Inorganic Chemical Technology

Prof. Nanda Kishore
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 23
Chlor-Alkali Industry - Soda Ash

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Chlor-Alkali Industry - Soda Ash. Chlor-Alkali Industry: this industry represents production of following major chemicals.

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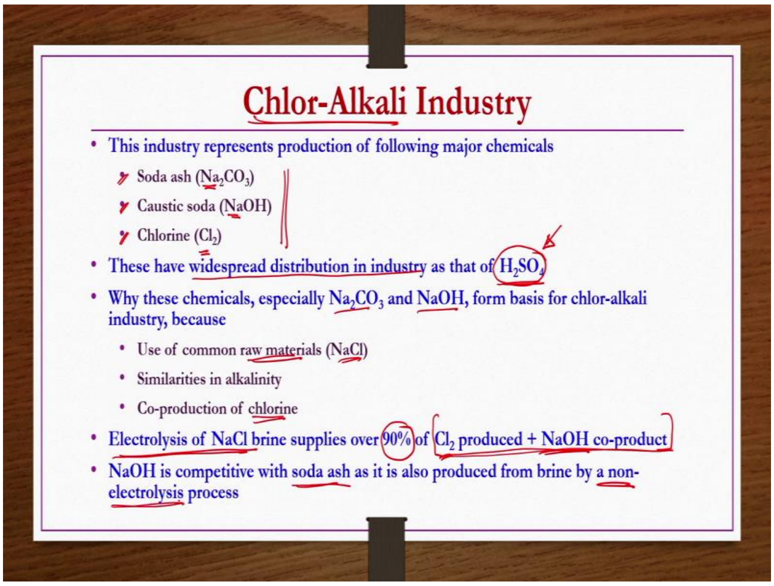

Chlor-Alkali Industry

- This industry represents production of following major chemicals
  - Soda ash (Na_2CO_3)
  - Caustic soda (NaOH)
  - Chlorine (Cl_2)
- These have widespread distribution in industry as that of H_2SO_4
- Why these chemicals, especially Na_2CO_3 and NaOH, form basis for chlor-alkali industry, because
  - Use of common raw materials (NaCl)
  - Similarities in alkalinity
  - Co-production of chlorine
- Electrolysis of NaCl brine supplies over 90% of Cl_2 produced + NaOH co-product
- NaOH is competitive with soda ash as it is also produced from brine by a non-electrolysis process

Actually, by chlor and alkali, you can see that alkali that terminology is coming because of the lithium, sodium, potassium, these kind of component and then chlor is because of the chlorine, right. So, specially the chlorine and then alkali related together we are discussing as a chlor-alkali industry because of the three major chemical productions in this industry.

There may be in fact there are many other products are also possible that we can see anyway as a co-products etcetera in this process when we are discussing about the production of these chemicals. But primarily three are very essential that are leading this you know this chlor-alkali industry. One is the soda ash or sodium carbonate. Another one is caustic soda or sodium hydroxide and then chlorine gas.

So, these are the three components or three chemicals which are you know primarily you know dominating this chlor-alkali industry. There may be other components as well. Because of the nature of the product here you know alkalis are there and then here chlorine gas is there. So, because of the nature of the chemicals these industries known as the chlor-alkali industry.

Then what if why should we study about this chlor-alkali industry? Because they have application widespread applications in the industry as that of H 2 SO 4. You can see the H 2 SO 4 treated as a barometer for the measurement of the development of chemical industry in India. And then such much important is H 2 SO 4 as we have already discussed.

These chlor-alkali industries also if you together not like individual component together all components if you take chlor-alkali industry and then make a comparison. So, then you can see even the products these chemicals whatever we listed here chlor-alkali industry major products they also have widespread distribution in the chemical industry. Such is important is this chlor-alkali industry and then especially out of which these three components are so much important.

That is the reason we have to study as a chemical engineers, ok. Why these chemicals especially sodium carbonate and sodium hydroxide form basis for the chlor-alkali industry because of the three reasons. The basic source whatever is there to prepare these chemicals is same that is sodium chloride. And there alkalinity also if you see there is a similarity and there is a co-production of chlorine as well, ok.

So, that is the reason you know these chemicals are very much essential and then they form basis for the chlor-alkali industry, ok. Now, whatever the Cl 2 and then NaOH that is sodium hydroxide and chlorine are available in the industry are produced in the industry out of which 90 percent is coming from the electrolysis of NaCl, ok. Whatever the Cl2 produced and then NaOH co-product produced in the chlor-alkali industry, right.

So, 90 percent of these components that are available in industries are these products that are available in industry are coming from the process where electrolysis of NaCl is being done, ok. So, in other words most of the chlorine and then NaOH rather most of this almost we can say almost all the chlorine and then sodium hydroxide are coming from the electrolysis of sodium chloride brine, ok.

NaOH is competitive with soda ash that is sodium carbonate as it is also produced from the same brine by a non-electrolytic process as well, ok.

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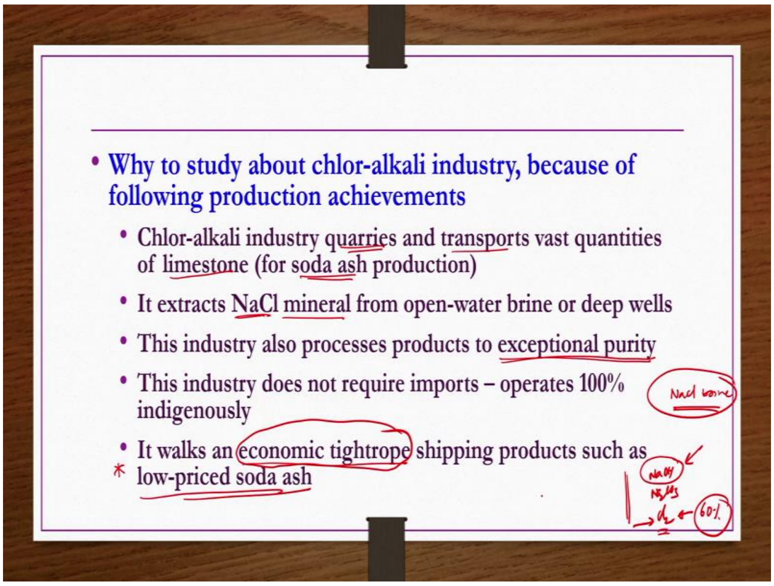

- Why to study about chlor-alkali industry, because of following production achievements
  - Chlor-alkali industry quarries and transports vast quantities of limestone (for soda ash production)
  - It extracts NaCl mineral from open-water brine or deep wells
  - This industry also processes products to exceptional purity
  - This industry does not require imports – operates 100% indigenously
  - It walks an economic tightrope shipping products such as * low-priced soda ash

Why to study about chlor-alkali industry because of the following production achievements that we are going to see. One is that chlor-alkali industry quarries and transports vast quantities of limestone for soda ash production. Limestone is also required for the process that we are going to see anyway when we discuss about the process. And then it extracts sodium chloride mineral from open water brine or deep wells that is other thing.

And this industry also processes products to exceptional purity. Actually, most of the industries the product when you produce, they are not very pure may be 10, 15 percent etcetera something like ammonia you see you produce in very small purity or then you have to improve its purity etcetera by the subsequent purification process etcetera.

But here this industry whatever the chemicals that are being produced they are often produced in exceptional purity that is high purity chemicals are produced in these industries. This industry does not require imports you only need NaCl brine solution. So, you do not need to depend because these things are available in almost all countries. So, in India we are not depending on any kind of imports for this industry completely indigenous industry.

Also, very important factor is that it walks an economic tightrope shipping products low price products such as soda ash. Soda ash is not very expensive. It is not expensive, but still it is produced in large quantities you know and then you know obviously, you know the economic tightrope walking would always be there and then you have to be careful to make a profitable plant, right.

So, other thing is that not only this production of these components also market also until recent past like up to 1980s or 1990s whatever the Cl 2 that is produced in this electrolysis of NaCl process to get sodium carbonate and sodium hydroxide etcetera you know only 60 percent is being consumed for production of organic chemicals or you know chlorinated organics or any other components or many other uses of this chlorine are also there we are going to see anyway.

Only 60 percent of chlorine gas is used for different purposes and then remaining has to be disposed of and then disposing of chlorine is not a easy task. Again, there you need to do so many kind of you know calculations and then installation process for the disposing of this chlorine etcetera all those things you have to study and do properly.

That is the case in India whereas, in USA its other way chlorine is used, but whereas, the sodium hydroxide is being is being disposed of because of lack of market for it, ok. So, it is not just you know people sometimes find very especially students find very exciting that you know we are producing so many chemicals from the one plant, but also if there is no market for so many co-products then there is no use, ok.

So, if you wanted to have a proper you know chlor-alkali industry which is economically benefitable for you it is better to have this industry in a industrial complex so that you know some of the co-products there may there itself may be used etcetera. So, that is one of the engineering problem that we are going to discuss anyway.

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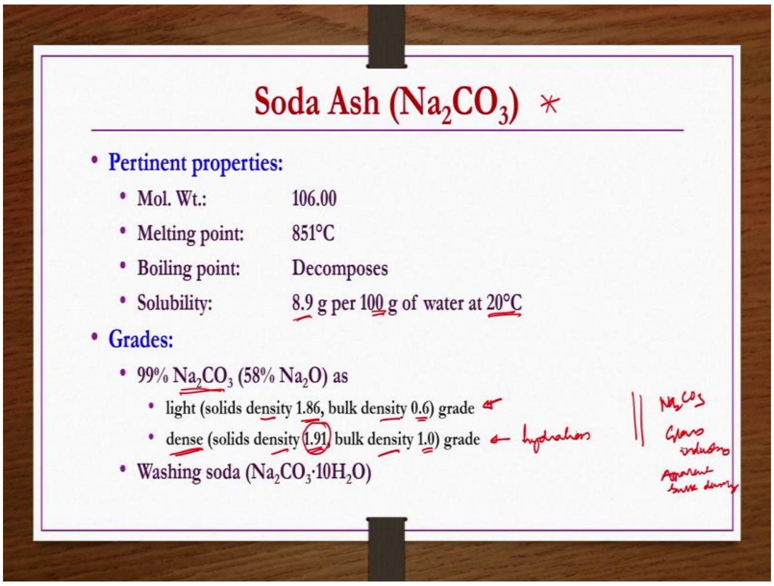

Soda Ash (Na_2CO_3) *

- **Pertinent properties:**
  - Mol. Wt.: 106.00
  - Melting point: 851°C
  - Boiling point: Decomposes
  - Solubility: 8.9 g per 100 g of water at 20°C
- **Grades:**
  - 99% Na_2CO_3 (58% Na_2O) as
    - light (solids density 1.86, bulk density 0.6) grade ←
    - dense (solids density 1.91 bulk density 1.0) grade ← hydration
  - Washing soda ($Na_2CO_3 \cdot 10H_2O$)

|| Na_2CO_3
Glass industry
Apparent
bulk density

Now, we start discussing about soda ash Na 2 CO 3. We start with pertinent properties molecular weight 106, melting point 851 degree centigrade, boiling point is not there because it decomposes, solubility it is not that high for example, at 20 degree centigrade only 8.9 grams of sodium carbonate is soluble in 100 grams of water, ok.

Grades, different grades are available, but especially you know two grades are there low dense and then high-dense grades are there. So, 99 percent Na 2 CO 3 or 58 percent Na 2 O as one technical grade. So, where you have light grade and then dense grade or heavier grade sodium carbonate or what do you mean by light grade solids density is 1.86, bulk density is 0.6. In the dense grade solids density is 1.91 and then bulk density is 1.0 gram per cc.

So, now you can see the density is slightly increased and then this is done because of the hydration. Because this sodium carbonate we are soon going to see in subsequent slides that this is primarily used for the glass industry. And then in the glass industry you need the you know dense or heavier grade sodium carbonate, ok.

So, how it gets usually in the plant you get these light grade product then it would be usually hydrated to increase its grade or increase its density, ok. Density is also two different densities you may be knowing that there are maybe different densities like you know apparent density, bulk density etcetera.

So, solids density, bulk density or two densities are given here. Another grade is nothing, but washing soda which is nothing but sodium carbonate 10H 2 O that is hydrated sodium carbonate is nothing but washing soda.

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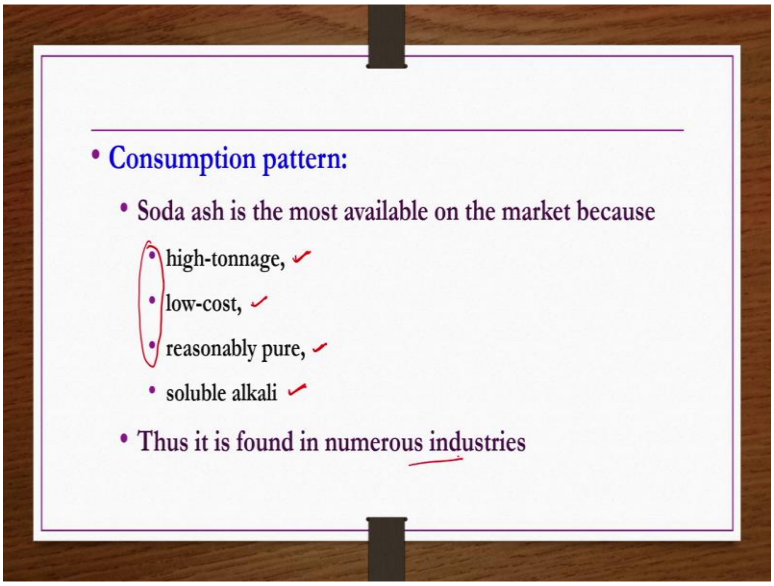

- Consumption pattern:
  - Soda ash is the most available on the market because
    - high-tonnage,
    - low-cost,
    - reasonably pure,
    - soluble alkali
  - Thus it is found in numerous industries

Consumption pattern soda ash is the most available on the market because it produced in high tonnages. High tonnage large volumes large quantities it is produced and then it produce at low cost that is also good. Reasonably pure, that is also very good, then soluble alkali soluble also.

But the thing is that so much of you know positives are there you know high tonnage and low cost reasonably pure sodium carbonate you are producing, but if it is not having marketing there is no point of producing such chemicals, ok. So, these are the one of the reason that is these are produced in high tonnage and low cost. So, that is the reason their cost is also low anyway that is good anyway. Thus, it is found in numerous industries as well.

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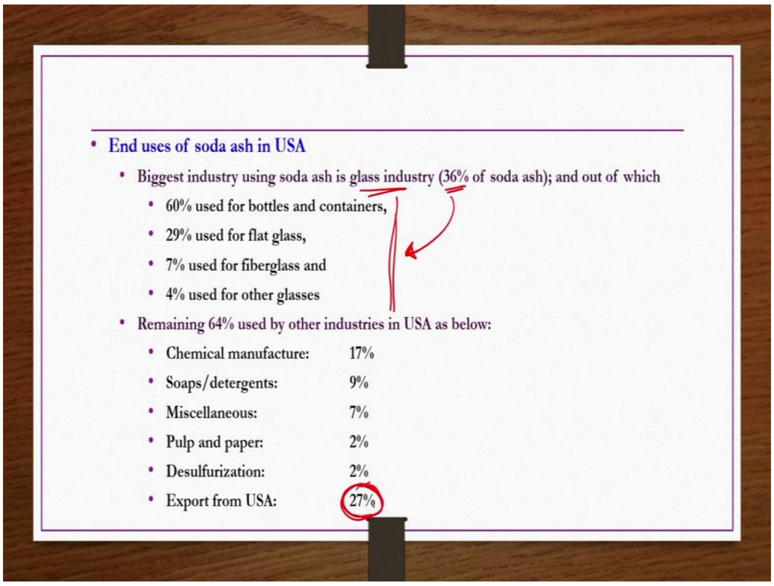

- End uses of soda ash in USA
  - Biggest industry using soda ash is glass industry (36% of soda ash); and out of which
    - 60% used for bottles and containers,
    - 29% used for flat glass,
    - 7% used for fiberglass and
    - 4% used for other glasses
  - Remaining 64% used by other industries in USA as below:
    - Chemical manufacture: 17%
    - Soaps/detergents: 9%
    - Miscellaneous: 7%
    - Pulp and paper: 2%
    - Desulfurization: 2%
    - Export from USA: 27%

End uses of soda ash we see it in USA and then India. In USA, majority of it used for the glass industry that is out of the soda ash that is produced in USA 36 percent is used for a you know glass industry and then remaining 64 percent is used for other purpose. 36 percent that is more than one third of soda ash produced in USA is consumed by the glass industry.

Out of this 36 percent if you see the breakup 60 percent used for the bottles and containers, 29 percent used for flat glasses, 7 percent used for the fiber glasses and then 4 percent used for other kind of glasses. So, out of this 36 percent you know if you do the breakage of consumption for different types of glasses. So, then you can have these kind of percentages.

Out of remaining 64 percent soda ash produced in USA, it is used for the chemical manufacture 17 percent, soaps and detergents 9 percent, miscellaneous 7 percent, pulp and paper 2 percent, desulphurization 2 percent, ok. And then export from USA to other countries is 27 percent, ok.

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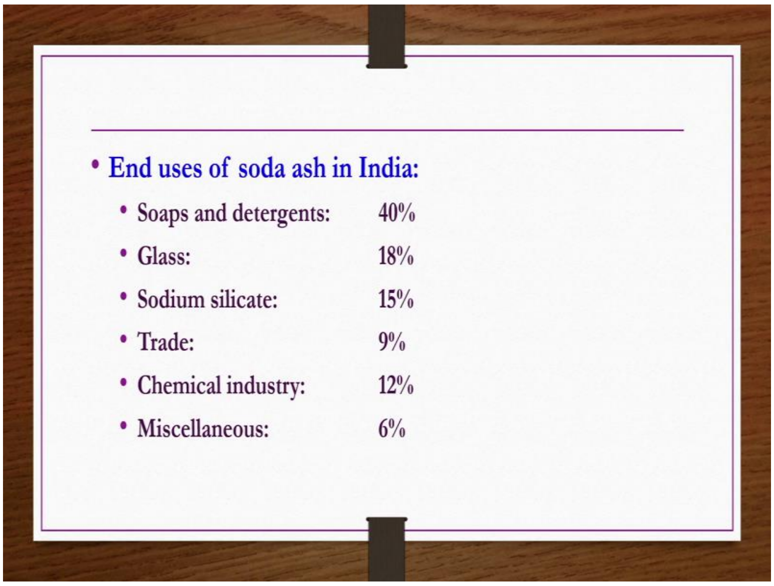

- End uses of soda ash in India:

Soaps and detergents:	40%
Glass:	18%
Sodium silicate:	15%
Trade:	9%
Chemical industry:	12%
Miscellaneous:	6%

End uses of soda ash in India: in India mostly, it is used for the soaps and detergents then followed by the glass and glass industries. Soaps and detergents 40 percent, glass industry 18 percent, sodium silicate 15 percent for other trade purpose 9 percent, chemical industry 12 percent, miscellaneous 6 percent.

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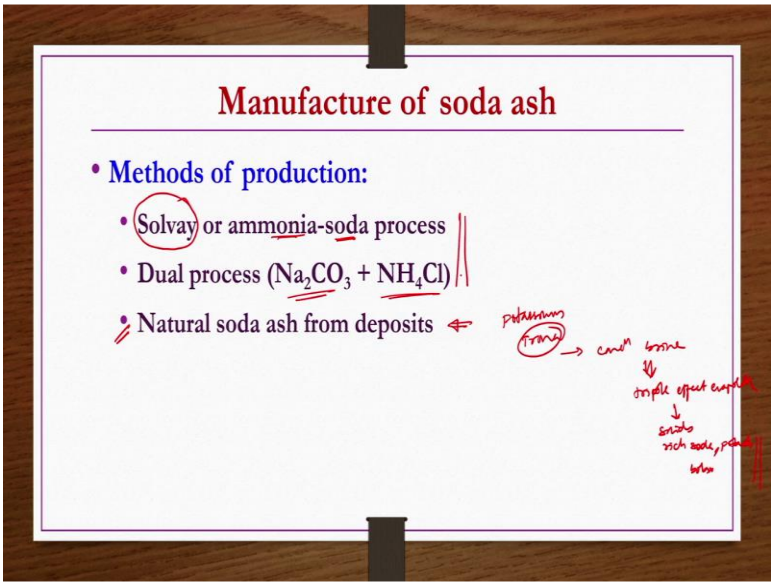

Manufacture of soda ash

- Methods of production:
  - Solvay or ammonia-soda process
  - Dual process ($Na_2CO_3 + NH_4Cl$)
  - Natural soda ash from deposits

potassium

Trona → concn brine

⇓

triple effect evap.

↓

solids

rich soda, potash

borax

Now, we see manufacture of soda ash, what are the processes are available. The classification we see methods of production, Solvay or ammonia soda process, ok. By name here ammonia soda you can see here ammonia is involved and then soda is being produced. So, that is the reason it is also known as the ammonia soda process.

Solvay is an Italian scientist who developed this one in 1860 or something like that, ok. Because of you know as a honor as a respect to him this process is also known as a Solvay process. Another one is the dual process where not only sodium carbonate, but also crystals of ammonium chloride are produced.

And then natural soda ash from deposits, this actually we have seen in the last week where we were discussing about potassium industries in which we discussed about trona process. Here in this industry what we have seen? Concentrating of the brines we have done and then after concentrating what you do, triple effective evaporators are used, right.

So, here one of the product is that solids you know solids is the rich in soda, potash etcetera. So, and then borax etcetera. So, what we have done? We have done subsequent purification of these products in three different stages and then differently because we are getting and recirculating all that we have seen. So, indirectly production of natural soda from deposits we have already seen. So, in this lecture we are going to discuss about these two processes.

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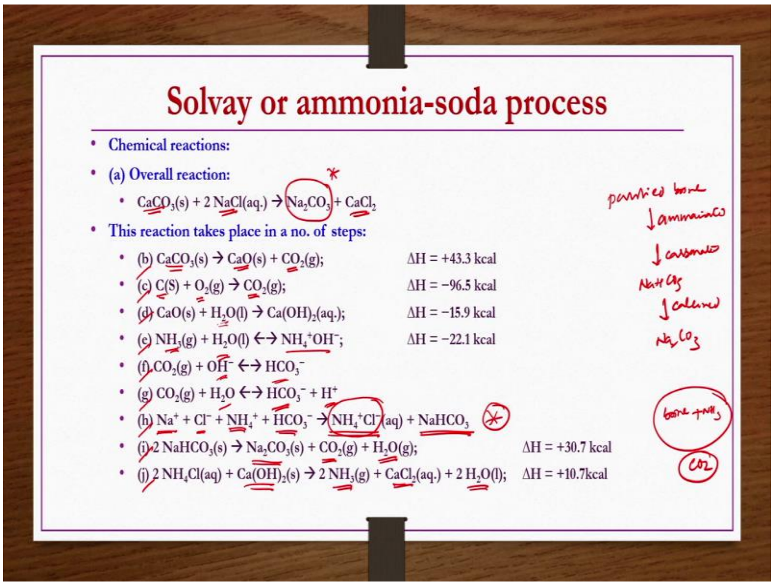

Solvay or ammonia-soda process

- Chemical reactions:
- (a) Overall reaction:
  - $CaCO_3(s) + 2\,NaCl(aq.) \rightarrow \boxed{Na_2CO_3} + CaCl_2$ *
- This reaction takes place in a no. of steps:
  - (b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$; $\Delta H = +43.3$ kcal
  - (c) $C(S) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -96.5$ kcal
  - (d) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq.)$; $\Delta H = -15.9$ kcal
  - (e) $NH_3(g) + H_2O(l) \leftrightarrow NH_4^+OH^-$; $\Delta H = -22.1$ kcal
  - (f) $CO_2(g) + OH^- \leftrightarrow HCO_3^-$
  - (g) $CO_2(g) + H_2O \leftrightarrow HCO_3^- + H^+$
  - (h) $Na^+ + Cl^- + NH_4^+ + HCO_3^- \rightarrow \boxed{NH_4^+Cl^-}(aq) + NaHCO_3$ ⊛
  - (i) $2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$; $\Delta H = +30.7$ kcal
  - (j) $2\,NH_4Cl(aq) + Ca(OH)_2(s) \rightarrow 2\,NH_3(g) + CaCl_2(aq.) + 2\,H_2O(l)$; $\Delta H = +10.7$kcal

purified brine
↓ ammoniated
↓ carbonated
$NaHCO_3$
↓ calcined
Na_2CO_3

brine + NH_3

CO_2

Solvay or ammonia soda process: chemical reactions of this process would be discussed first. Overall reaction, calcium carbonate reacts with the sodium chloride to give product, sodium carbonate and then ways to take dispose of that is calcium chloride is also produced.

But this is the overall reaction. In order to get this one there are so many reactions are occurring in between before getting this final product. So, those reactions we will see in a sequential manner. This reaction takes place in a number of steps. First reaction is calcium carbonate decomposing into the calcium oxide and carbon dioxide gas.

Then another one is that coke or carbon reacts with oxygen to give carbon dioxide. Because in this process what we have this process is that purified brine whatever is there that would be ammoniated then followed by that carbonated to get sodium bicarbonate and then that will be calcined to get sodium carbonate. This is the process.

So, carbon dioxide is required. So, then this reaction has to take place. And then calcium oxide reacts with water to give calcium hydroxide. Ammonia gas reacts with water to give ammonium hydroxide it is a reversible reaction and then carbon dioxide reacts with the hydroxyl group to give bicarbonate ion.

Then carbon dioxide reacts with water to give another bicarbonate ion by releasing a proton. Then sodium chloride or sodium ion and chloride ion of sodium chloride reacts with the ammonium ion and then bicarbonate ions to give ammonium chloride and then sodium bicarbonate. So, this is the; this is the important reaction where sodium bicarbonate is forming. So, this sodium bicarbonate would be calcined to get sodium carbonate, ok.

So, this sodium bicarbonate decomposes to sodium carbonate by releasing carbon dioxide and then water vapor. And then whatever this ammonium chloride is formed that reacts with the calcium hydroxide to give the ammonia for the recycling because ammoniation has to be done by the ammonia and then it also produces calcium chloride wastage that has to be disposed of along with that one there would be water formation also.

Now, these reactions should be occurring in a sequence as it is written that is the reason these numberings are given. So, these numberings are going to be very essential while discussing the process. Why? Because let us say ammoniation is there. Whatever the ammonia is there that should be completely absorbed by the brine then only you have to release CO 2.

Otherwise, you know ammonium chloride formation will take place and then that is if it is prepared and then start forming crystallizations or precipitation of ammonium chloride is taking place. So, then sodium carbonate will not crystallize. Such kind of conditions are there that is the reason these reactions sequence is very important and then we are going to see them in the flow chart as well.

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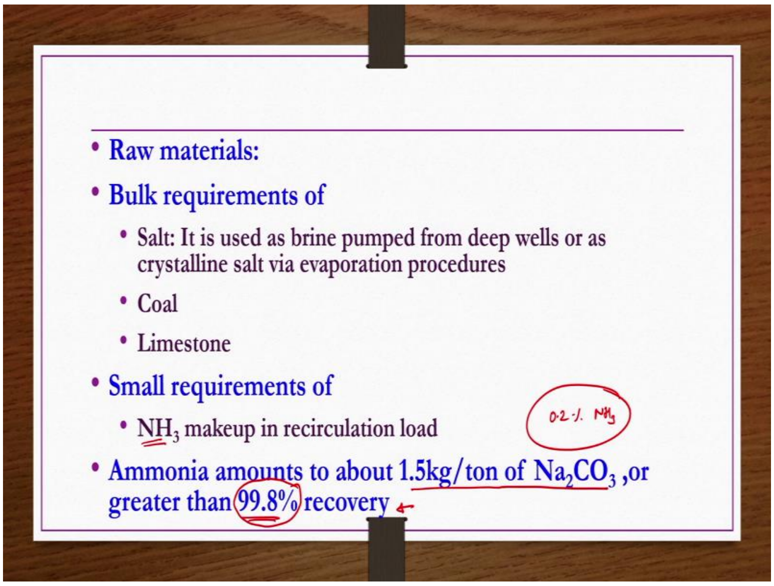

- Raw materials:
- Bulk requirements of
  - Salt: It is used as brine pumped from deep wells or as crystalline salt via evaporation procedures
  - Coal
  - Limestone
- Small requirements of
  - NH_3 makeup in recirculation load
- Ammonia amounts to about 1.5kg/ton of Na_2CO_3 ,or greater than 99.8% recovery

0.2 % NH_3

Coming to the raw materials obviously, bulk requirements of salt it is used as brine pumped from deep wells or as crystalline salt via evaporation procedures. Then coal is required because you need CO 2, then limestone is required because you have to decompose the ammonium chloride to get the ammonia and then calcium chloride. So, for that purpose this limestone is required and then small requirements of ammonia makeup in re-circulation load is also there.

Ammoniation step is there, but its consumption is very low. How much only 0.2 percent of ammonia whatever you are supplying as per the requirements of the calculation that much only being consumed rest everything is being keep on recirculations. Ammonia amounts to about 1.5 kg ton of sodium carbonate or greater than 99.8 percent recovery or that means, whatever the ammonia you are supplying to the process out of which 99.8 percent has to be recovered.

Only 0.2 percent is being consumed for the absorption of ammonia in you know brine solution before going to the carbonation step, ok.

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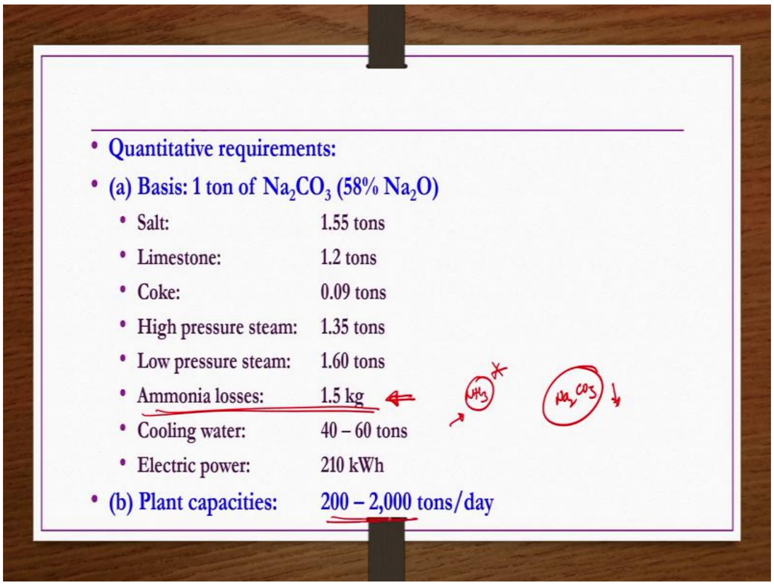

- Quantitative requirements:
- (a) Basis: 1 ton of Na_2CO_3 (58% Na_2O)

Salt:	1.55 tons
Limestone:	1.2 tons
Coke:	0.09 tons
High pressure steam:	1.35 tons
Low pressure steam:	1.60 tons
Ammonia losses:	1.5 kg
Cooling water:	40 – 60 tons
Electric power:	210 kWh

- (b) Plant capacities: 200 – 2,000 tons/day

NH_3

Na_2CO_3

Quantitative requirements basis 1 ton of sodium carbonate that is 58 percent Na 2 O, salt 1.55 tons, limestone 1.2 tons, coke 0.09 tons, high pressure steam 1.35 tons, low pressure steam 1.6 tons, ammonia losses 1.5 kgs, cooling water 40 to 60 tons, electric power 210 kilo watt hour. Ammonia losses also it has to be carefully designed and then utilized because you are using ammonia which is expensive to produce a low cost chemical like you know sodium carbonate.

It is more expensive it is less expensive; it is in fact it is cheaper in order to produce a cheaper chemical if you are using expensive chemical. So, you have to be very careful while using that expensive chemical. You have to make sure that there should not be you know considerable losses you cannot avoid some losses that is a different thing, but that loss should not be so high that it is making the process economically unfeasible. Plant capacities usually 200 to 2000 tons per day.

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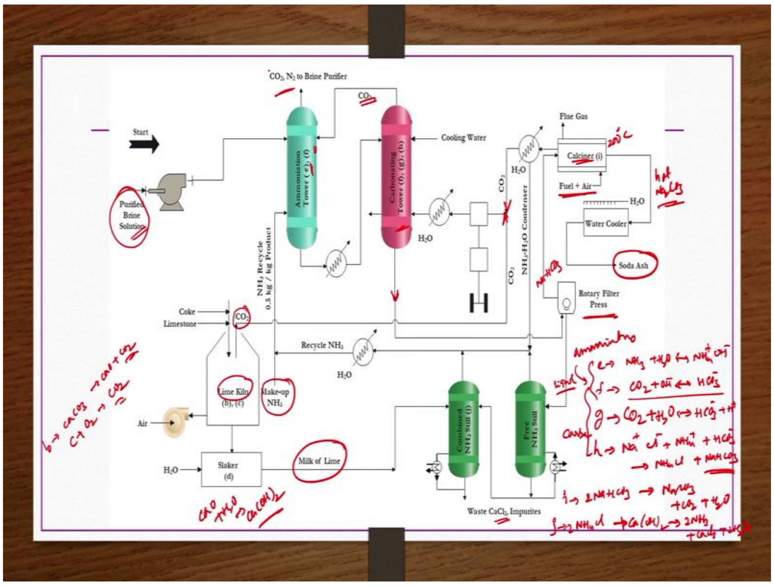

Now, this is the flow sheet that we have having here. So, purified brine solution whatever is there that is pumped to a ammoniation tower where reactions e and then f are taking place, right. So, where this reaction is e is nothing but ammonia reacting with water to get ammonium hydroxide. Actually, they are produced in you know such a way that they can be easily decomposed and then it is a reversible reaction.

And then f reaction is nothing but carbon dioxide is reacting with the hydroxyl ion to give bicarbonate ion, ok. This is also reversible reaction, right. Here to this ammoniation tower you are supplying ammonia from the bottom ok, and from the top CO 2 you are supplying. This CO 2 has to be supplied after ammonia is being absorbed by the brine and then sent to the carbonation tower, ok.

Once the saturation of this ammonia absorption in the brine has come because it is in a continuous flow. So, that continuously saturation of ammonia absorption in brine has to be maintained and then once that saturation has reached then only you have to supply the CO 2.

So, ammoniated as well as the partially carbonated brine whatever is there that is taken to the carbonating tower right, in which reactions f, g, h are taking place f is this reaction we have already seen, g reaction is nothing but CO 2 reacting with water and then reversibly giving carbonate and by releasing proton. And then h reaction is nothing but

Na plus and then Cl minus reacting with this ammonium ion of here actually these are in ionic conditions.

We are writing in such way and then it reacts also with a bi bicarbonate ion to give ammonium chloride and sodium bicarbonate. So, this is the product that is forming here. So, these three reactions are taking place in carbonation tower and then these two reactions are taking place in ammoniation tower or ammoniating tower.

Actually, we have shown only one tower for each of them there may be multiple towers as per the requirements ok, 3, 4, 5 or. So, they are possible, ok. So, now the product whatever is there from the bottom of this carbonation tower is taken to a rotary filter press where the pressing has pressing of the slurry has been done.

And then whatever the liquor is there that is taken to the pre ammonia steel and then whatever the solids are there they are nothing but the sodium bicarbonate solids. There will be calcined in a calciner at 200 degree centigrade where reaction i is taking place that is nothing but 2 moles of sodium bicarbonate forming 1 mole of sodium carbonate and then releasing CO 2 and then water vapour, ok.

For this calcination purpose fuel gases may be used in general. So, hot sodium carbonate whatever you are getting after the calcination that is water cooled and then taken to the packaging, ok. So, now here for ammoniation tower you need ammonia so that ammonia there is a makeup ammonia anyway there initially because recycling is not possible at t is equal to zero time of the process starting.

So, whatever the liquor that is taken here that is taken to the free ammonia steel. And then here whatever the chlorides are there in the liquor they will be removed as a calcium chloride impurities and then almost like pure ammonia is taken to the combined ammonia steel where the reaction j is occurring that is reaction j is nothing but this is reaction i reaction.

j is nothing but decomposition of ammonium chloride that is 2 moles of ammonium chlorides reacting with calcium hydroxide to give 2 moles of ammonia and then calcium chloride plus two moles of water. So, this ammonia is again you know after you know treating with this steam it is recycled and then sent to the ammoniation tower.

Similarly, here you need CO 2 for this process. So, in a lime kiln where this reaction b is nothing but calcium carbonate is decomposing into the calcium oxide plus CO 2 or this coke is getting combust to give carbon dioxide. So, this CO 2 gases whatever are forming here in this reactor they are you know processed through you know steam chambers and then sent to the carbonating tower through this lime, ok.

Now, here in this process calcination when you are doing calcination of sodium bicarbonate when you are doing you are not only getting Na 2 CO 3 but also you are getting water vapor and then CO 2, that CO 2 after removing the water is also being sent to the carbonating tower, ok, fine. So, this is the process that is occurring in the solid process.

Now, here in the in this process or whatever these slakers etcetera are there that is calcium oxide formation they will be reacting with water here in this reaction in this reactor to form calcium hydroxide or milk of lime because that is required for this decomposition of ammonium chloride to produce ammonia, ok. This is the process briefly explained in the flow chart.

Here in this process additional thing is that in the ammoniation tower CO 2 and then N 2 would also be forming they will be sent back to the brine purification section because for the brine purification you may need this CO 2.

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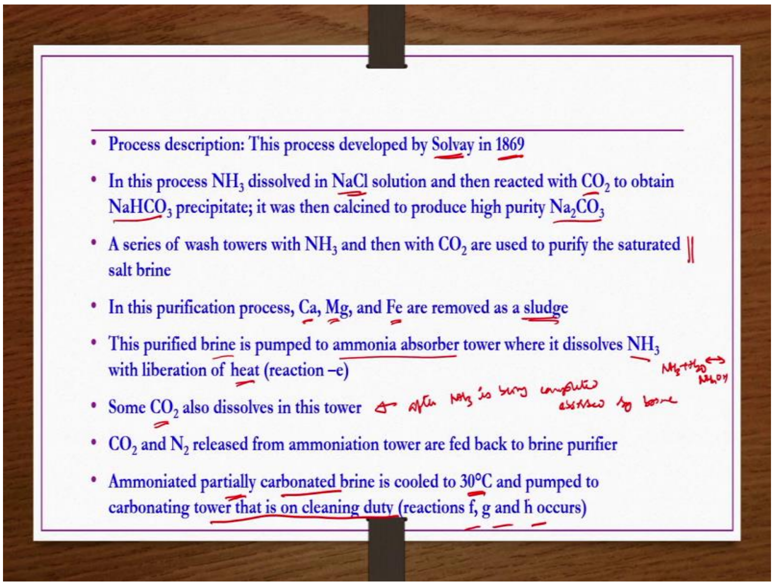

- Process description: This process developed by Solvay in 1869
- In this process NH_3 dissolved in NaCl solution and then reacted with CO_2 to obtain $NaHCO_3$ precipitate; it was then calcined to produce high purity Na_2CO_3
- A series of wash towers with NH_3 and then with CO_2 are used to purify the saturated salt brine
- In this purification process, Ca, Mg, and Fe are removed as a sludge
- This purified brine is pumped to ammonia absorber tower where it dissolves NH_3 with liberation of heat (reaction –e)

$NH_3 + H_2O \leftrightarrow NH_4OH$

- Some CO_2 also dissolves in this tower ← after NH_3 is being completely absorbed by brine
- CO_2 and N_2 released from ammoniation tower are fed back to brine purifier
- Ammoniated partially carbonated brine is cooled to 30°C and pumped to carbonating tower that is on cleaning duty (reactions f, g and h occurs)

Now, the same process we are going to discuss as a description part. This process developed by Solvay in 1869. So, because of him this process is also known as the Solvay process which is also has nothing but ammonia soda process. In this process ammonia dissolved in sodium chloride solution and then reacted with CO 2 to obtain sodium bicarbonate precipitate it was then calcined to produce high purity sodium carbonate.

A series of wash towers with ammonia and then CO 2 are used to purify the saturated brine. So, in the flow sheet we have seen only one, but there may be multiple. In this purification process calcium, magnesium, iron are removed as sludge. This purified brine is pumped to ammonia absorber tower where it dissolves ammonia with liberation of heat. So, here is this reaction p is taking place where ammonia is reacting with the water reversibly to give ammonium hydroxide, right.

Now, this is exothermic reaction it liberates the heat. Some CO 2 also dissolves in this process because in the continuous process CO 2 is also being supplied, but the CO 2 is supplied after ammonia is being completely absorbed by NaCl brine, ok. CO 2, N 2 release from the ammoniation tower are fed back to the brine purifier.

Ammoniated, but partially carbonated brine is cooled to 30 degrees centigrade and pumped to carbonating tower that is on cleaning duty where reaction f, g, h are occurring. f Reaction f and g are nothing but the formation of bicarbonate ions and then h is nothing but the formation of sodium bicarbonate, ok.

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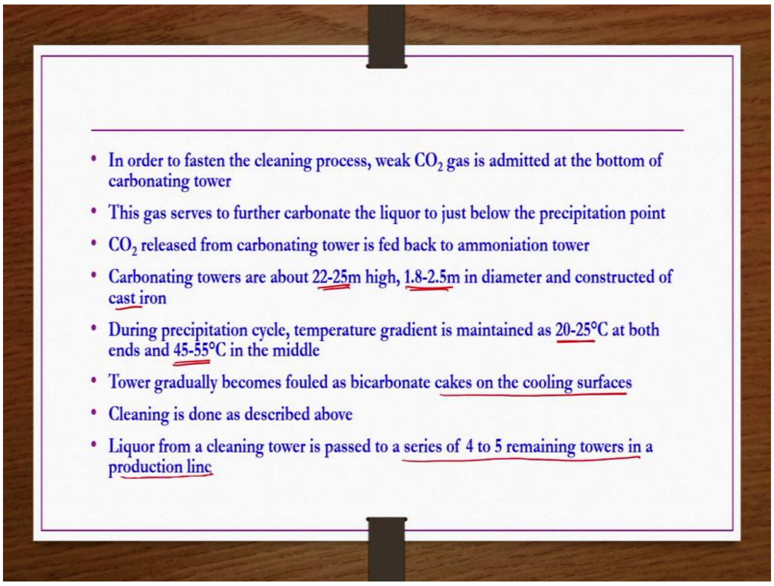

- In order to fasten the cleaning process, weak CO_2 gas is admitted at the bottom of carbonating tower
- This gas serves to further carbonate the liquor to just below the precipitation point
- CO_2 released from carbonating tower is fed back to ammoniation tower
- Carbonating towers are about 22-25m high, 1.8-2.5m in diameter and constructed of cast iron
- During precipitation cycle, temperature gradient is maintained as 20-25°C at both ends and 45-55°C in the middle
- Tower gradually becomes fouled as bicarbonate cakes on the cooling surfaces
- Cleaning is done as described above
- Liquor from a cleaning tower is passed to a series of 4 to 5 remaining towers in a production line

In order to fasten the cleaning process weak CO 2 gas is admitted at the bottom of carbonating tower. This gas serves to further carbonate the liquor to just below the precipitation point. CO 2 released from carbonating tower is fed back to ammoniation tower. Carbonating towers are about 22 to 25 meters high and then 1.8 to 2.5 meters in diameter and they are constructed of cast iron.

During precipitation cycle temperature gradient is maintained 20 to 25 degrees centigrade at both ends and 45 to 55 degrees centigrades in the middle. It is these conditions are maintained so that you know precipitation of ammonium chloride should not take place only you know precipitation of a sodium carbonate should take place.

Tower gradually becomes fouled as bicarbonate cake formation takes place on the cooling surface. Cleaning is done as described above. Liquor from a cleaning tower is passed to a series of 4 to 5 remaining towers in a production line.

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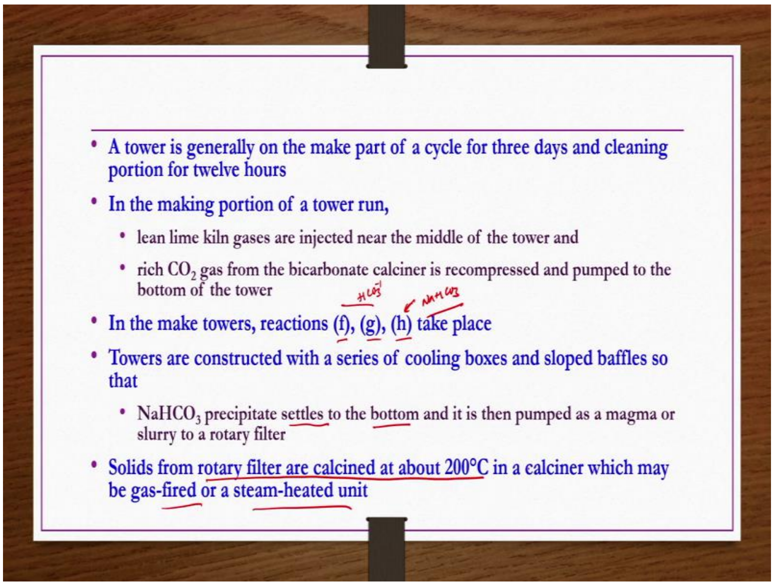

- A tower is generally on the make part of a cycle for three days and cleaning portion for twelve hours
- In the making portion of a tower run,
    - lean lime kiln gases are injected near the middle of the tower and
    - rich CO_2 gas from the bicarbonate calciner is recompressed and pumped to the bottom of the tower

HCO_3^{-1} $NaHCO_3$

- In the make towers, reactions (f), (g), (h) take place
- Towers are constructed with a series of cooling boxes and sloped baffles so that
    - $NaHCO_3$ precipitate settles to the bottom and it is then pumped as a magma or slurry to a rotary filter
- Solids from rotary filter are calcined at about 200°C in a calciner which may be gas-fired or a steam-heated unit

A tower is generally on the make part of cycle for three days and cleaning portion for twelve hours because that sodium carbonate is continuously forming as a cake on the walls of the towers. So, that has to be scrapped continuously. Whatever continuously you are scrapping or whatever effectively you are scrapping that sodium bicarbonate precipitation from the walls of the tower, there is still a requirement of cleaning.

So, three days production process is there or make process is there and then twelve hours would be there you know for the cleaning purpose after completion of three days. In the making portion of a tower run, lean lime kiln gases are injected near the middle of the tower and rich CO 2 gases from the bicarbonate calciner is recompressed and pumped to the bottom of the carbonating tower again as we have seen in the flowchart.

In the make towers reactions f, g, h taking place that is formation of bicarbonate ions and then formation of a sodium bicarbonate as a product is the h reaction. Towers are constructed with a series of cooling boxes and sloped baffles so that sodium bicarbonate precipitate settles to the bottom and it is then pumped as magma or slurry to a rotary filter. Solids from the rotary filter are calcined at about 200 degrees centigrade in a calciner which may be gas-fired or a steam-heated unit.

Fuel gases you can use or steam also you can use for this calcination of sodium bicarbonate so that to get the sodium carbonate.

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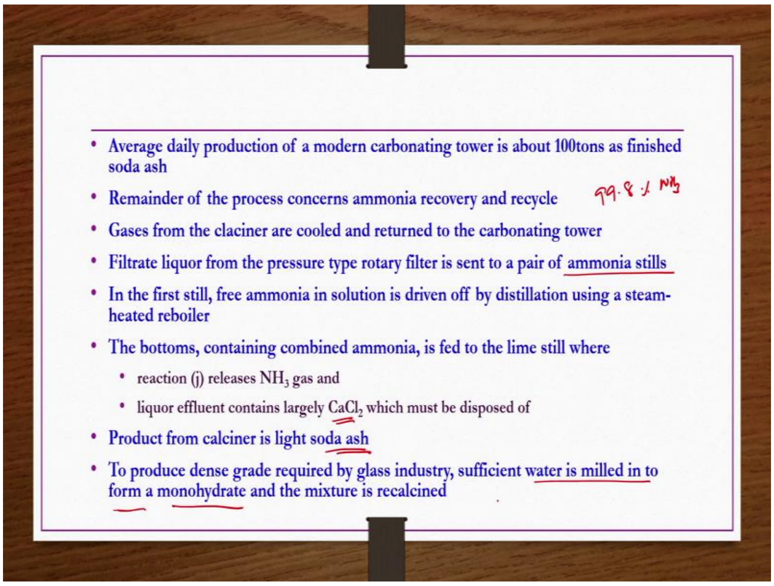

- Average daily production of a modern carbonating tower is about 100tons as finished soda ash
- Remainder of the process concerns ammonia recovery and recycle 99.8 % NH_3
- Gases from the claciner are cooled and returned to the carbonating tower
- Filtrate liquor from the pressure type rotary filter is sent to a pair of ammonia stills
- In the first still, free ammonia in solution is driven off by distillation using a steam-heated reboiler
- The bottoms, containing combined ammonia, is fed to the lime still where
  - reaction (j) releases NH_3 gas and
  - liquor effluent contains largely $CaCl_2$ which must be disposed of
- Product from calciner is light soda ash
- To produce dense grade required by glass industry, sufficient water is milled in to form a monohydrate and the mixture is recalcined

Average daily production of a modern carbonating tower is about 100 tons as finished soda ash remainder of the process concerns about the ammonia recovery and the recycle. Remember this process is not going to be effective if you are not effectively recovering the ammonia. What do you mean by effectively recovering ammonia?

More than 99.8 percent of ammonia has to be recovered only 0.2 percent should be consumed or including the consumption and then losses it should not be more than 0.2 percent, ok. Why? Because ammonia is more expensive than the product sodium bicarbonate. Gases from the calciner are cooled and returned to the carbonating tower.

Filtrate liquor from the pressure type rotary filter is sent to pair of ammonia stills so that decompose this ammonium chloride by using calcium hydroxide. So, that products ammonia and calcium chloride waste would be forming, ammonia would be recovered and then calcium chloride waste would be dispersed off.

In the first still free ammonia in solution is driven off by distillation using a steam heated reboiler. The bottoms containing combined ammonia is fed to the lime still where reaction j releases ammonia gases, ok. Reaction j is nothing but ammonium chloride reacting with the calcium hydroxide to give ammonia and then calcium chloride.

Liquor effluent contains largely calcium chloride which must be disposed of. Product from calciner is light soda ash ok, light grade soda ash. So, then what you have to do? If you wanted to have a dense or heavy grade soda ash which is required for the glass industry you have to you know sufficient water is milled into the into form a mono hydrate and then mixture is recalcined to get the you know heavy grade soda ash. We are going to see how these are going to be used in the glass industries etcetera when we talk about the glass industry.

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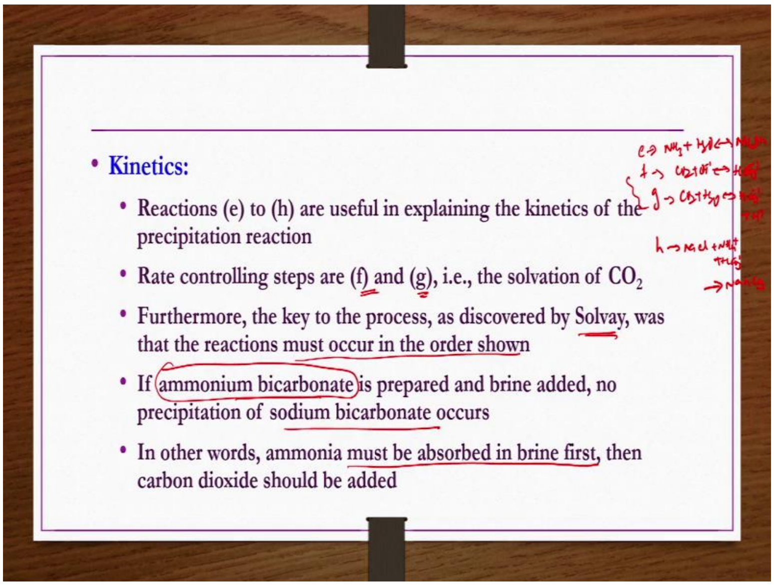

- **Kinetics:**
  - Reactions (e) to (h) are useful in explaining the kinetics of the precipitation reaction
  - Rate controlling steps are (f) and (g), i.e., the solvation of CO_2
  - Furthermore, the key to the process, as discovered by Solvay, was that the reactions must occur in the order shown
  - If ammonium bicarbonate is prepared and brine added, no precipitation of sodium bicarbonate occurs
  - In other words, ammonia must be absorbed in brine first, then carbon dioxide should be added

$e \rightarrow NH_3 + H_2O \leftrightarrow NH_4OH$

$f \rightarrow CO_2 + OH^- \leftrightarrow HCO_3^-$

$g \rightarrow CO_2 + H_2O \leftrightarrow HCO_3^- + H^+$

$h \rightarrow NaCl + NH_4^+ + HCO_3^- \rightarrow NaHCO_3$

Kinetics: reactions e to h are useful in explaining the kinetics of the precipitation reaction because e to h reactions e to e reaction we have already seen ammonia reacting with water to give ammonium hydroxide reversibly.

And then f reactor is CO 2 is reacting with the OH minus to give bicarbonate ion and then g is also CO 2 reacting with a water to give bicarbonate ion by releasing a proton and then h is nothing but this Na plus and then Cl minus reacting with the NH 4 plus and then HCO 3 minus to give sodium bicarbonate these are the reactions.

So, these are very essential reactions you know. So, you know they are very important to explain the kinetics of the precipitation reaction. Rate controlling steps are f and g these two are the rate controlling steps because of the solvation of CO 2, because here carbonation is the one of the important step. Because ammoniation followed by carbonation is leading to the formation of the sodium carbonate.

But the ammoniation how much it is being absorbed is very small only small quantity of ammonia is being absorbed by the brine before it is being carbonated, ok. So, that is the reason this f and g are the very important and rate controlling steps ok, also energy consumption should be high for these two steps that is the reason they are rate controlling steps.

Furthermore, the key to the process as discussed or discovered by the Solvay was the reactions must occur in the order shown as we have discussed. If ammonium bicarbonate is prepared and brine is added no precipitation of sodium bicarbonate occurs. So, you should avoid ammonium bicarbonate formation. How you can do?

You have to make sure the reactions to occur in the sequence as we have discussed then only ammonium bicarbonate will not occur otherwise there is a chance of ammonium bicarbonate formation which you do not want. In other words, ammonium must be observed in brine first then carbon dioxide should be added. So, that it will avoid formation of ammonium bicarbonate.

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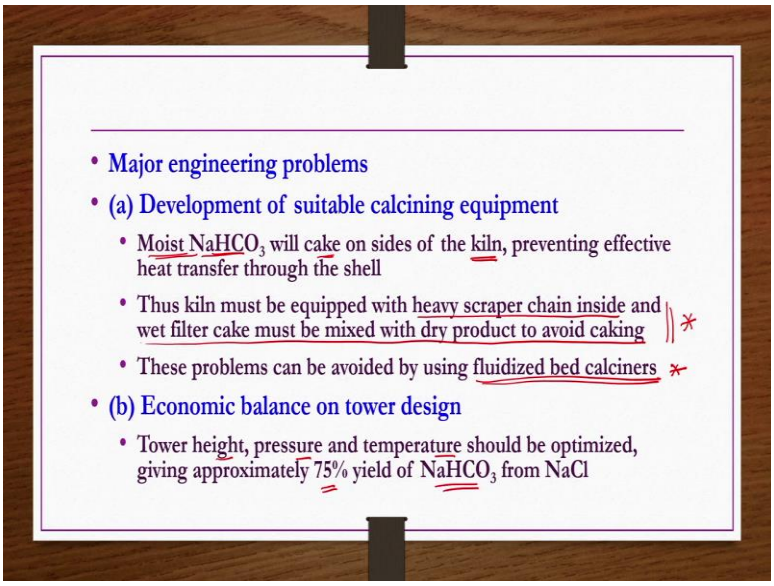

- Major engineering problems
- (a) Development of suitable calcining equipment
    - Moist $NaHCO_3$ will cake on sides of the kiln, preventing effective heat transfer through the shell
    - Thus kiln must be equipped with heavy scraper chain inside and wet filter cake must be mixed with dry product to avoid caking *
    - These problems can be avoided by using fluidized bed calciners *
- (b) Economic balance on tower design
    - Tower height, pressure and temperature should be optimized, giving approximately 75% yield of $NaHCO_3$ from NaCl

Now, we see major engineering problems: development of suitable calcining equipment. Sodium bicarbonate is in the wet condition actually that is being calcined to get the sodium carbonate. So, this calcining you will be doing in a kilm, right. So, that on the walls of the kilm this cake formation may be taking place.

So, if the cake formation of sodium carbonate is taking place on the walls of the kilm then effective heat transfer may not take place. So, that is one important issue. Thus kilm must be equipped with heavy scraper chain inside and wet filter cake must be mixed with a dry product to avoid caking. So, this is the solution, ok.

These problems can also be avoided by using fluidized bed calciners some of the plants recent or modern plants are having these things, but the conventional older plants are not having this facility. Economic balance on tower design is very much essential because in this process the towers series of ammoniation towers and then carbonation towers are there.

So, how effectively you are designing economical balance is very much essential, ok. So, tower height, pressure and temperature should be optimized. So, that giving approximately 75 percent yield of sodium bicarbonate from sodium chloride by the process that we have discussed.

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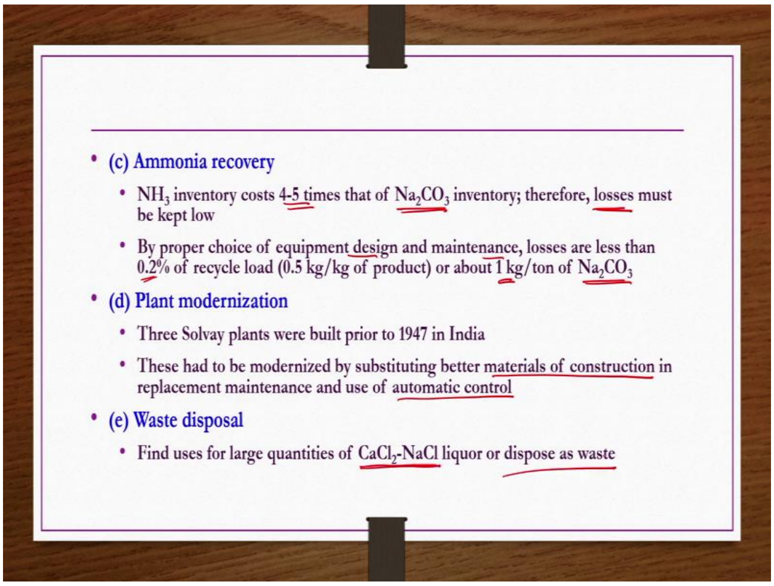

- (c) Ammonia recovery
  - NH_3 inventory costs 4-5 times that of Na_2CO_3 inventory; therefore, losses must be kept low
  - By proper choice of equipment design and maintenance, losses are less than 0.2% of recycle load (0.5 kg/kg of product) or about 1 kg/ton of Na_2CO_3
- (d) Plant modernization
  - Three Solvay plants were built prior to 1947 in India
  - These had to be modernized by substituting better materials of construction in replacement maintenance and use of automatic control
- (e) Waste disposal
  - Find uses for large quantities of $CaCl_2$-NaCl liquor or dispose as waste

Then ammonia recovery as mentioned ammonia inventory is expensive it costs 4 to 5 times than that of sodium carbonate inventory. So obviously, you must avoid losses or you must kept as low as possible otherwise the product is not going to give you enough money because ammonia is more expensive than this sodium carbonate.

However, by proper choice of equipment design and then maintenance losses are less than 0.2 percent of recycled load or about 1 kg per ton of sodium carbonate. When you produce one ton of sodium carbonate only 1 kg of ammonia is being used such a way you have to design, ok.

Plant modernization: most of the plants in India were very old. So, then these had to be modernized by better materials of construction in replacement maintenance and then use of automatic control as well. Waste disposal, find uses for large quantities of calcium chloride, sodium chloride, liquor or dispose as waste.

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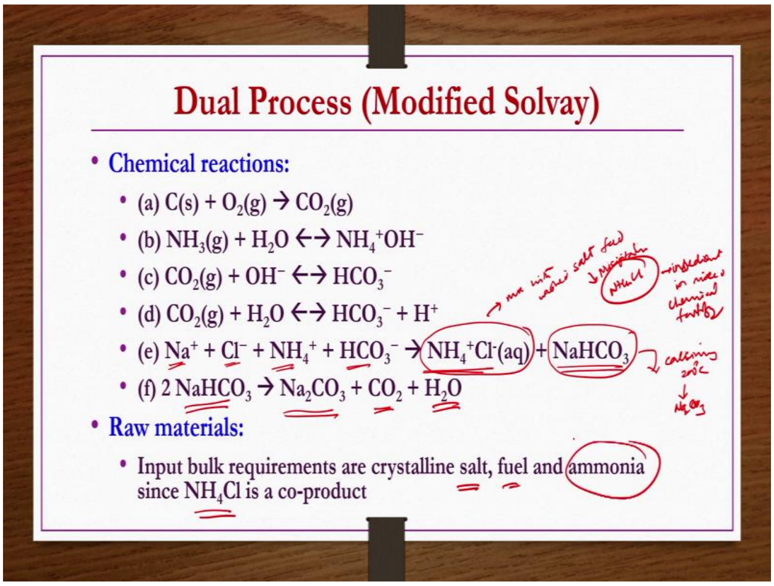

Dual Process (Modified Solvay)

- Chemical reactions:
  - (a) $C(s) + O_2(g) \rightarrow CO_2(g)$
  - (b) $NH_3(g) + H_2O \leftrightarrow NH_4^+OH^-$
  - (c) $CO_2(g) + OH^- \leftrightarrow HCO_3^-$
  - (d) $CO_2(g) + H_2O \leftrightarrow HCO_3^- + H^+$
  - (e) $\underline{Na^+} + \underline{Cl^-} + \underline{NH_4^+} + \underline{HCO_3^-} \rightarrow \boxed{\underline{NH_4^+Cl^-(aq)}} + \boxed{\underline{NaHCO_3}}$
  - (f) $2\,\underline{NaHCO_3} \rightarrow \underline{Na_2CO_3} + \underline{CO_2} + \underline{H_2O}$
- Raw materials:
  - Input bulk requirements are crystalline salt, fuel and ammonia since NH_4Cl is a co-product

→ mix with another salt feed
↓ precipitate
NH_4Cl
→ ingredient in mixed chemical fertilizer
calcining
200°C
↓
Na_2CO_3

Now, we discuss about the modified solvay process or dual process, ok. So, in this modified process what we do? Rather reacting ammonium chloride with calcium hydroxide to give ammonia and then recycling, what we are doing? We do mixing of this ammonium chloride with a salt and then we try to do the crystallization by refrigerating it at 0 degree centigrade continuously so that you can also have ammonium chloride as co-product in the production of sodium carbonate, ok.

So, but however here economics one has to see because when you are decomposing ammonium chloride using the calcium hydroxide to get ammonia. So, ammonia is recovered and reused recycled, but now if you are not doing that one over then what happens? You are getting ammonium chloride. The what is the value for the ammonium chloride that also you have to see.

So, the better thing about this ammonium chloride is that it is a ingredient to produce mixed chemicals, right. Mixed chemical fertilizers we have seen. So, in the production of those mixed chemical fertilizers this ammonium chloride sometimes is used as a ingredient. So, one has to see market for the for this ammonium chloride. Accordingly, you have to select whether should you go for the Solvay process or modified Solvay process.

Chemical reactions: carbon react with oxygen to give carbon dioxide or coke reacts with the oxygen to give carbon dioxide and then ammonia reacts with water to give the ammonium hydroxide and then carbon dioxide reacts with hydroxyl group to give bicarbonate ion. And then carbon dioxide reacts with water to give bicarbonate ion by releasing a proton.

Whereas, this ammonium hydroxide out of which ammonia ion reacts with the sodium ion and then chloride ion of sodium chloride along with the bicarbonate ion to produce ammonium chloride as well as the sodium bicarbonate. So, now here in the this part doing the calcination calcining of this sodium bicarbonate at 200 degree centigrades to get Na 2 CO 3 that is same there is no change.

Now, modification is in this point. Here what you do? You mix with a washed salt feed to improve its precipitation. When you do this one its precipitation will take place. And then you can get ammonium chloride crystals you know solid product that you can use as ingredient in mixed chemical fertilizers productions or it may be having other applications as well, ok.

So, this sodium bicarbonate further decomposes to sodium carbonate by releasing the carbon dioxide and then water vapors. Raw materials, input bulk materials are crystalline salt, fuel and then ammonia since ammonium chloride is a co-products. So, its consumption would be more.

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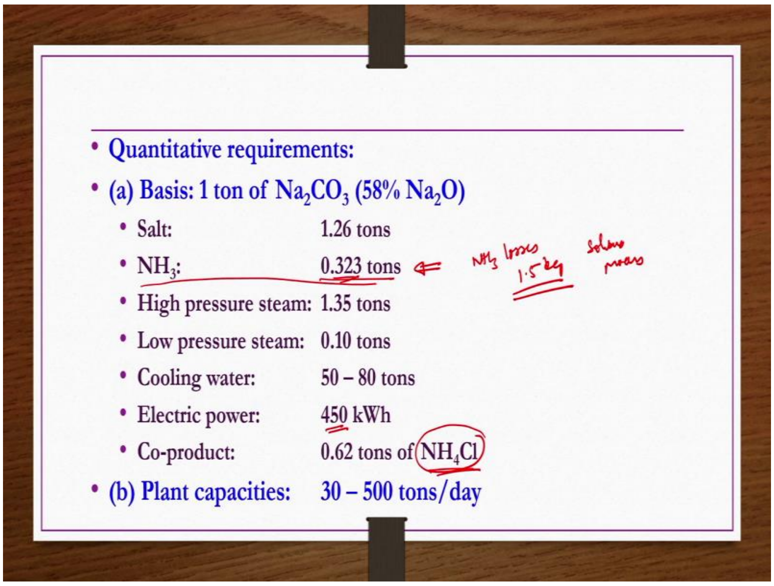

- **Quantitative requirements:**
- **(a) Basis: 1 ton of Na_2CO_3 (58% Na_2O)**
  - Salt: 1.26 tons
  - NH_3: 0.323 tons ⇐ NH_3 losses 1.5 kg Solvay process
  - High pressure steam: 1.35 tons
  - Low pressure steam: 0.10 tons
  - Cooling water: 50 – 80 tons
  - Electric power: 450 kWh
  - Co-product: 0.62 tons of NH_4Cl
- **(b) Plant capacities: 30 – 500 tons/day**

That how much it is we are going to see here in quantitative requirements. In quantitative requirements we are going to see these quantities. Basis one ton of sodium carbonate that is 58 percent Na 2 O if you wanted to produce salt you need 1.26 tons, ammonia see 0.32 3 tons and then high pressure steam 1.35 tons, low pressure steam 0.10 tons, cooling tower 50 to 80 tons and then electric power; power is also improved 450 kilo watt hour, co-product 0.62 tons of ammonium chloride and then plant capacity usually 30 to 500 tons per day.

So, in the previous process what we have seen original Solvay process ammonia losses are there, how much? Only 1.5 kgs only 1.5 kgs of ammonia losses is there in the original Solvay process. Now, here ammonium chloride you are getting as a product. So, its consumption proper consumption is there and then how much it is per 1 ton of sodium carbonate production you need 0.3 tons of ammonia.

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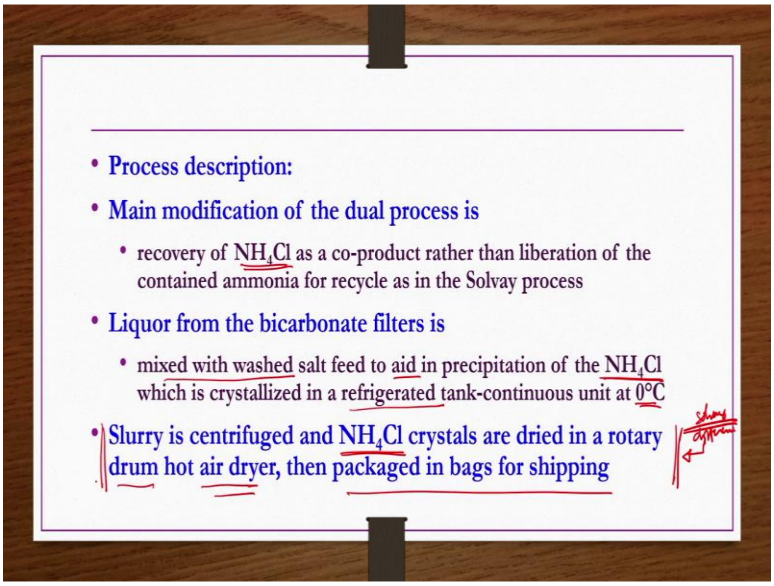

- Process description:
- Main modification of the dual process is
  - recovery of NH_4Cl as a co-product rather than liberation of the contained ammonia for recycle as in the Solvay process
- Liquor from the bicarbonate filters is
  - mixed with washed salt feed to aid in precipitation of the NH_4Cl which is crystallized in a refrigerated tank-continuous unit at 0°C
- Slurry is centrifuged and NH_4Cl crystals are dried in a rotary drum hot air dryer, then packaged in bags for shipping

Slurry
different

Process description main modification of the dual process is recovery of ammonium chloride as a co-product rather than liberation of the contained ammonia for recycle as in the Solvay process, liquor from the bicarbonate filter whatever is there that we in the initial Solvay process react with the calcium hydroxide to get ammonia, but here we are not doing that one.

That would be mixed with washed salt feed to aid in precipitation of ammonium chloride which is crystallized in a refrigerating tank-continuously at 0 degree centigrades. Slurry is centrifuged and then ammonium chloride crystals are dried in a rotary drum hot air dryer, then packaged in bags for shipping.

So, now you can see only this is the different in the flow sheet right, other than that one rest of the Solvay process is same. So, that is the reason separate flow sheet has not been shown compared to the Solvay process only this step is different and then you know only that is one step only.

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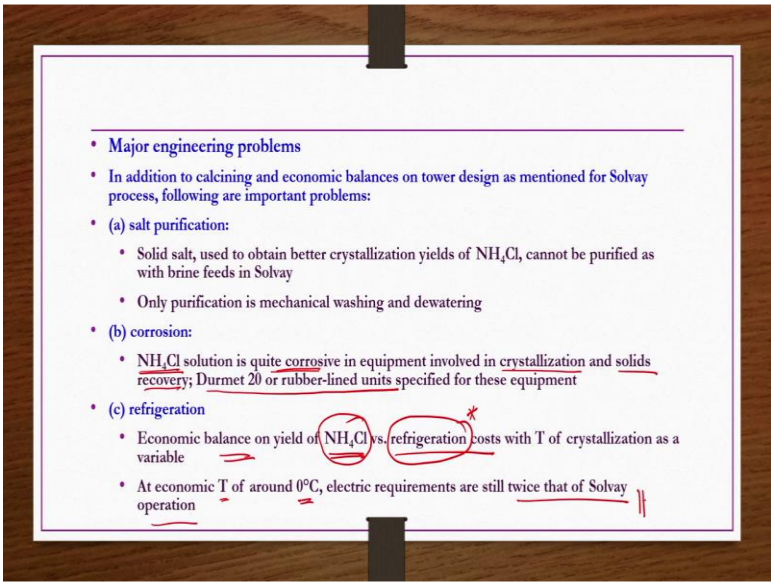

- Major engineering problems
- In addition to calcining and economic balances on tower design as mentioned for Solvay process, following are important problems:
- (a) salt purification:
  - Solid salt, used to obtain better crystallization yields of NH_4Cl, cannot be purified as with brine feeds in Solvay
  - Only purification is mechanical washing and dewatering
- (b) corrosion:
  - NH_4Cl solution is quite corrosive in equipment involved in crystallization and solids recovery; Durmet 20 or rubber-lined units specified for these equipment
- (c) refrigeration
  - Economic balance on yield of NH_4Cl vs. refrigeration costs with T of crystallization as a variable
  - At economic T of around 0°C, electric requirements are still twice that of Solvay operation

Major engineering problems: in addition to calcining and economic balances on tower design as mentioned as mentioned in Solvay process that we have just discussed following are important problems. One is the salt purification. Solid salt used to obtain better crystallization yields of ammonium chloride and cannot be purified as with a brine as with sodium chloride brine feeds in Solvay process only purification is mechanical washing and dewatering is possible.

Corrosion is another important problem. Ammonium chloride solution especially is quite corrosive in equipment involved like in crystallization and then solids recovery section. So, the solids recovery section and crystallization unit should be constructed by using Durmet 20 or rubber lined units, ok.

Refrigeration next problem is the refrigeration; we have seen that you know continuously refrigeration has to be done at 0 degree centigrades. So, economic balance on yield of ammonium chloride versus refrigeration cost. In order to get ammonium chloride, you have to use the refrigeration, but if the refrigeration cost is very high compared to the your product cost then it is not going to be useful. So, then economic balance is very much important.

So, at economic temperature of around 0 degree centigrade electric requirement are still twice that of Solvay operation, ok.

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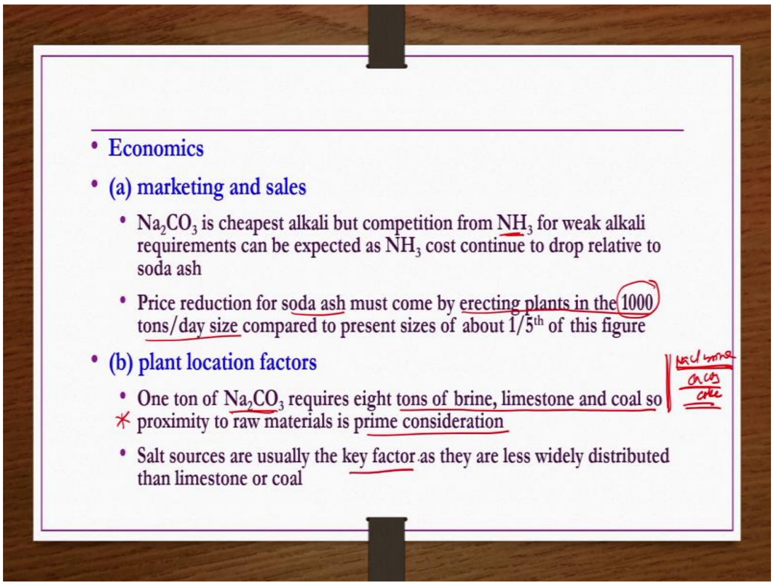

- Economics
- (a) marketing and sales
  - Na_2CO_3 is cheapest alkali but competition from NH_3 for weak alkali requirements can be expected as NH_3 cost continue to drop relative to soda ash
  - Price reduction for soda ash must come by erecting plants in the 1000 tons/day size compared to present sizes of about 1/5th of this figure
- (b) plant location factors
  - One ton of Na_2CO_3 requires eight tons of brine, limestone and coal so proximity to raw materials is prime consideration
  - Salt sources are usually the key factor as they are less widely distributed than limestone or coal

NaCl brine

$CaCO_3$

coke

Economics, marketing and sales are important. Sodium carbonate is the cheapest alkali, but competition from ammonia for weak alkali requirements can be expected because ammonia prices or cost is continuously dropping relative to the sodium carbonate cost. Price reduction for soda ash must come by erecting plants in the 1000 tons per day size. The present size are approximately 200, 300 tons per day etcetera like that only in India.

So, the size has to be you know increased to at least you know 1000 tons per day. So, that you know price reduction in you know soda ash production you know it can be reduced. Plant location factors: because here NaCl, brine is there and then other calcium carbonate and then coke etcetera requirements are there, right.

So, transportation should not be a kind of additional load. So, the plant has to be located where you can get these materials you know at a reachable distance or you know less distance. One ton of sodium carbonate requires 8 times of brine, limestone and coal. So, proximity to raw materials is prime consideration, is very much essential. Because transportation costs are very high nowadays. Salt sources are usually the key factor as they are less widely distributed than limestone or coal.

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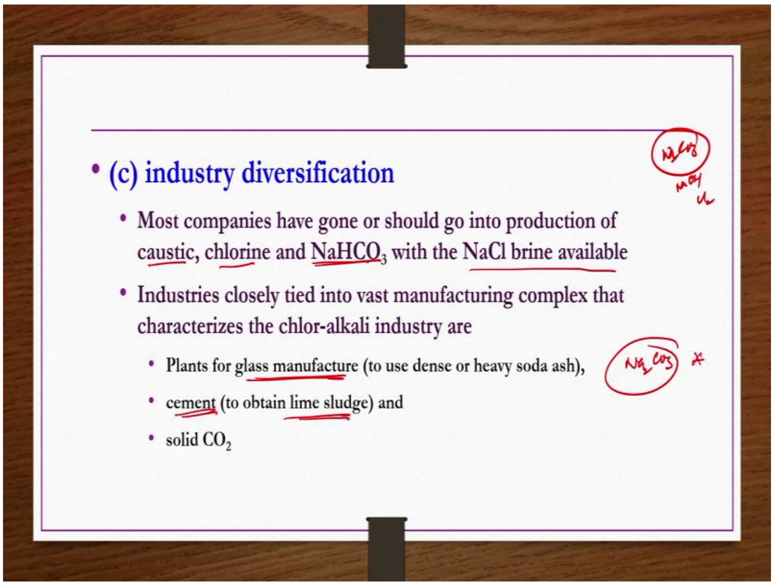

- (c) industry diversification
  - Most companies have gone or should go into production of caustic, chlorine and $NaHCO_3$ with the NaCl brine available
  - Industries closely tied into vast manufacturing complex that characterizes the chlor-alkali industry are
    - Plants for glass manufacture (to use dense or heavy soda ash),
    - cement (to obtain lime sludge) and
    - solid CO_2

Na_2CO_3

$NaOH$

Cl_2

Na_2CO_3 *

Then industry diversification: as we have seen these Na 2 CO 3 it is not very expensive chemical and then it is produced in high tonnages. So, in addition to this one NaOH and then chlorine etcetera also produce. So, then industry diversification is required, ok. So, most companies have gone or should go into the production of caustic, chlorine and then sodium bicarbonate with NaCl brine available not only just a sodium carbonate then only you can make a you know better profit from this plant.

Industries closely tied into vast manufacturing complex that characterizes the chlor-alkali industry. They are plants for the glass manufacture. We have seen that around 18 20 percent of Na 2 CO 3 soda ash is used for the glass industry. So, we are going to discuss glass industry very soon. So, then where we then we can discuss how it is being used there. It is also used in the cement industry to obtain lime sludge and then solid CO 2 production.

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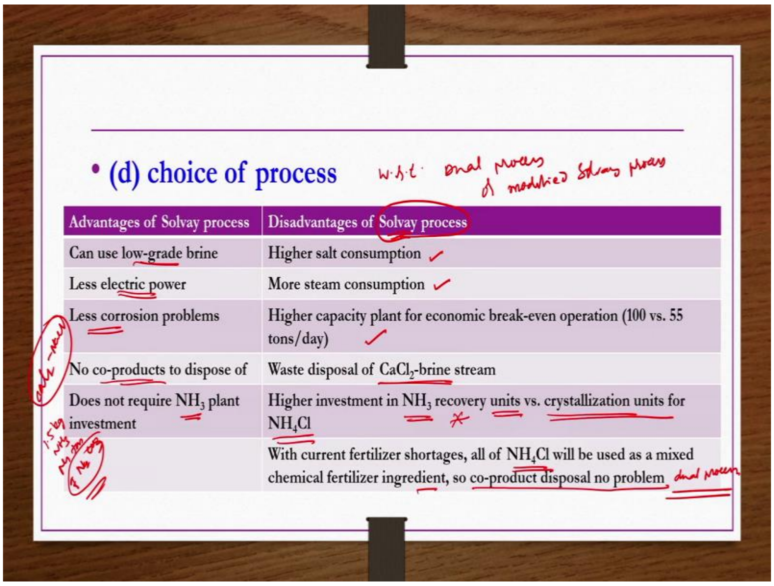

- (d) choice of process

w.r.t. Dual process
or modified Solvay process

Advantages of Solvay process	Disadvantages of Solvay process
Can use low-grade brine	Higher salt consumption ✓
Less electric power	More steam consumption ✓
Less corrosion problems	Higher capacity plant for economic break-even operation (100 vs. 55 tons/day) ✓
No co-products to dispose of	Waste disposal of $CaCl_2$-brine stream
Does not require NH_3 plant investment	Higher investment in NH_3 recovery units vs. crystallization units for NH_4Cl
	With current fertilizer shortages, all of NH_4Cl will be used as a mixed chemical fertilizer ingredient, so co-product disposal no problem dual process

1.5 kg NH_3 per ton of Na_2CO_3

Choice of processes: Now, you have a three processes actually. Here we discussed only two processes because the natural process of soda ash getting from the brines, we have already discussed in the potassium industries. Now, here we discussed Solvay and modified Solvay process or Solvay process versus dual process. So, choice is very much essential, right.

So, now here advantages, disadvantages we are written, they are with respect to the dual process. Advantages of the Solvay process with respect to the or compared to the dual process or modified dual processes are given here. Compared to the dual process or modified dual process.

Solvay process having the advantage of low grade brine can be used, less electric power required, less corrosion problem because ammonium chloride, you know crystallization and then solids recovery is not there because ammonium chloride is much more corrosive than any of the other chemicals used here in this process.

And then no co-products to dispose of whatever the sodium chloride and then NaCl liquor is there that is only you need to think of to dispose, ok. Does not required ammonia plant investment; you need only 1.5 kgs of ammonia per ton of Na 2 CO 3 production.

But compared to the modified Solvay process, a dual process what are the disadvantages of the Solvay this process? Higher salt consumption, more steam consumption, higher capacity plant for economic break even operations, waste disposal of calcium chloride and sodium chloride streams, then higher investment in ammonia recovery units because in the Solvay process if you are not recovering ammonia effectively up to 99.8 percent or more.

So, then that is not going to be economically you know profitable. So, that is big concern in the Solvay process, ok. Whereas in the modified Solvay process you have the crystallization units for ammonium chloride. So, here again you have the investment. So, the investment cost you have to do. Recovery of ammonia is less investment or less capital requirement or crystallization of ammonium chloride is requiring less capital that you have to see as per your resources and then make a decision.

With current fertilizer shortage all of ammonium chloride will be used as a mixed chemical fertilizer ingredient. So, co-product disposal problem is not there in the dual process or modified Solvay process. So, these are these advantage disadvantages are with respect to dual process or modified Solvay process.

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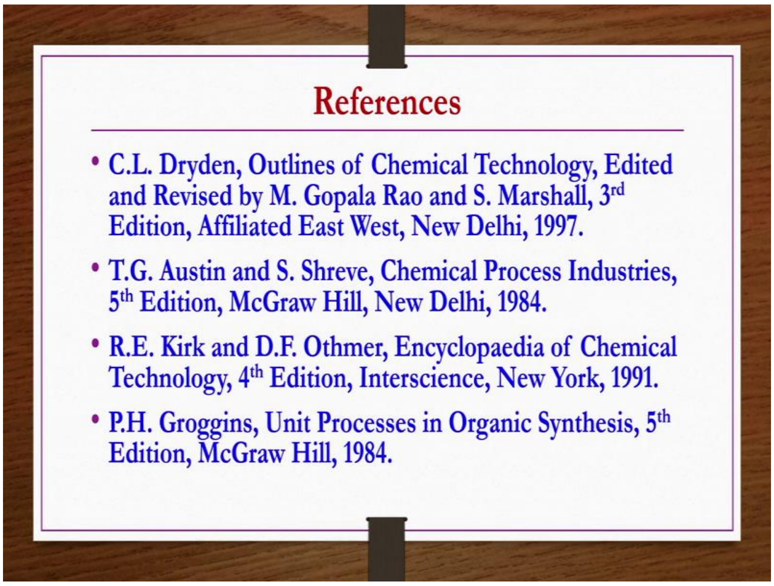

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References for this lecture are provided here.

Thank you.