Industrial Inorganic Chemistry
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Lecture – 27
Chloralkali Electrolysis

Good morning everybody. So, once again come back to this class of Industrial Inorganic Chemistry where to where talking about the halogens.

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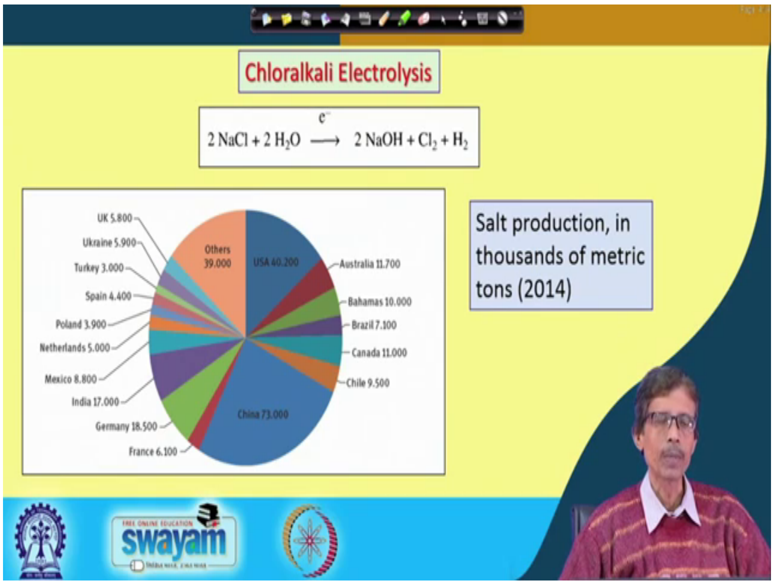

Chloralkali Electrolysis

$$2\,NaCl + 2\,H_2O \xrightarrow{e^-} 2\,NaOH + Cl_2 + H_2$$

Salt production, in thousands of metric tons (2014)

And one most important industrial preparation will be talking today we had started this discussion last time is your Chloralkali Electrolysis. So, it has 2 component basically what you can understand, the first thing what you can have is the you must have the chloralkali supply what is that chloralkali that we have discussed earlier also. That it is nothing, but your sodium chloride only is not a different type of alkali metal ion is only sodium and the chlorine for the chloralkali. We will go for the typical electrolysis process and interestingly the raw material what we can have throughout the globe and how people can produce the different types of these salts basically.

That means the sodium chloride, because this sodium chloride will be using for this particular electrolysis that we have seen last time also that during this electrolysis we get sodium hydroxide we get chlorine as well as we get hydrogen. So, is a very important starting material from industrial point of view because if you are only intended to produce chlorine from sodium chloride because we have huge reserve of sodium chloride from the ocean from the surface of the earth also. That can be converted immediately to it is another value added material which is your sodium hydroxide and chlorine as we produce and we will also see how we can utilise this particular chlorine for making some other chlorine based compounds chlorine based inorganic compounds such as we all know that is the bleaching powder.

How we can make the bleaching powder out of this chlorine or if this particular chlorine is not utilised readily as it is we can convert it to it is corresponding hydrochloric acid; that means, hydrogen chloride or we can put it in the cylinders to preserve it to carry somewhere else where it can be utilised nicely. So, in terms of the salt production in thousands of metric tons what we see from this pie chart or the pie diagram is that major share is from the China. So, China has the huge reserve starting from the ocean source or the surface source or from the earth crust, next is USA and you see compare to that 73000 and 40200 in metric tons of this production of the salt; that means, sodium chloride only.

Production of this salt and their production for India is not very less even so, it is 17000. So, the amount of this thing we have. So, we have the huge reserve of sodium chloride what we produce annually, but if we do not have the right industry which can be used for the production of these 3 components say starting from sodium hydroxide to hydrogen gas also. We cannot utilise this particular material in a nicer way such that it can be used for other industrial sectors writing like starting from your pharmaceutical sector to making new organic molecules or new inorganic compounds.

So, if we have a huge reserve so, we always focus our attention to convert this particular species; that means the sodium chloride to sodium hydroxide through this electrolytic process. So, the immediate electrolytic process is helpful for us because this electrolytic process always we know that it can also be very much helpful in clearing the purity of these materials. So, the purity of these things if we get chlorine and hydrogen as the gas or the sodium hydroxide from the solution part we can have a guaranteed strength or we can have a guaranteed purity for all these material. That means 3 components we will get out of one particular starting material which is your sodium chloride.

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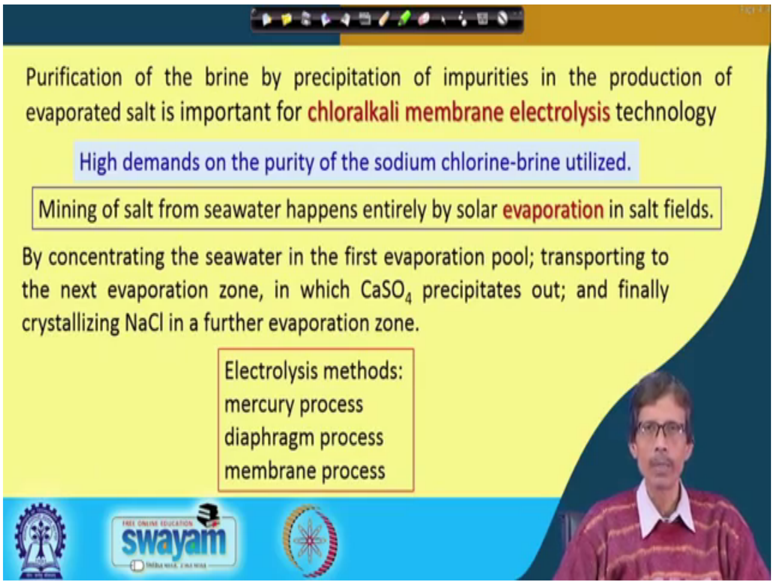

Purification of the brine by precipitation of impurities in the production of evaporated salt is important for chloralkali membrane electrolysis technology

High demands on the purity of the sodium chlorine-brine utilized.

Mining of salt from seawater happens entirely by solar evaporation in salt fields.

By concentrating the seawater in the first evaporation pool; transporting to the next evaporation zone, in which $CaSO_4$ precipitates out; and finally crystallizing NaCl in a further evaporation zone.

Electrolysis methods:
mercury process
diaphragm process
membrane process

So, what we do, we do typically from the starting material also; that means, the purification of the brine how we make that is the brine water that means the sea water also the concentrated sea water. So, if we can have also by precipitation of impurities in the production of evaporated salt; that means, salt we all know that is one important technique for purification of a table salt what we consume as sodium chloride is through a particular evaporation or the evaporated technique. So, getting this particular salt is very important for the one type of electrolysis which we call as the chloralkali membrane electrolysis technology.

So, typically when we introduce membrane for this particular electrolysis because as we have seen that we can have 3 components one is sodium hydroxide, the second is the chlorine and third is the hydrogen. So, you have to separate these 3 and you get all of them individually with not much contamination from the others. So, hydrogen gas what we are intended to get is in the pure form say 90 percent or the 95 percent purity it should not be contaminated with that of our chlorine what is produced simultaneously. So, the simultaneous production of these 3 things luckily we can have the 2 components; that means the chlorine and the hydrogen in two different chambers and sodium chloride hydroxide what is being produced is also remaining in the electrolytic chamber.

So, or getting these sodium chloride brine; that means, the sodium chloride what is present in the brine high demands on the purity of the sodium chloride bar brine what you can use for your production. So, what we get, we can get the salt from mining or from the sea water happens entirely by the solar evaporation in salt fields. We have huge salt fields whether you go to the Gujarat coast or any other coastal area even in West Bengal also we have in the this some part we can have also the salt production earlier, but now we have not interested or we are not doing this thing, even the industrial people should come forward to get this particular starting material in a cheaper way.

So, mining of salt from sea water basically and particular thing is that is straightway you go for the evaporation of the salt in the salt field. So, what we do it go for the concentration concentrating basically concentrating of a sea water in the first evaporation pool. So, if you have the evaporation pool we put sea water we allow to enter the sea water inside that pool then we transport that to the next evaporation zone. So, the first evaporation pool can go for little bit of evaporation and which is then allowed to go to the second zone in which calcium sulphate precipitates out, but from calcium sulphate is already there in sea water.

So, during that precipitation what we should know that we are looking for a very highly concentrated solution of sodium chloride and by that time if your calcium sulphate k s p values are different from the k s p value of sodium chloride all we know the calcium sulphate will precipitate fast before your sodium chloride is crystallizing out. So, in that particular zone we should be able to take care of the calcium sulphate from the brine or the sea water. So, the brine will also supply some amount of calcium sulphate cake to you and finally, we push the concentrated solution of sodium chloride to the next zone and allow it for further evaporation which is known as the further evaporation zone and that further evaporation zone is looking for we are looking for that the crystallization of sodium chloride.

That means even if you have some amount of impurity in it would not be crystallize at that particular point only the bulk amount of the material the solid material what is getting separated from that saturated solution during crystallization is your sodium chloride. So, taking that sodium chloride in your hand so, you are now having a good supply of the raw material; that means the purified sodium chloride. It is a reasonably pure in your hand and we can use the electrolysis technique and these electrolysis methods are of 3 types depending upon the ease depending upon the availability of the material and depending upon the cost involved for introducing a particular process for the industry.

So, industrial people should have the know how for that particular process and the modification is going on with time. So, first one if we consider that the mercury process why we use the mercury the mercury we know that the mercury itself can be a electrode and it can be in the liquid form and it can be a corresponding electrode in the liquid form we because we know that the mercury can serve as a good cathode in electrolytic chamber or during electrolysis. So, mercury pool and we also know somewhere we have seen that the sodium amalgam can also be helpful if in presence of mercury some amount of sodium amalgam is formed over the surface of that thing so, we will have a mercury process.

So, the development of that particular technique we can introduce a diaphragm for the separation of the material what is coming out is known as the diaphragm process and finally, we have more sophisticated membrane to be used and this will be known as also your membrane process.

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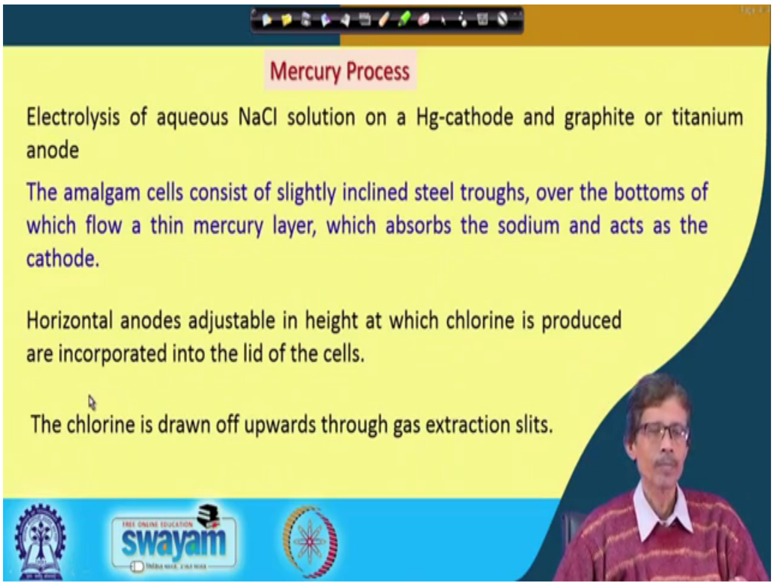

Mercury Process

Electrolysis of aqueous NaCl solution on a Hg-cathode and graphite or titanium anode

The amalgam cells consist of slightly inclined steel troughs, over the bottoms of which flow a thin mercury layer, which absorbs the sodium and acts as the cathode.

Horizontal anodes adjustable in height at which chlorine is produced are incorporated into the lid of the cells.

The chlorine is drawn off upwards through gas extraction slits.

So, the first one is the mercury process what we can use is the electrolysis of aqueous sodium chloride solution on a mercury cathode. So, you have the mercury cathode electrode and graphite or titanium as the anode.

So, we should know the material; that means, sometimes we know if we go simple electrochemistry, starting from your polarography to cyclic voltammetry we always should know that what sort of electrode we are using. So, polarography was invented was introduced long back where the mercury cathode or the mercury cathode electrode was very much utilised over there and that particular electrode was known as dropping mercury electrode which is known as d m e. So, dropping mercury electrode was very popular during the development of that particular technique that means the polarographic technique.

In a similar fashion industry people have also utilize the huge amount of mercury pool also as a mercury cathode and graphite as we all know that the carbon rod from our dry cell batteries we all know that the graphite can also be a very useful anode and the titanium metal itself or the metal rod. So, either the carbon rod or the titanium rod can be useful for making the anode for this particular electrolysis. So, in presence of pure mercury and some amount of sodium if we give we get the amalgam of the sodium.

So, amalgam cell will consist of slightly inclined steel troughs. So, steel containers is nothing, but the steel trough over the bottoms of which a flow of thin mercury layer, we are not using huge amount of mercury because the mercury is also not allowed environmentally is not very useful also from the industrial point of view because it will deadly for the environment deadly for the human health or they deadly for the animal kingdom also. So, we should also restrict the restriction was there if it has been develops around hundred years back people were also very much careful in not misusing the mercury for this particular purpose.

So, in that case the mercury which absorbs the sodium and acts as a cathode. So, not the pure mercury it is only absorbing that is basically solubilising there. So, mercury liquid basically on the surface is solubilising some amount of sodium because we know that the sodium chips or the sodium metal we can cut with a simple knife and we can make small pieces of it and if we put on this or mix some very fine particles of the sodium from the sodium metal itself and we can put over that particular pool of the mercury you get the corresponding converted layer of mercury as the sodium amalgam.

And then we can have the horizontal anodes so, not any vertical anode, but is the horizontal anodes adjustable in height because you can adjust the height is within the chamber because you can have large pool of the product of sodium hydroxide within the chamber. And you should also allow the passage of the chlorine; that means, the corresponding accumulation of the chlorine gas inside the chamber and are incorporated into the lid of the cells. So, if you have the lid of the cell; that means, the cover of the cell so, the horizontal anodes are attached to that particular lid because the connection electrical connection to that particular lid will be also useful.

Now when chlorine is produced one of the gaseous component during electrolysis is produced is drawn of upward through the gas extraction slits. So, gas passage slits rather not extraction is a can industrial people also use sometimes we as a typical chemist we do not use the extraction, extraction we used as solvent is getting used for extracting some solid material or something like that. So, is a gas passage so, gas passage slits are basically over available through which the chlorine is only allowed to pass close to that particular electrode which is producing your chlorine gas.

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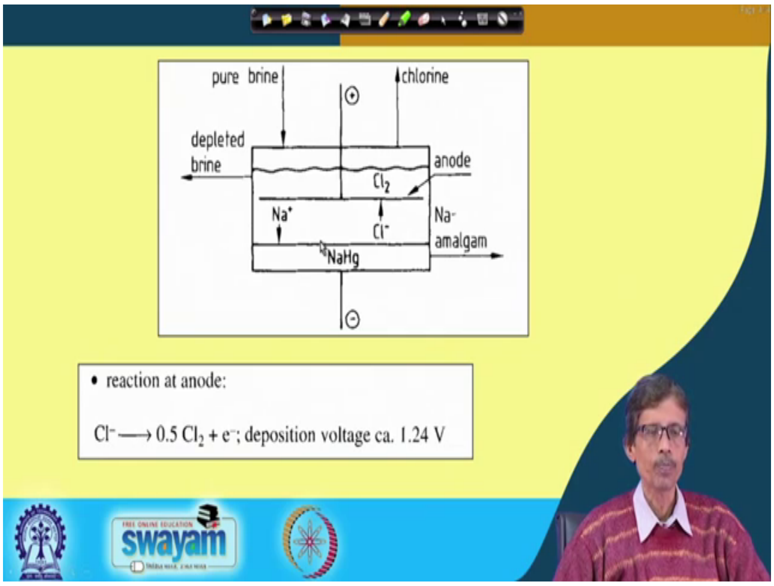

- reaction at anode:

$Cl^- \longrightarrow 0.5\ Cl_2 + e^-$; deposition voltage ca. 1.24 V

So, is the rough flow sheet diagram where, you see you always should think of the chamber. So, chamber you have so, a rectangular box always you can draw you can draw it in a 3 dimensional fashion also because this is a 3 dimensional thing because it is a tank basically.

So, electrolysis chamber or what you can consider is a tank and as I told you that you have the corresponding not vertical electrode, but you have the horizontal electrode. So, you see now see these things that is that you have this. So, when you have the sodium amalgam. So, is a pool at the bottom of the chamber so, since you consider that pool as the electrode so, what do you think, that will it be a vertical electrode or a horizontal electrode, because you cannot put the mercury in a column fashion or mercury in a vertical way. So, you cannot put because you can have some extra chamber out of for that and you should have the direct contact with a material what is being used for your electrolysis.

So, since at the bottom you have the sodium amalgam in it. So, it is connected to that particular side; that means the negative end of the electrolysis cell. So, which is your horizontal sodium amalgam electrode required for the corresponding production of one particular material. Similarly above it which has also been we discuss that it is adjustable the height can be adjustable. So, the anode you have the corresponding anode and that particular anode either made of your carbon rod or the titanium rod is there.

So, what we get basically that during this particular process if we focus our attention that we will be taking only the chlorine over there. So, this chloride ions basically because the sodium ions what is getting over there is attracted over the sodium amalgam. So, chloride ions will be attracted to the anode and it will produce your chlorine and whatever you have; that means, the depleted brine because the concentration of the sodium chloride will be reduced within this brine and this is the corresponding point where we can introduce pure brine water or the brine solution inside the chamber.

So, what we see this particular part basically will take care of the production of the chlorine and whatever amount of sodium is forming your sodium amalgam that will react with water producing sodium hydroxide and the hydrogen afterwards. So, this particular reaction what we consider if we can consider that what is happening at the anode the reaction basically for the production of the chlorine. So, Cl minus or twice of Cl minus will be producing 1 Cl 2 or half of the Cl 2 molecule with electron and deposition at a voltage of 1.24 volt.

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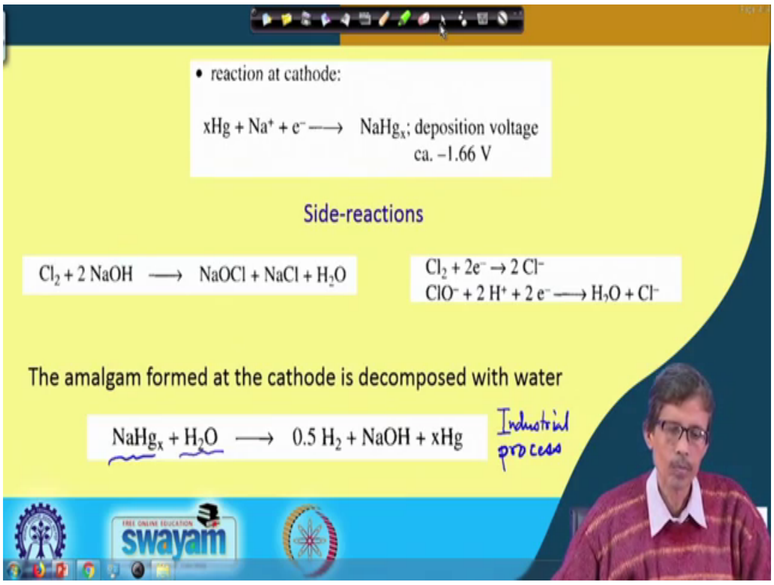

- reaction at cathode:

$xHg + Na^+ + e^- \longrightarrow NaHg_x$; deposition voltage ca. –1.66 V

Side-reactions

$Cl_2 + 2\,NaOH \longrightarrow NaOCl + NaCl + H_2O$

$Cl_2 + 2e^- \rightarrow 2\,Cl^-$

$ClO^- + 2\,H^+ + 2\,e^- \longrightarrow H_2O + Cl^-$

The amalgam formed at the cathode is decomposed with water

$\underset{\sim}{NaHg_x} + \underset{\sim}{H_2O} \longrightarrow 0.5\,H_2 + NaOH + xHg$

Industrial process

And at the cathode what we are getting. So, on the surface of this particular mercury or the sodium amalgam pool already you have the x number of atoms of mercury will be attracting your sodium and which is being reduced by the electron what is available from the anode side will be giving you so, NaHg x this is basically your sodium amalgam and deposition voltage for that particular species is minus 1.66 volt.

So, during this particular process what we are producing, we are producing only the chlorine gas and your sodium amalgam, but some of the reactions we should also consider which is the side reactions while you produce sodium hydroxide all together. So, we will producing sodium hydroxide as well as hydrogen, but some side reactions which will be destroying our target material like chlorine as well as sodium hydroxide because these two things will be there.

And during the passage of this chlorine which is leaving your chamber by that time your chlorine gas can react with the produced sodium hydroxide forming you sodium hypochlorite that we will also discuss afterwards how we can make very quickly the sodium hypochlorite which is a very good bleaching reagent and which is also very much industrially important. So, not only sodium hypochlorite, but you will get back the starting material; that means your sodium chloride.

So, you have this for this particular process basically your Cl 2 is getting reduced to chloride by accepting 2 electron and your hypochlorite ion is also responsible for accepting electron as well as proton because these protons are not utilized for your hydrogen production. So, it will instead produce water molecule and more number of chloride ions and those chloride ions can also be recycled back to your production further. So, amalgam formed at the cathode next what amalgam you have now you know hand. So, your NaHg x in your hand and chloride is giving you the chlorine gas and chlorine gas is leaving your chamber and we are not getting that chlorine for your other purpose; that means, the chlorine for your reaction is sodium hydroxide.

So, amalgam formed at the cathode is next allowed to decompose with water. So, you allow the reaction of amalgam with water. So, the control of the another reactant; that means, the water is also very important, sometime back in this particular class we have discussed that water is a very good reagent for some reactions. We do some reactions by dissolution of some material in water and we do some we know that some organic reactions we do with a number of hydrogen water molecules, which is attaching to this particular reaction of organic chemistry such as your hydrolysis reaction.

Similarly if you judiciously allow the reaction of your sodium amalgam with water molecule you will be getting 2 other products immediately, which is giving you a mercury back; that means, the free mercury will be produced along with your hydrogen as well as sodium hydroxide for your chloralkali electrolysis process. So, that is the thing if you step wise if you break these thing; that means, how you break the formation of your chlorine gas and the next time whatever amount of sodium amalgam you form. So, you use mercury as the corresponding pool as the electrode then you convert it to sodium amalgam and then sodium amalgam you allow it to react with water to produce your hydrogen and sodium hydroxide and mercury back.

So, this particular reaction what you are talking thinking of you should always remember to understand this one very importantly that if somebody is asking you that how sodium amalgam will react with water molecule, because this is the process what is a industrial process is typically a industrial process. So, in that industrial process; that means, you have a huge or the bulk amount of this particular one that will be getting for production of hydrogen as well as sodium hydroxide. So, this particular reaction you always try to remember in terms of it is corresponding reactivity of sodium amalgam.

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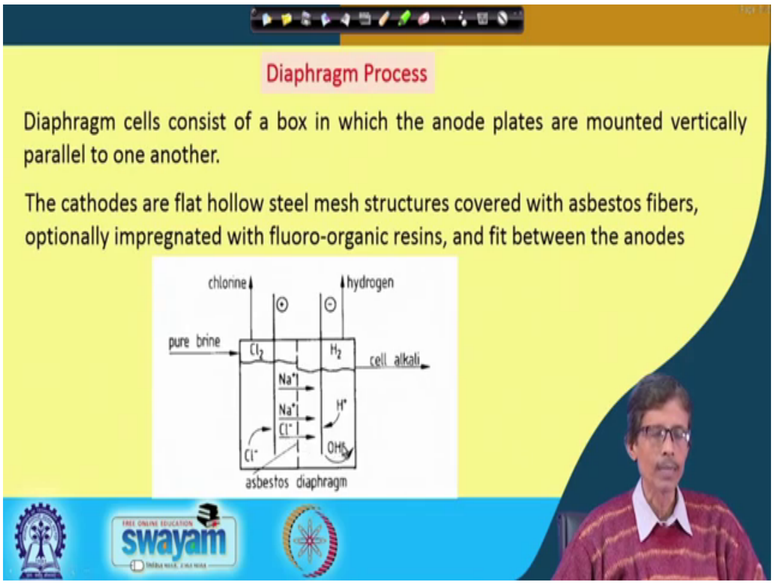

Diaphragm Process

Diaphragm cells consist of a box in which the anode plates are mounted vertically parallel to one another.

The cathodes are flat hollow steel mesh structures covered with asbestos fibers, optionally impregnated with fluoro-organic resins, and fit between the anodes

So next we will see that the other procedure the second procedure which is diaphragm process. So, we will now introduce diaphragm for the production of these 3 important components and now since the electrolysis cell is bearing diaphragm we will call it as a diaphragm cell and that is why you should also try to remember the definition the exact text book definition what we sometimes call with examples we give the definition as well as with some example what is known as your diaphragm cell. So, it is nothing, but a box in which the anode plates are mounted vertically parallel to one another.

So, now we are going back from a regime of electrodes in horizontal directions to a vertical direction. So, what you have now the direction is we are changing now for this particular case we will have the vertically parallel electrodes in than the cell. So, the cathodes are nothing, but cathodes are flat hollow steel mesh structures. So, steel mesh we all know that very fine net basically so, those very fine net and all these things whatever we have in this particular process so, that can also function as the good diaphragm.

So, diaphragm is basically a very fine net and it is made up of something. So, cathodes are flat hollow steel mesh structure which is covered with asbestos fibers. So, steel is not allowed to do it will be covered with asbestos fiber another inert material. So, as a optionally impregnated with fluoro organic resins. So, it is coated with the asbestos fibers then it is further can be fixed with fluoro organic resins which is very much inert in this particular reaction medium or electrolysis medium which is rather a very harsh condition for the reaction.

And fit between the anodes so, you have the corresponding cathodes and those cathodes are fitted between these two anodes. So, you can have number of anodes as well as number of cathodes in your hand so, all these things one after another you can put and you get this one. So, your electrodes now in vertical direction and this vertical directions you have the diaphragm cell what is known as your diaphragm cell and what you get over there is that you fix it in a different way so, you have the pure brine introduction from the side not from the top.

So, from the left hand side if you put the brine inside and you have the asbestos diaphragm so, you have the steel covered steel mesh then it is covered with asbestos and final coating. So, you have the mesh because what you can separate these two anodes and the cathode. So, separation of these anodes and cathodes by the asbestos diaphragm is giving you the corresponding diaphragm cell. So, during that particular process again simultaneously now is there is no need to react with your produced sodium amalgam, but you allow to react that particular one together the sodium chloride electrolysis.

So, diaphragm cell will have definitely that particular advantage that that together will be producing 2 gaseous material and you have plenty of sodium ions and the hydroxide ions within the reaction chamber. So, you have this corresponding one as a saturated solution of sodium hydroxide within the cell.

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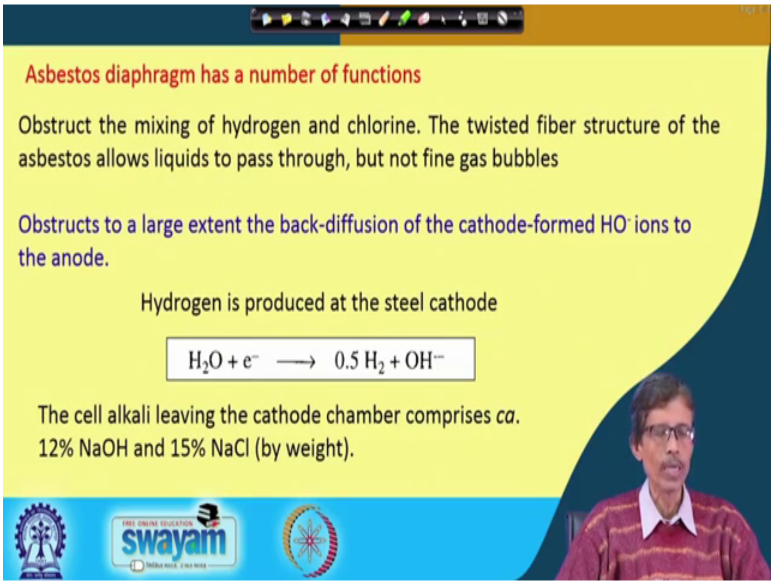

Asbestos diaphragm has a number of functions

Obstruct the mixing of hydrogen and chlorine. The twisted fiber structure of the asbestos allows liquids to pass through, but not fine gas bubbles

Obstructs to a large extent the back-diffusion of the cathode-formed HO^- ions to the anode.

Hydrogen is produced at the steel cathode

$$\boxed{H_2O + e^- \longrightarrow 0.5\,H_2 + OH^-}$$

The cell alkali leaving the cathode chamber comprises *ca.* 12% NaOH and 15% NaCl (by weight).

So, then this asbestos diaphragm has a number of functions why we are using this asbestos diaphragm that is why you will get the corresponding diaphragm cell. So, asbestos diaphragm is disturbing or is enervating the mixing of hydrogen and chlorine or H 2 or Cl 2 gas the twisted fiber structure because you know that the asbestos fibers that how it looks like. So, the twisted fiber structure of the asbestos allows liquids to pass through.

So, basically asbestos fiber is functioning as a sealed and it is only allowing the solution which contains either sodium ion or the hydroxide ion. So, there will be a possibility of mixing of these two ions in liquid phase such that you get the sodium hydroxide uniformly throughout the entire chamber, but it will not allow the finer gas bubbles of any of these two; that means, it is not allowing chlorine gas to pass or hydrogen gas to pass. So, that is the major advantage of using your diaphragm which is made of asbestos.

It also obstructs a large extent of back diffusion of the cathode form hydroxide ions to the anode, because the accumulation of this hydroxide ions which is forming at the cathode. So, it is not allowing any kind of back diffusion of this hydroxide ion to the anode because otherwise this hydroxide ion will be reactive at the anode. So, is basically when it is in solution it will be restricted to that particular chamber only. So, in a general way what you can understand that, when you introduce some diaphragm for electrolysis it is basically very much helpful for getting a pure quality through mixing a liquid and the gases separated out from these two electrodes anode or the cathode.

So, hydrogen what is being formed is produced at the steel cathode. So, we should take out that particular hydrogen produced at that particular cathode chamber because it is accepting electron to produce the hydrogen at that cathode and that is why we are telling it is the cathode formed hydroxide ion. So, hydroxide ion; that means, OH minus OH minus will be there that hydroxide ions will be there at the cathode only until should not pass to the anode.

And by doing so, the cell alkali leaving the cathode chamber; that means, the concentration of that particular alkali what is leaving behind that particular cathode chamber comprises of 12 percent of NaOH and 15 percent of NaCl by weight because you have already a high concentration of sodium chloride. So, sodium chloride concentration will come down and sodium hydroxide concentration will go up, when you take out this particular material for a cycle when the production of chlorine and production of hydrogen is exhausted rather. We will take out the solution and the solution will give you the different percentages what is the even over there as sodium hydroxide percentage and the sodium chloride percentage and that will be utilized further for purification.

Because the partial crystallization or the selective crystallization of these two because these two quantities when you take out from solution they are solid. So, solid cakes of sodium hydroxide and solid cakes of sodium chloride will possible to produce from there and you can separate these two because the fractional crystallization will allow one of the material to precipitate or crystallize first then the other. So, the separation through crystallization only is possible and you get 2 solid products out of this particular reaction chamber ok. So, next we will continue the third category in our next class ok.

Thank you very much.