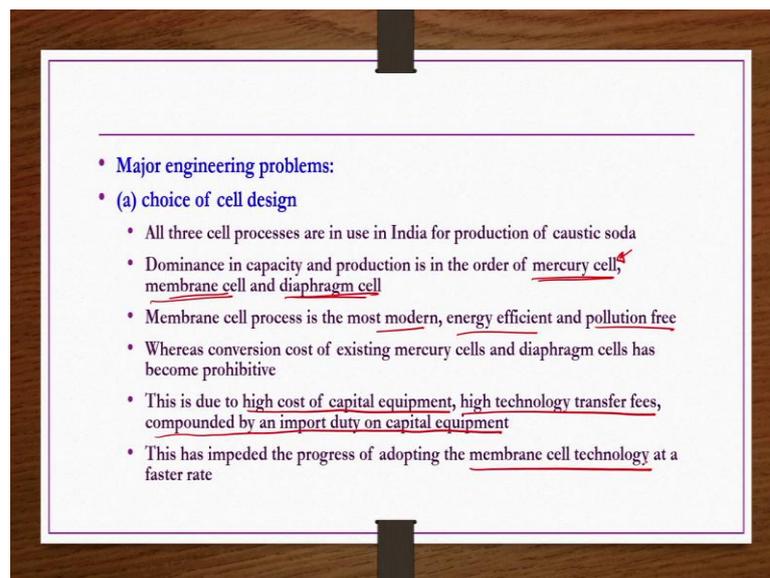
To produce solid salt needed for mercury cells centrifuge to salt is added to salt saturator where depleted cell brine contacts the salt and provides a replenished feed to electrolyzing compartment of mercury cell this is we have seen in the flow chart ok. Whatever the salt precipitates are there. So, that were centrifuge dried and then sent to the salt saturator where depleted brine is also being sent so, that to make up the required NaCl concentration.

Wet chlorine gas from anode is cool to remove water and further dried in sulfuric acid scrubber that also we have seen. Gas is condensed by one of the following pressure temperature combinations in the flow sheet we have shown only refrigeration, but how what are the condition three possible are available.

One is the high pressure 7 to 10 atmospheric pressure water cooling option and then medium pressure 2 to 3 atmosphere and refrigeration at minus 20 degree centigrade option. And then low pressure 5 to 10 centimetres H₂O refrigeration at minus 40 degree centigrade in order to condense the chlorine gas. So, depending on the availability of the sources one has to choose the process. Rotary compresses with sulfuric acid seals are specified for this liquefaction process.

Hydrogen evolved at cathode is either burned for the boiler fuel or used as H₂ source at plant locations where diversification of processes can utilize hydrogen in chemical synthesis. So, that is about the electrolytic process using the diaphragm cells, mercury cells and then membrane cell processes their comparisons, their merits and demerits etcetera.

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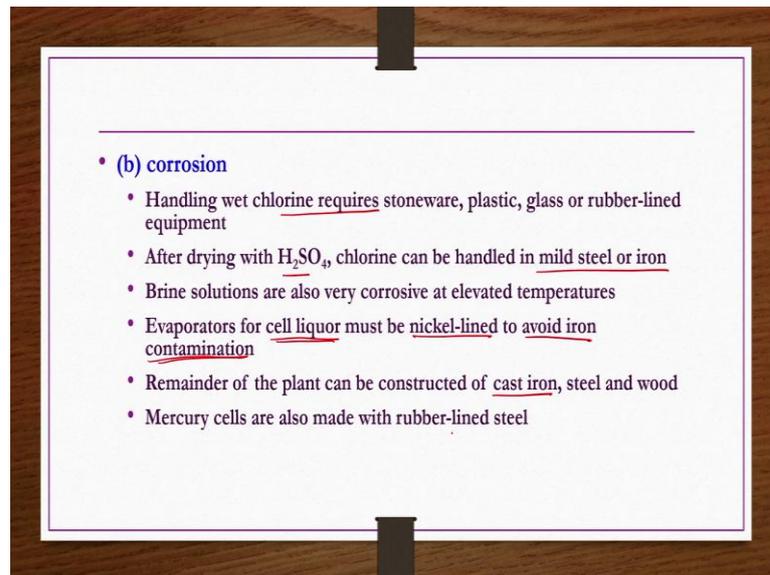


Now, we will be discussing major engineering problems associated with these kinds of electrolytic processes, major engineering problems, choice of cell design which cell should be used. In India almost all three types of cell processes are being utilized for the production of a caustic soda NaOH. Dominance in capacity and production is in the order of primary mercury cell followed by the membrane cell and then followed by the diaphragm cell.

So, this is the most utilized here in India. Membrane cell process is the most modern energy efficient and pollution free ok whereas, conversion cost of existing mercury cells

and diaphragm cells has become prohibitive. This is due to high cost of capital equipment, high technology transfer fees compounded by an import duty on capital equipment because of these things. Adopting the membrane cell technology has not at the expected pace ok.

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Then second engineering problem to concern about is the corrosion because chlorine, sodium hydroxide both of them are corrosive as well as sodium chloride also at elevated temperature is corrosive. So, then accordingly the corrosion issue should be handled. Handling wet chlorine requires stoneware, plastic, glass or rubber lined equipment. After drying with H_2SO_4 , chlorine can be handled in mild steel or iron.

Brine solutions are also very corrosive at elevated temperatures. Evaporators for cell liquor must be nickel lined to avoid iron contamination because NaOH is highly corrosive. Remainder of the plant can be constructed by cast iron, steel and wood. Mercury cells are also made with rubber lined steel.

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Economics

- (a) **plant location:**
 - Need careful analysis of such factors as cheap power and salt sources, coupled with the rising cost of transportation
 - In some cases, it has more advantages to locate within a plant complex or near the product market because of the relative costs of transporting salt and finished products || NaOH
Cl₂
 - For e.g., 1/3rd of caustic soda plants are attached to paper and rayon mills
- (b) **caustic-chlorine-hydrogen balance**
 - Utilization of Cl₂ at a rate of around 65% of production as was case in India was not considered economic
 - Excess chlorine has to be burned to HCl or otherwise destroyed
 - Hydrogen disposal is a much easier problem ← H₂
 - Outlets for saleable chlorine must be developed to balance caustic-chlorine co-production

Now, coming to the economics, plant location is very much essential because lot of solution is required and then transportation of the salts etcetera has to be reduced. So, location, need careful analysis of such factors as cheap power and salt sources coupled with the rising cost of transportation.

In some cases, it has more advantages to locate within a plant complex or near the product market because of the relative cost of transporting salt and then finished products. Let us say we have seen NaOH and then Cl₂ both of them are used in pulp and paper industries ok. So, in this pulp and paper industries so, there itself if you have a electrolytic process, the there itself we can use them as a product directly ok. So, still there would be transporting requirement would be there only for salt, not for the product.

So, that kind of a arrangements one has to make. For example, one-third of caustic soda plants are attached to paper and rayon mills. Caustic chlorine hydrogen balance is required. Whatever, it is not about the co-product. Often it has been misunderstood by the researchers as well as the industrialist that if you produce more number of components, chemicals in one plant it which going to be more beneficial.

That is not true here because in India, whatever the chlorine and then sodium hydroxide produced by electrolytic process, chlorine only 65 percent of the chlorine is being used directly wherever applications are there as per the end uses we have shown. Rest of the 35 percent etcetera is burned to produce HCl or disposed of and then disposing the

chlorine is a tough problem compared to the disposing of hydrogen. So, if you do not have market and then even if you are getting a co-product is not going to be you know economically you know beneficial for you, ok there should be balance.

Utilization of chlorine at a rate of 65 percent production as was case in India was not considered economic. Excess chlorine whatever is there that has to be burned to HCl formation or otherwise destroyed. You know destroyed a decomposition is a big problem because this chlorine is toxic gas you cannot release more than 2 ppm into the air.

Hydrogen disposal is a much easier problem, but nowadays rather disposing hydrogen you should see how to store it because hydrogen energy is the need of the hour. Outlet for saleable chlorine must be developed to balance caustic chlorine co-production.

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• A substantial new usages of chlorine will be (PVC) and chlorinated hydrocarbons prepared from petrochemical intermediates

• In advanced countries, the balance is in the reverse, with caustic soda being the disposal problem

• This explains why other chlorine processes are important

• (c) lime-soda process

• Since this process produces no chlorine, it might appear attractive for Indian conditions

• Cost of soda ash is too high and electrolytic process is the choice until Na_2CO_3 costs drop to less than one-half that of NaOH per unit weight

• The situation is even more favourable for electrolysis as more Cl_2 co-product is utilized

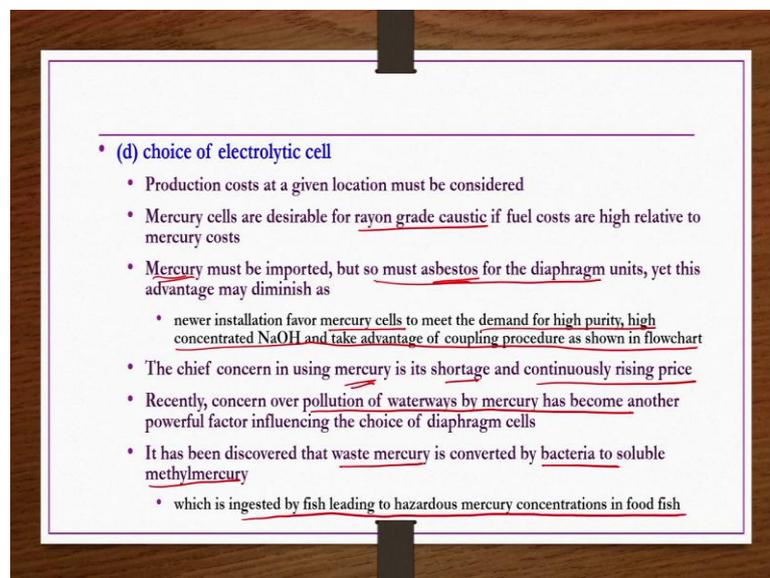
Handwritten annotations: 'USA' in a circle, 'Cl₂' in a circle with an arrow pointing to 'caustic soda', and 'NaOH' in a circle with an 'X' over it.

Additionally, recently you know most of the chlorine is also being used for this poly vinyl chloride manufacturing as well as chlorinated hydrocarbons prepared from petrochemical industries for that purpose also chlorine is being used nowadays. In advanced countries balance is the reverse that is caustic soda being the disposal problem. In USA especially chlorine is being consumed whatever is produced it is being consumed there is no excess there is no disposal problem of chlorine, but NaOH is not being consumed.

So, there is a problem of disposal of this NaOH in USA whereas, in India it is reverse. In India chlorine disposal is a problem and then NaOH is a common chemical that is being consumed whatever is produced. This explains why other chlorine processes are important for other countries.

Lime soda process since this process produces no chlorine it might appear attractive for Indian conditions because we are having excess chlorine or chlorine requirement is less. Cost of soda ash is too high and electrolytic process is the choice until sodium carbonate cost drops to less than half of that of the sodium hydroxide per unit weight. The situation is even more favourable for electrolysis as more Cl₂ co-product is utilized.

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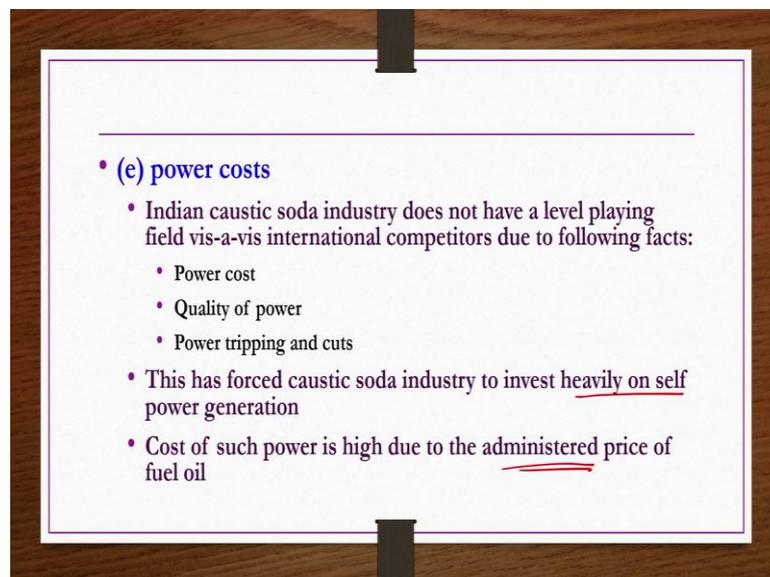
If it is not utilized then it is a problem choice of electrolytic cell. Production cost at a given location must be considered whether are you going to take asbestos cells or mercury cells or membrane cells. Mostly asbestos and mercury cells are being imported. So, accordingly you know one has to see production cost. Mercury cells are desirable for rayon grade caustic because it produces 70 percent NaOH and for this rayon grades you know higher concentration NaOH solution is required ok.

Mercury must be imported, but so must be asbestos also for the diaphragm cell. Only Not only the mercury asbestos are also being imported, but this advantage may be diminishing as newer installation favor mercury cells to meet the demand for high purity,

high concentrated NaOH and take advantage of coupling procedure as we have seen in the flow chart.

The chief concern in using mercury is its shortage and continuously rising price. In addition, pollution of waterways by mercury has become another issues nowadays. So, it should also be considered. It has been discovered that waste mercury is converted by bacteria to soluble methyl mercury, which is ingested by fish leading to hazardous mercury contaminations in food fish.

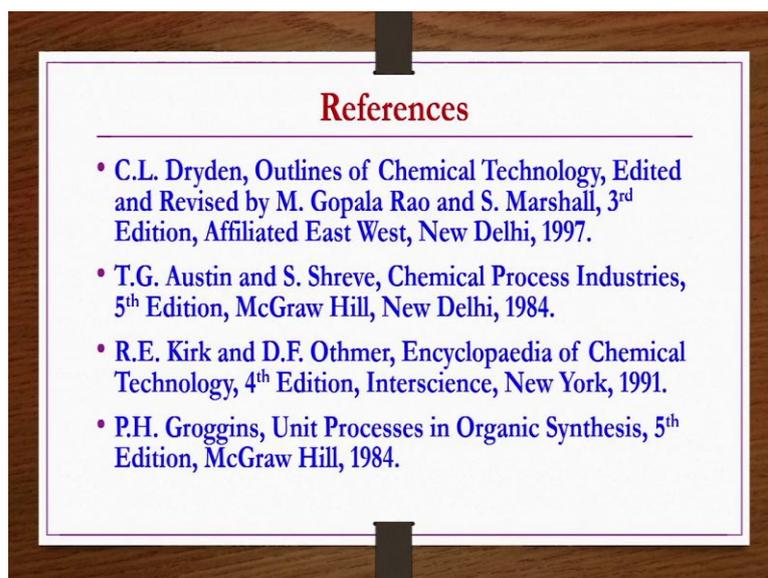
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Power cost its most essential because of the power cost Indian caustic soda industry is not at par with the advanced countries sodium hydroxide industries. The reason is that power cost quality of power and then power tripping and cuts that we are facing in India that is right.

So, in order to avoid these problems caustic soda industry are heavily depending on self-power generation, but that is also expensive because for the self-power generations you need fuel and then fuel prices are often administered and then gradually increasing ok. So, all these factors one has to take under into consideration before selection of the process and then location as well.

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References for today's lecture are provided here.

Thank you.