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Lecture - 21 Potassium Industries

Welcome to the MOOCs course Inorganic Chemical Technology, the title of today's lecture is Potassium Industries. We have started discussing about fertilizer industries, especially after having the knowledge of how much importance is chemical engineer is having in fertilizer industry.

We started with discussing about fertilizers, their sources, different types of fertilizers, etcetera, those things we started and then we started with nitrogen fertilizers or nitrogen fertilizer industries, then we discussed about the phosphorus fertilizer industries also. Now, we start about the Potassium Industries.

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So, what are the sources of potassium? As we have already seen at the beginning of the fertilizer's lecture, we do not have a indigenous sources for the potassium and phosphorus. So, obviously, we have to find out from where we can get, etcetera.

So, the ancient sources of potassium was ashes of wood and then plant wastes' burnings. Whatever the agricultural field waste after collecting the crops, etcetera, then whatever the agricultural wastage is there, that is usually burnt and then after burnt whatever the ashes are there, they are one source of a potassium in general. And, then also forestry waste also. sometimes you know when you when the forestry waste then also you may get ashes and in that ash may have adequate amount of potassium in general. That is what happens, ok.

Now, how it is available in the nature? It is available in the nature in two different form forms as insoluble form, as highly soluble form, right. For example, as insoluble, potash bearing silicates, it is available in nature as well as highly soluble salts like potassium chloride in underground deposits and in sea water also available this potassium.

So, the minerals of potassium if you would like to see, primary potash minerals include sylvinite, which is a mixture of sylvite. Sylvite is nothing but potassium chloride and halite, which is nothing but sodium chloride in different proportions. In different proportions of KCl and NaCl is nothing, but the sylvinite, it is one of the primary potash minerals ok.

Carnalite, that is KCl, MgCl 2 6H 2 O; then kainite, that is KCl MgSO 4, 3H 2 O; langbeinite, that is K 2 SO 4, 2MgSO 4 and then nitrate, that is potassium nitrate. In these different forms, these the potash minerals are available in general ok. We have already discussed in our previous class that India do not have any exploitable deposits of potassium. There may be some sources of potassium, but they are not sufficient enough that you can do the exploitation of a you know those deposits to get potassium.

So, then what are the possible sources of potassium in India? So, as we have already seen, bitterns left over salt recovery. In the salt recovery or salt making process, whatever the remaining highly concentrated solution is remaining, highly viscous concentrated solution is remaining, that is nothing, but the bittern, that is known as the bittern. It is a very good source of not only potassium, but also several other minerals ok, that is one source.

And, then as we are saying that you know ashes of woods maybe a source of potassium as per the ancient sources. So, then that means, that they must be available in some plants, etcetera, like that also. So, whatever the fermentation, after fermentation, molasses, distillery slops, etcetera are there so, they must also be having some amount of potassium. So, what we can say? These are two possible sources for potassium, ok.

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Potassium, if you see some more details about the potassium, then raw materials, first is the sylvinite that is coming in sedimentary deposits, sedimentary deposits of sylvinite is one resource. Langbeinite is another raw material and then deposits of solid sodium salts permeated by a saturated complex brine.

So, actually these different raw materials, actually there are many sources. You know we are listing as per the requirements in general, as per the product that is we are getting from these raw materials, you know we have just put them as a different category, that is it. Let us say sylvinite is a mixture of sylvite and halite as we know, and it is processed to get high-grade potassium chloride. If you wanted to get high-grade potassium chloride, it is better to mine and treat the sylvinite to get high-grade potassium chloride.

Let us say, if you wanted to get potassium sulfate, then langbeinite is a good source. It is processed to make potassium sulfate. Similarly, deposits of solid sodium salts may be processed to separate high-grade potassium chloride and borax together with numerous other saline products also, ok. So, some of these things we are going to see anyway, what are the products.

If you take the statistics until 1980, whatever the potash that is available or potassium salts production was there. So, out of those potassium salt, KCl was occupying 79 percent and then remaining 9 percent is K 2 SO 4, ok.

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Now, we see worldwide major producers of potassium, right. Potassium, especially towards the fertilizer industries, what it is? How much K 2 O, how much dissolved or soluble K 2 O that is present in fertilizer that is taken as a kind of a reference for the potassium that is present in fertilizers. So, in terms of millions of metric tons of K 2 O produced, if you see, United States of Soviet Russia and Canada are almost you know close to each other, right.

Then East Germany -3.2 and West Germany -2.3; USA -2.2; France -1.8 are the leading countries producing these many millions of metric tons of K 2 O, right.

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Now, how do you get the metallic potassium? That is the question because the potassium that you are getting from the saline or brine solution, etcetera that they are mostly potash or other minerals, right. When you take the brine solution and then do the processing, you get the different types of potassium salts. In general, KCl, K 2 SO 4, etcetera these kind of things you can get and then those things we are going to see anyway.

But, if you wanted to have a metallic potassium K, so, then what are the methods that are available that we see. So, usually electrolysis of fused KCl method is followed to get the potassium, metallic potassium which is similar to sodium, but more reactive compared to the sodium, ok.

However, it is not followed this method is not followed commercially to produce metallic you know metallic potassium because whatever the K that is produced that attacks the electrodes and then remain dispersed in the fused salt. That is the reason this method, you know though it is one of the initial methods found to get the metallic potassium, it is not followed commercially because of this reason. Ok.

So, then how do you produce metallic potassium? Metallic potassium is prepared from potassium chloride by double decomposition with sodium. How? Sodium plus KCl reversibly reacts to give potassium plus sodium chloride. Ok. This is a reversible reaction. This is one of the important methods that people follow.

This potassium is used in the high temperature, heat transfer alloy. This this sodium potassium or NaK is a very good high temperature heat transfer alloy, right. So, in the production of this, usually this metallic sodium is used and then it is also used for the production of KO 2. This KO 2 is used in life support systems and then it is very reactive. So, then it is stored under unreactive gas such as nitrogen. Ok.

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Potassium chloride whatever the potassium chloride is produced out of which 90 percent is produced as fertilizer grade. Fertilizer grade having anything from 50 to 97 percent purity etcetera. So, some fertilizers required only 50 percent, 50 - 51 percent KCl is sufficient. So, but however, fertilizer grade is having KCl 97 purity. Ok.

So, whatever the KCl is produced, 90 percent of KCl is produced under fertilizer grade. But, however, if you wanted to produce other potassium derive other potassium derivative, then you have to go for a chemical grade potassium chloride that is 99.9 percent pure.

In fertilizer industries, this KCl is also known as the muriate of potash. Chemical grade or 99.9 percent KCl. 99.9 percent pure KCl is often used for the manufacturing of most other potassium salts. We will be seeing some of them in the next class as well.

So, what is potash? Potash is a general name given to a group of minerals and chemicals containing potassium, right. So, it is a general name. Potash is not only just KCl, but in

in general, though in fertilizer industries, it is called as muriate of potash. Potash is a common name, very common name given to a group of minerals and chemicals that are containing potassium, ok.

And, it is very important and basic nutrient requirement for the growth of plants. And then obviously, it is a very important ingredient in the fertilizer industries, ok. In general, most of the potash is produced as potassium chloride, however, because as we have seen, you know it is primarily produced for the fertilizers purpose. So, then it is produced in a you know KCl form.

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Now, we see manufactured by Trona process. Manufacturing by Trona process in the sense actually, whatever the saline brine solution is there, that is processed through several steps to get several products, right. So, whatever the saline solution or the brine solution that we take and then do the processing to get different products like potash, borax, soda, soda ash etcetera, these kind of components – that process is known as the Trona process.

How it is done? So, it is you know solution is taken from the lakes. For example, from Searles lake, which is in California, shipping of potash along with the other numerous other potassium derived products was begun in 1916. This lake is composed of four layers. The upper layer of crystalline salt is 20 to 30 meters deep. Second layer is about 4

to 5 meters of mud and then third layer is about 8 meter of salt and fourth layer is mud interspersed with minor salt seams.

So, brine, whatever you required for the processing to go to follow this Trona process to get different products, you know that has to be collected from this lakes and in general what they do? They take something between you know from the first and third layers, ok. So, in processing, brine is pumped from the interstices in the salt body from first and third layers.

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Approximate composition of ormes		
Expressed as	Upper deposit %	Lower deposit %
KCl 🖊	4.85	3
NaCl /	16.25	16.25
Na ₂ SO ₄	7.20	6.75
Na ₂ CO ₃	4.65	6.35
Na ₂ B ₄ O ₇	1.50	1.77
Na ₃ PO ₄	0.155	
NaBr /	0.109	
Miscellaneous 🦯	0.116	0.35
Total salts (approximately)	34.83	34.60
H ₂ O	65.17	65.40

So, now, we understand the brine is one of the important component or basic raw material from which we are producing all this soda, soda ash, borax etcetera, right. So, it is important to see what is the composition or approximate composition of brines in the lower and upper layers of the lake.

So, if you see upper deposit percentages and lower deposit percentages, it is expressed as composition of different chemicals like potassium chloride, sodium chloride, sodium sulfate, sodium carbonate, borax or borates of sodium, sodium phosphate, sodium bromide and then other miscellaneous. You can see there is no trend which is having higher component etcetera, it s a all kind of mixed trend.

So, when you see the summation of these salts, then you say approximately 35 percent whether it is lower deposits or upper deposit. Approximately 35 percent is consisting of

these salts and then remaining 65 percent, approximately 65 percent remaining is nothing, but the water H2O.

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So, now, we see the Trona procedure. What it is actually? In this Trona procedure, what we do? We get you know three major products. Rather three major products, we should say that a group of three major you know categories – one is the soda category, another one is the potash category, another one is the borax category. Ok. So, that procedure we are going to see in detail now.

This procedure gives more details of division of procedures leading to products such as potassium chloride, borax or hydrated borate of sodium which is having this composition. Soda ash or soda crystals or sodium carbonate which is Na 2 CO 3, right.

So, in this process, large tonnage of common salt is also produced, but this salt is not having enough market because of that one what we do in often it is washed back into the lake, ok. So, this procedure is found upon many years of intensive research where in exact conditions were worked out and then applied in the plant, ok. So, we are going to see flow sheet of this process anyway.

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Now, before going into the flow chart, we will have a outline of Trona procedure, right. So, here so, this is the outline. Now, what do you see? It is looks very difficult to understand here. So, what I will do, I will try to divide this one into two parts, right. So, this one part and then this is the other part. So, that is basically this entire outline whatever is there, it is very difficult to read here.

So, the upper part I am taking to the next slide and discussing and then lower part I will be taking to further next slide and then discussing it.



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Ok, so upper part is nothing but we start with the raw lake brine plus borax mother liquors also because in this process, what happens? You know actually, primarily whatever the brine is there that you concentrate and then in three different stages, you get three different products. One is the soda level, another one is the potash level and then the last level is the borax level, right.

After the borax production, crystallization whatever remaining mother liquor is there, that mother liquor is also fed back to the initial brine solution containing vessel right, ok. So, these two are taken and then warmed by condensing vapors in vacuum crystallizers and then followed by it is concentrated in triple effect evaporators by evaporating the water, ok.

So, then what happened? You get the two main streams, one is rich in potassium chloride and then borax or borates of sodium, another one is the remaining salts like this one burkeite, this is known as this is one of the mineral which is known as the burkeite and then this is halite and then this this is di lithium sodium phosphate which is impurity.

Of course, from here also we get product. So, but these both the streams are hot in conditions. So, what we do? First, we take this KCl and then borate of sodium thing and then what you do? You do vacuum crystallization at 38 degree centigrade. When you take this part and do the vacuum crystallization, then what happens? KCl will be centrifuged and then that can be dried and shipped.

So, whatever the mother liquor after you know KCl being centrifuged that remaining mother liquor whatever is there, that would be rich in borax. That would be rich in borax. Of course, there may be some KCl, minute KCl may also be there, never worry about that one.

So, this mother liquor that can be filtered again that can be filtered again to get the crude borax whereas, the filtrate is there that can be sent back to the mother liquor which is being cooled to 24 degree centigrades. So, this process can be continued until the filtrate is not having any borax, ok. So, this crude borax can be taken as it is for the product or it can be refined and then you know refined borax can be taken as a product. So, alright.

So, now, KCl is one product that you got. Refined borax is the second product. Now, the other side the other steam which is having the burkeite, halite and then impurities,

lithium impurities that is taken and separated by countercurrent washing. We using the steam hot steam, countercurrent washing is done, so that whatever the halite is there that can be taken as underflow, sodium chloride solution and washed away.

Overflow whatever is there that will be you know washed with lake brine again and then recovered brine is taken you know collected and sent back to the initial position. So, this overflow after filtering with brine whatever is there solution that you get that is having a dissolved burkeite solution that is burkeite dissolved in water that solution you get plus this whatever di-lithium sodium phosphate is there that will be floating on the surface of the liquid.

On the surface of burkeite solution as there these are you know floating. So, these floating impurities are taken and then impure these thing are hot leads to get products from here also. So, after removing or taking of the floating impurities you have only burkeite liquor solution that you cool it to 22 degree centigrades and do the filtration. One phase you get sodium sulfate hydrated sodium sulfate, another one is the liquor which you can heat and then treated with sodium chloride.



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So, here after this step what you get you know burkeite solution you say that can be taken back to the initial position and then filtrate whatever is there that is cool to 30 degree centigrade and filtered again. So, there again you get some NaCl that can be sent

back to the lakes. Further, if you cooled it to 5 degree centigrade and do the filtration you will get the sodium carbonate or hydrated sodium carbonate crystals you get, right.

So, these crystals you know you can do the calcination etcetera to get the sodium carbonate which is having 58 percent Na 2 O. So, this is the third product ok. Whatever the sodium sulfate hydrated sodium sulfate is there to that you can add NaCl to lower the transition to lower temperature of 17 degree centigrade and do the filtration. So, then you get the refined Na 2 SO 4 that you can dry and then send it to the products bagging and this is your fourth product.

Whatever the sodium chloride mother liquor is there that is sent to the lake again. Now, the impurities whatever di-lithium sodium phosphate impurities are there that you do the you know leaching with the hot water. So, then what you get? You get a burkeite liquor that you can take to the initial feeding recycling purpose and then you get impurities concentrated impurities which is having 20 percent lithium oxide you get that you can dry and then take it as a product.

This may be a one product or what you can do this product you do the acidification reaction using the sulfuric acid to get the phosphoric acid and lithium sulfate 6, 7. This lithium sulfate if you treat further with sodium carbonate you will get lithium carbonate after centrifugation and drying of this centrifuged product like this. So, this is eighth product.

So, now you can see so many products are there as per the requirement you know you can get the products. Actually, these products are grouped in three categories one is the soda category, another one is the potash category another one is the borax category. So, now next flow sheet whatever we are going to see that is having all these steps, right. So, we discussed the same details through flow sheet as well.

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However, in broadest outline if you wanted to present this Trona procedure then it involves concentration of potassium chloride and borax in hot brine and, then simultaneous separation of salt and burkeite which is a mineral that is having the composition Na 2 CO 3 to Na 2 SO 4.

And, then delayed crystallization of borax will lead to KCl that can be obtained by rapid cooling of concentrated brine in vacuum coolers and crystallizers. And, then after centrifugation potash mother liquor is a refrigerated and furnishes borax. All these steps we are going to see by a flowchart where we can discuss in detail.

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Now, this is the flowchart. Actually, this is having three sections first section is the concentration and then soda products. Second section is the potash recovery, third section is the borax recovery or third category this is. So, this we are going to see we take one by one. Ok.

So, whatever the hot brine is there that is fed to the lower bottom of a third effect evaporator of triple effect evaporators. So, 1, 2, 3 triple effect evaporators, three evaporators are there. So, this hot brine is fed through a by using a steam so that it can be under sufficiently hot condition when it goes into the evaporator because this evaporator is being provided with the steam.

So, now because of the hot steam what happens? You know the solution we get heated up and then volatile components would be taken to a hydro cyclone to recover if any particles are there in the volatile components and then fed back to the evaporator.

Whereas, the volatiles mostly water which is not having any you know sediments or solid particles etcetera they will be condensed and collected as solution. The same thing happening in all three of these evaporators, right. So, this is in triple effect evaporator basically we are concentrating the brine solution. So, whatever the underflow that you get from the each of these cones, each of these effects are taken to the corresponding cones 1, 2, 3.

The underflow of cone is taken to the second cone like that subsequently to the third cone it is been done, right. So, from the bottom or the third cone bottom what you get? You get the salts you get the salts which is having some solutions also. So, then what you do? You do the vacuum filtration so that to remove the you know liquor etcetera right.

So, and then solids whatever are there that you collect. These solids are nothing but they are rich in soda products. So, this solids you take to soda products plant, ok. Whereas, the after vacuum filtration, brine solution etcetera is there that is nothing but the mother liquor 2 which is taken to the hot brine container again. Whereas, the overflow of these three cones whatever is there that is taken to a clarifier, right. This overflow is rich in potash content.

So, this overflow of these cones are taken to a clarifier there you know further purification of are you know concentration of this overflow will take place, right and then that is taken to a concentrated storage here for the recovery of potash. Because this overflow of this clarifier whatever is there you know rich in potash products. So, that is taken to concentrated storage here and then this concentrated solution whatever is there.

So, that undergoes three stage vacuum centrifugation so that to concentrate it or remove the liquors etcetera, right. After the third vacuum crystallizer whatever the underflow is there that is taken to a settler where solids are you know crystals of potash are being separated out and dried and then sent to the bagging section. Whereas, the liquor which is coming as the overflow of the settler is nothing, but the mother liquor one which is rich in which is rich in borax.

So, this mother liquor is taken to mother liquor tank where mother liquor 1 and 3 both are there. This mother liquor now it is rich in borax, right. This is undergoing some kind of steps like refrigeration, crystallization followed by thickening etcetera and then when you do the filtration you get the filtrate whatever is there that is nothing but mother liquor 2.

So, further you take it to the you know after the filtration whatever the solids that you get they are nothing, but the crude borax and then further refining of this crude borax if you do you get the refined borax and then in the process of crude borax refining whatever the mother liquor is remaining that is mother liquor 3 that is taken to the this tank until this is not having any borax component. So, this is the overall Trona procedure in a flowchart manner ok. So, getting the soda products getting the potash products and then getting borax products, ok. Now, we see step by step their description as well.

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Concentration and soda-products separation. Raw brine is mixed with end liquors from borax crystallizing house and pumped into 3rd effect of triple effect evaporators where brine is hot-concentrated and salted out in three effects counter to the steam flow.

Suspended salts whatever are there they are nothing but NaCl and then burkeite mineral are removed from the liquors of each effect by continuously circulating the hot liquor through cone settlers which are also known as the salts separators or salt traps. Whatever the three cones we have seen here these are nothing but the salt separators or you know salt trap.

Underflow from 1st effect cone containing salt passes through an orifice into the 2nd effect cone, receiving a counter current wash with the clarified liquor from the 2nd effect cone. Combine salts of 1st, 2nd and 3rd cones receive a hot counter current wash with raw brine as they leave 3rd cone. Combined underflow is filtered, and then filtrate returned to the evaporators as we have seen in the flowchart.

Cake whatever is there that is having salt NaCl and then mineral Na 2 CO 3.2 Na 2 SO 4 which is nothing but burkeite is sent to the soda products to recover Na2CO3. Soda

products plant in that we recover Na 2 CO 3 from this cake. Final hot, concentrated liquor is withdrawn from overflow of 1st effect cone into an auxiliary settler called a clarifier ok.

Overflow from this clarifier is pumped to storage at the potash plant because this is this overflow is very rich in potash component, ok. So, underflow from clarifier is filtered and treated in the same manner as the previous underflows we have seen.

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So, whatever the overflow coming from the clarifier is nothing but you know mother liquor which is rich in potash component. So, that part we see now here. So, this concentrated storage undergo three stage vacuum centrifugation followed by settling, followed by drying of the crystals of potash etcetera. This already we have discussed, description we see.

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Hot concentrated liquor leaving the clarifiers is saturated with KCl and borax. KCl is obtained by cooling quickly to 38 degree centigrade and crystallizing in three-stage vacuum cooler crystallizers. Enough water is added to replace that evaporated so that NaCl remains in the solution.

Suspension of solid KCl in the mother liquor is passed to a cone settler, where the thickened sludge is obtained as underflow. KCl is dried in rotary dryers yielding 97 percent KCl that is fertilizer grade potash. This salt is conveyed to storage, to bagging plant or to a recrystallizing procedure as per the requirement.

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Third stage is separation of borax. So, whatever the overflow of this component is there actually rich in potash with some borax also. So, here that is taken here and then we have done this three-stage vacuum crystallization to get the potash here. So, the remaining liquor whatever is there that is now having only borax rich in borax. This is gone through this stage to get the crude borax or refined borax as per the requirement, ok.

So, now this part also we have seen, now description of the same we will see now.

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Overflow, combined with filtrate is pumped to borax plant for removal of borax. Potash mother liquor is cooled in vacuum crystallizers as shown in the flow chart. Water lost by evaporator is returned to boiling solution to prevent concentration of this solution with consequent crystallization of KCl with crude borax.

Borax crystallizes out a crude sodium tetraborate pentahydrate. This crude borax is filtered off and washed. Filtrate is returned to the start of evaporator cycle along with the brine solution. When necessary, crude borax is refined by recrystallization, otherwise this salt is centrifuged dried and packaged for the market. So, that is the Trona procedure. Now, the same Trona procedure we see in a different manner rather than flowsheet we see in a different pictorial manner.

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So, lake brine whatever is there that is having composition like this. There may be other things also water, NaCl, di-lithium, sodium phosphate, sodium carbonate, sodium sulfate, potassium chloride, sodium borate etcetera all these things are borax etcetera all these things are there. They are there in a mineral form, they may not be there in the pure form.

So, this lake brine what you do? You do the concentration of this one. How you do? By using triple effect evaporator. So, when you use the triple effect evaporator to concentrate this lake brine solution you can take off the evaporated water and then concentrated solids whatever is there or you know slurry whatever is there that is you know taken to the soda products plant.

And then liquor whatever is there which is the concentrated liquor that is taken to the potash plant because this liquor is rich in both potash and borax ok. These soda products are further processed to get you know sodium sulfate, sodium carbonate, lithium carbonate, phosphoric acid etcetera ok. Now, this concentrated liquor which is rich in potash and then borax is taken to the potash plant, right.

So, mother liquor of this potash plant is taken to a borax plant whereas, the solids that you get here from the potash plant are further processed to get agricultural grade, potassium chloride, granular potassium chloride, chemical potassium chloride as per the requirement and then liquid bromine also plus potassium sulfate also if you need to get the mixed fertilizers etcetera, right.

So, mother liquor of this potash plant whatever is there that is nothing, but mother liquor number one which is sent to the borax plant here. So, here now this mother liquor is primarily rich in borax. So, the borax is taken to the borax refinery and then mother liquor of this plant whatever is there that is nothing but mother liquor number 2 which is sent back to the concentration process along with the lake brine.

This borax is sent to the borax refinery where you can get different types of a borax components, ok. This is all about the Trona process or procedure. We have been discussing in different forms the same thing now.

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Now, major engineering problems if you wanted to list out, the first most important issue is the proper design of a triple effect evaporator because everything is happening from the concentrated product that you get after evaporating water from the brine and that you are doing in the evaporators triple effect evaporators.

So, evaporation is at the rate of several million kgs of water per day is taking place. So, then triple effect evaporators whatever you have taken that is going to be very essential, very important point. Now, in this process obviously, you are supplying the energy to evaporate the or boil of the water from the evaporator.

So, then heat transfer is involved and then this heat transfer is very much essential because when salt crystallize out at the same time along with this you know water being evaporated both of them are taking place at the same time. So, effective heat transfer is very much essential, proper heat transfer calculation one has to do.

So, this problem solved by removing the piping from inside the evaporators and doing the heating in outside heaters under mild hydrostatic pressure with minimum evaporation. Superheated solution is flashed into evaporators also and then heat transfer is also facilitated by vacuum cooling through vaporization instead of using cooling liquids in coils, which could become fouled with encrusted solids in general. Ok. So, vacuum cooling is again another option, right. Because of considering all these things cost of energy increased actually when you do the careful analysis to incorporate all these things the cost of energy is very much high. However, you know later on several studies have been carried out and then reduction of energy use has been found, but those details are not yet been disclosed. Ok.

So, this is all about the Trona process or Trona procedure along with its engineering problems etcetera, right.

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So, the references for this lecture are provided here. So, details of these slides whatever we discussed in this present lecture can be found from these two books.

Thank you.