Inorganic Chemical Technology
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Lecture - 22
Potassium Industries - 2

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Potassium Industries Part 2. Before going into the details of today's lecture, what we will be doing? We will be having a kind of recapitulation of what we have seen in the previous lecture.

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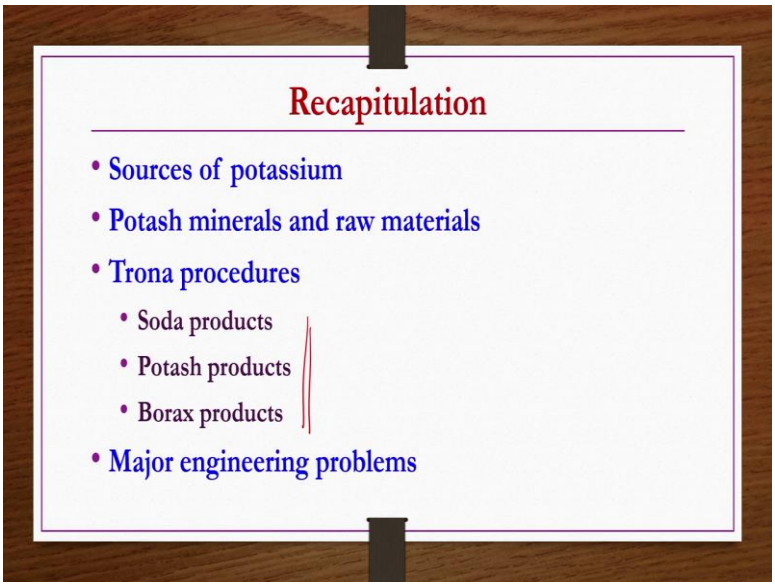

In the previous lecture, we started with potassium industries with sources of potassium, potash minerals and raw materials and then trona-procedures, where we have a three different steps to get soda products, potash products, borax products. Whereas these all these three are we get from the lake brine by doing different kind of processes that is what we have seen. And then we have also seen major engineering problems of this trona-procedure.

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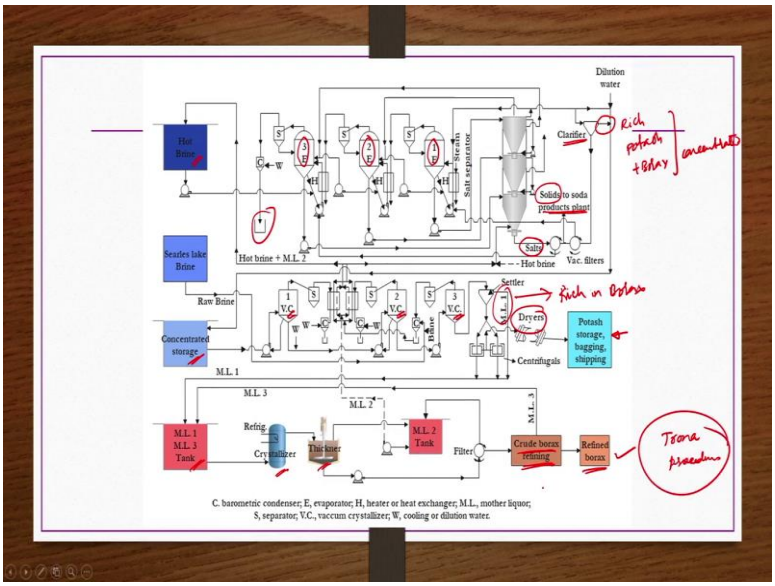

Briefly, if we recapitulate this trona-procedure, then what we have? We have a brine, we make it hot by using this steam and then it is fed to triple effect evaporator. So, that it can be concentrated. Whatever the concentrated brine after passing through this triple effect evaporator, it will be much more concentrated and then water would be evaporated off, ok that water would be condensed and collected anyway, right.

So, the underflow of these individual effects are taken to individual cones and then individual cones whatever the underflows are there, then from the top it will go to the second one and then like that to the bottom one. So, from the bottom most cone will get salts, which is having some water etcetera or you know moisture etcetera so, then what you do what we take it to the vacuum filter and then get the solids.

These solids are rich in soda. So, then this would be taken to the soda plant to get the soda products, right. In the clarifier, we will be taking the overflow of each of these cones. In this overflow also if at all there is solid present, concentrated the salts are solids are presents. Then what we do? We will separate them as a underflow of this clarifier and then pass through a vacuum filter to remove the moisture or water or brine etcetera.

And then dry solids will take to the soda products plant to get the soda products. Whereas the brine or mother liquor etcetera recovered from these processes or individual effective operators as well as from this vacuum filter they are fed back to the hot brine.

Whereas the overflow of this clarifier is rich in potash plus borax and then it is very concentrated.

This concentrated liquor is taken to the concentrated storage. From there it passes through three stages vacuum crystallization. Where from the underflow of each of these you get a concentrated slurry kind of thing that is taken to a settler where solids are settled at the bottom and then dried and then those are nothing but the potash products we taken for storage, bagging etcetera those kind of purposes.

Whereas the overflow of the settler whatever is there because the underflow of this individual vacuum crystallizers are going to the settler. In the settler you get the solids as a underflow and then that is dried and taken as a potash. Whereas the overflow what we do? This overflow would be rich in borax.

So, this mother liquor which is nothing but the overflow of the settler from the settling tank that is taken to a mother liquor tank and then this passes through different stages of refrigerative crystallization thickening etcetera and then followed by the filter to get the crude borax. Whatever the filtrate is there or mother liquor is there that is fed back to the mother liquor storage tank. This crude borax may be further refined to get the refined borax. So, this trona procedure now we get so many products like this, ok.

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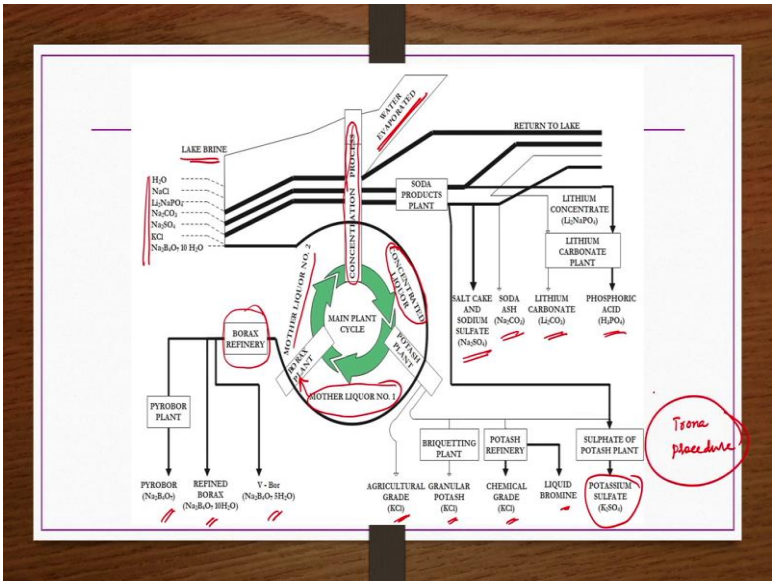

The same thing we have also seen in a different pictorial manner. So, let us say lake brine whatever we are having that is having several minerals including sodium chloride, dilithium sodium phosphate, sodium carbonate sodium sulphate, potassium chloride, borax etcetera so many things would be there. So, they may not be in pure form.

So, then what we are doing? We actually purifying this lake brine in a triple effect evaporator ok which is known as the concentration process which we do in triple effect evaporator where we evaporate water and then concentrate this brine. This concentrated brine is further filtered to get the solids as a soda products right. The solids are you know may be further treated to get individual product like sodium sulphate, sodium carbonate, lithium carbonate phosphoric acid etcetera.

Whereas the concentrated brine after filtration right solids are taken as this potash products whereas, the liquor concentrated liquor after this filtration is there that is known as the concentrated liquor and then that is rich in both potash and borax. So, then that will be taken to a potash plant where it will be further filtered and then mother liquor is sent to the borax plant.

After filtration in the potash plant whatever these solids are there they will be further process to get agricultural grade, potash or granular potash or chemical grade potash liquid bromine etcetera you can get these kind of products. So, here by taking some fraction of soda products and then some fraction of potash products do proper processing then you may also get a potassium sulphate as well, ok.

So, mother liquor of potash plant whatever is there that we take to the borax plant and then here again you do the filtration. When you do the filtration, you get the solids you know those solids taken to the borax refinery whereas, the filtrate or mother liquor is there that is fed back in the cycle along with the brine to further go the process.

Whereas this borax components are there they may be individually fractionated to different types of borax products. So, this is also again the same trona procedure, but a different pictorial presentation, ok.

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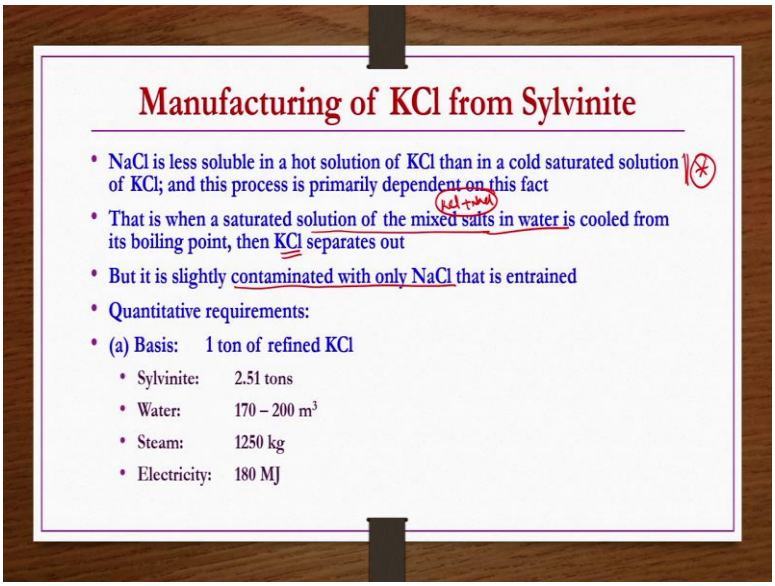

Now, what we will be doing in this lecture? In this lecture we will be having a discussion how to get the potassium chloride by different approaches as well. So, first one is manufacturing of KCl from sylvinite. Here the basis of this process is that NaCl or sodium chloride is less soluble in hot potassium chloride solution than in cold saturated potassium chloride solution, right.

So, this basic fact whatever is there this is the basis for KCl production from sylvinite. This we take as a basis. So, when a saturated solution of the mixed salts where mixed in the sense KCl plus NaCl this salt is there, it is under boiling condition. So, when it is boiling condition right then if you cool it from its boiling point then KCl will be separated out in the solution.

However this KCl will not be very pure, but slightly contaminated with NaCl only slightly contaminated with NaCl ok. So, quantitative requirements if you see for this process if you wanted to produce 1 ton of refined KCl you need sylvinite 2.5 1 tons water 170 to 200 meter cubes steam 1250 kgs electricity 180 mega joules these are the requirements.

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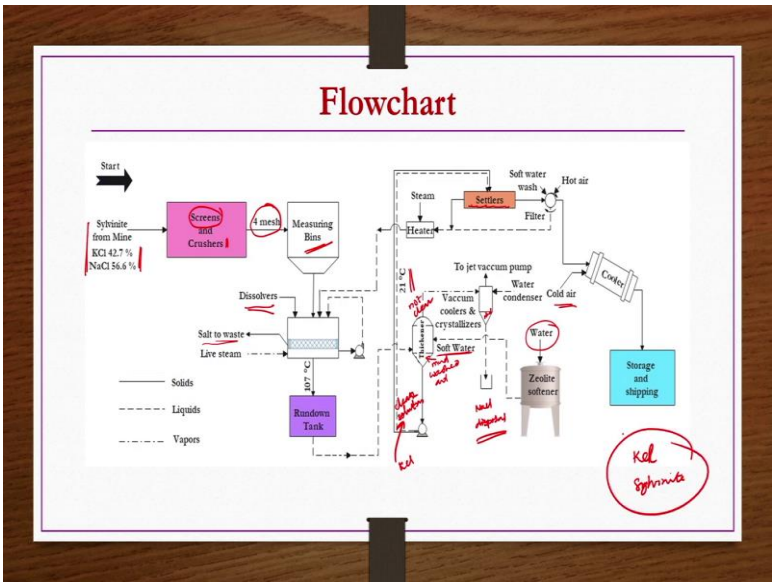

Now, flow chart of this process if you see whatever the ore sylvinite ore is there that you get from the mines let us assume it is having this kind of composition that is KCl approximately 43 percent NaCl approximately 53 percent, ok. So, this would be pass through a size reduction equipment and then pass through screens of a 4 mesh size.

So, whatever the material that is passing through 4 mesh is taken as a desired product and then stored in a measuring bins. Whatever the ore which is having more than a 4 mesh size they will be fed back to the crusher for the further size reduction, ok. Now, the size reduced ore is taken to a dissolver right in which this ore as well as the steam interact in a counter current way, ok

So, here a proper dissolving takes place and then there are series of dissolvers actually it is only one is shown here there are series of dissolvers and then this whatever the liquor form when you dissolve it by using steam here you know it forms a kind of liquor and then that passes from one dissolver to the other dissolver by means of a mechanical elevating equipments, ok.

So, here whatever undissolved salts etcetera are there they will be separated out as a waste. This mother liquor is heated to approximately 110 or 105 degree centigrade something like that and then stored it. This hot mother liquor is taken to a thickener where mud etcetera would be there you know if at all mud etcetera would be there in the ore because that will also be coming in the mother liquor also.

If it is present in the ore it will be coming into the mother liquor also. So, that mud would be settled out in this thickener at the bottom and then this mud would be washed out using water, right. So, when since you are producing KCl as much pure as possible. So, then you try to have the soft water, ok. So, then this zeolite softness are used for making water soft and then it is fed to the thickener. So, that to flush out or wash out the mud, ok.

Then the liquid whatever is there the liquid not so clear liquid that would be having both KCl and NaCl that would be taken to a vacuum cooler and crystallization section, right. Here NaCl whatever are there the crystals etcetera are there they will be settled out and then collected at the bottom as a underflow of this vacuum coolers and crystallization section and then this NaCl would be disposed of fine.

Then whatever the clear liquid is there here the clear liquid or clear solution is there that is having KCl that is taken or heated to 25 to 30 degree centigrade something like that it will be heated to the temperature and pass it through a settler. Where KCl would be collected from the bottom at the crystals here and then they will be taken to a filter where you know this KCl crystals are washed with soft water again if it all in it orbits etcetera present.

So, to wash off and then filtrate whatever is there that will be passing through a heater and then going to the dissolver section so, that to make the dissolving process comfortable, right. This dried product hot dry product whatever is there that would be cooled in a cooler using a cold air and then taken to the storage and shipping purpose. So, this is how you can produce KCl from sylvinite ore ok.

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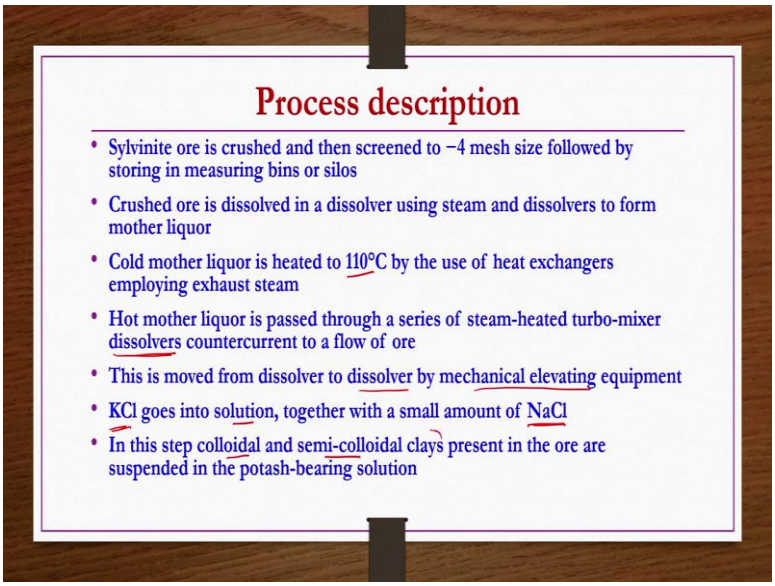

This is one process the description of the process is given here sylvinite ore is crushed and then screen to 4 mesh size followed by storing in measuring bins or silos crushed, ore is dissolved in a dissolver using steam to form mother liquor cold mother liquor is heated to 110 degree centigrades by use of heat exchangers employing exhaust steam.

Hot mother liquor is passed through a series of steam heated turbo mixers dissolvers counter current to a flow of ore. This is moved from dissolver to dissolver by mechanical elevating equipment and then KCl goes into the solution together with a small amount of NaCl ok. In this step colloidal and semi colloidal clays present in the ore are suspended in the potash bearing solutions in general.

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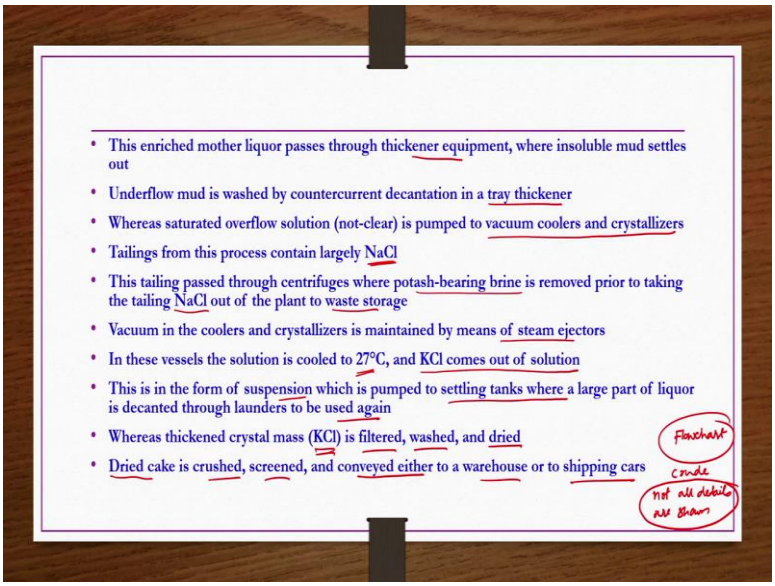

This enriched mother liquor passes through thickener equipment where insoluble mud settles out and underflow mud is washed by counter current decantation in a dry thickener whereas, saturated overflow solution not so, clear solution is pumped to vacuum coolers and crystallization sections. Tailing from this process contain largely NaCl this tailing passed through centrifuges where potash bearing brine is removed prior to taking the tailing NaCl out of the plant to waste disposal or waste storage.

Vacuum in the coolers and crystallizers is maintained by means of steam ejectors in these vessels the solution is cooled to 27 degree centigrade and KCl comes out of solution this is in the form of suspension which is pumped to settling tanks where large part of liquor is decanted through launders to be used again whereas, thickened crystal mass KCl is filtered washed and dried.

Dried cake is crushed, screened and conveyed either to a warehouse or to shipping cars. Now, here flow chart you know whatever we have seen in the previous slide is a bit crude that is not all details are shown ok in order to make it simple for understanding it has not been I mean all details have not been shown important things are only shown.

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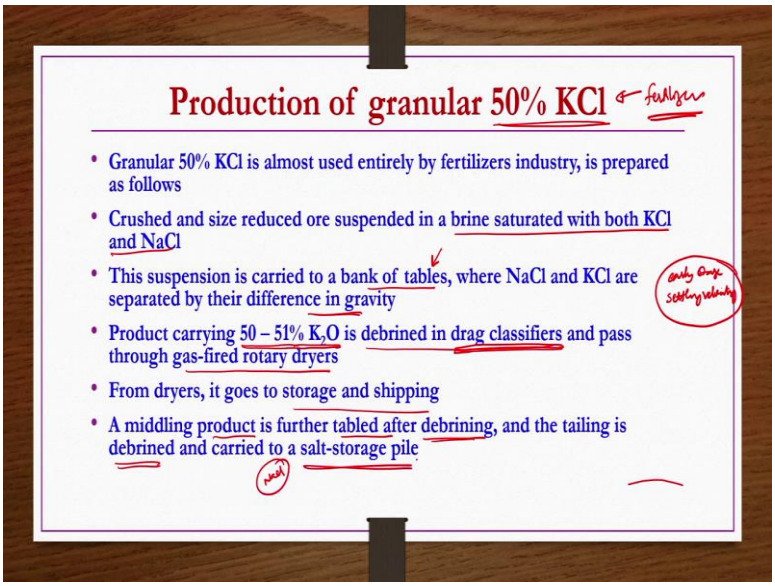

Now, granular 50 percent KCl production, how do you do? Because 50 percent KCl is often used as it is for a fertilizer purpose or in fertilizer industries, ok. Granular 50 percent KCl is almost used entirely by fertilizers industry is prepared as follows it is very simple process crushed and size reduced ore suspended in brine saturated with both NaCl and KCl, ok.

This suspension is carried to a bank of tables, tables are a kind of unit operations where this operation takes place based on the difference in gravity or based on difference in the density. However, in these tables the settling of this you know one of the phases from the other or one component from the other is not taking place based on its a resettling velocity rather it takes by early stage settling velocity. So, these details about tables etcetera you may be studying in mechanical unit operations course, ok.

Now, by doing this separation you have a one a stop, another one is the bottom product and then middle one is the middling product is there if you are using two tables. Product carrying 50 to 51 percent K 2 O is debrined in drag classifiers. Drag classifiers are again a kind of sedimentation tanks where this operation of the component takes place based on the drag differences and pass through gas filter rotary dryers for the drying. From dryers it goes to the storage and shipping.

A middling product is further tabled whatever the middling product is there further tabled and then it will be debrined and the tailing is whatever is there that is also

debrined and then after debrining this middling and then tailing product that is bottom products they are mostly containing the NaCl they will be taken to a salt storage pile very simple process.

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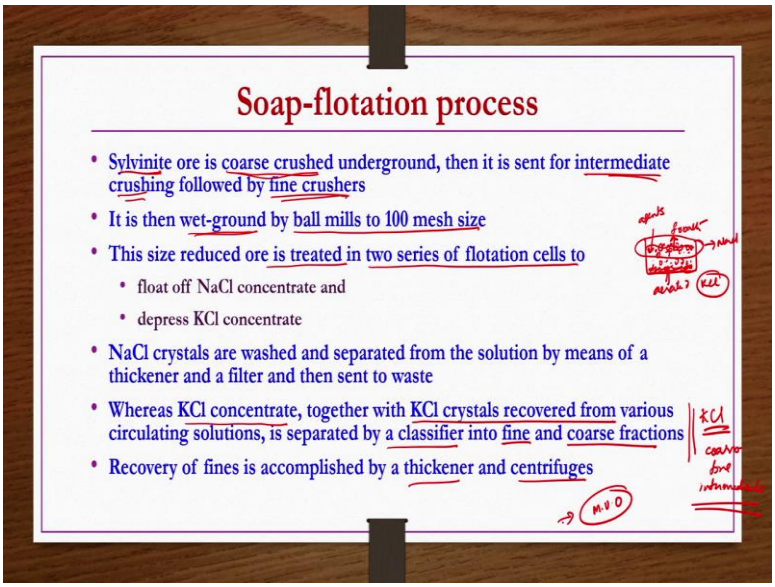

Soap floatation process is another process where you can produce a KCl easily ok. What we do here sylvinite is the ore that we take it is crushed in a three different types of crushers one is the coarse crushers followed by the intermediate crushing then followed by the fine crushers.

Crushers actually you know they usually produce the particles of certain sizes like you know few centimeters or few mms only ok from the ore serving the few meter size ok. So, they are further size reduced to some micron size or fraction of millimeters etcetera by grinders.

So, this fine crushers are finely crushed material or finely crushed sylvinite ore after fine crushers are again wet-ground by ball mills to a 100 mesh size ok. This size reduced ore is treated in two series of floatation cells right, where you get float of NaCl concentrate and then depress KCl concentrate right.

Here floatation cells actually you know you have a container in which you take this ores crushed ores and then you will be providing some solution water or some kind of you

know brines are also sometimes provided. To this one agents floatation agents would be added and then they will also be aerated.

So, that bubbles will form in this you know container and then to these bubbles you know lighter weight or you know whichever particle is having smaller density they will be attached and then along with these bubbles those particles would be carried to the top of the top surface as a froth whichever is having the heavier density those are settling at the bottom as a kind of different product.

So, now here in this case this froth whatever is there that is containing primarily NaCl that is taken washed off and then you know decanted or you know disposed as a waste or may be taken to a salt storage piles ok. Whatever the settled ones heres are there they are nothing but KCl products.

So, they will be collected and then passed through different purification steps and then taken as a 50 percent or 90 percent purity KCl whatever you required. The purification process will depend on how much purity you need it. So, NaCl crystals are washed and separated from the solution by means of a thickener and a filter and then sent to waste whereas, KCl concentrate together with KCl crystals recovered from various circulating solutions is separated by a classifier into fine and coarse fractions.

Recovery of fines is accomplished by a thickener and centrifuges ok. So, in this process this KCl whatever you get you may be getting in different sizes right coarse fine intermediate kind of thing. So, as per the requirement you know you can apply appropriate mechanical unit operations and then do this operations etcetera. If you need to do an enlargement then you and size enlargement unit operations you have to apply and get it.

All those details we are not discussing because most of them these details of unit operations are not part of the course, they are part of mechanical unit operation course. So, here we are discussing only the process to get a given product. Now, here in this case KCl is the product.

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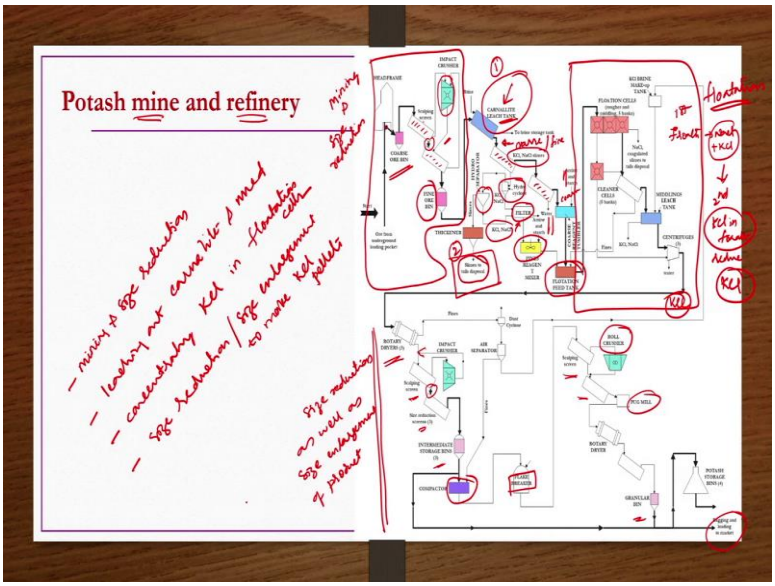

Now, potash mine and refinery process we see here. So, the flow sheet is shown here for this process. Now, this flow sheet if you see primarily, it looks very big because it is as the name suggests Potash mine and refinery mining and then refining all the details are presented that is the reason it is looking very big.

So, now let us say this part whatever is there it comes under mining and size reduction part you do the mining and then do the size reduction of the ore as per your requirements. And then this part is a kind of floatation section just now we have seen. So, where you take NaCl as a froth and then KCl you take as a concentrate settling at the bottom right.

Whereas, the remaining this part is having both size reduction as well as size enlargement of product crudely or you know very briefly if you see the details here whatever the mine ore is there that you take to crushers. Crushes are you know big size equipment where they reduce the feed material from few meters average size to few centimeters average size. So, they are known as the coarse crusher.

So, then head framer and then gyratory recrushers etcetera some of the crushers are there so, that you will be studying later in your mechanical unit operations course. After the crushing the material is taken to a coarse ore bin because that material itself is coarse. Crushers will not produce you in a very fine product some fraction may be there, but majority average size if you take, they will be very coarse in size.

So, this material is taken to a series of screens, right. So, from this coarse your aim is to get the fines fine ores, ok. So, when you do the series of screens let us say this screen is having you know something like 50 mesh size it may be having 100 mesh size. More the mesh number smaller is the opening of the screen, ok.

So, the coarser particles will be retained on the top and then finer would be coming from the bottom. These finer products now we cannot say finer we can say intermediates they will be fed back to the other screen here with which is having the smaller opening compared to the previous screen whichever previous step was there.

So, here again the fines would be collected and then fines would be taken to the fine ore bin whereas, the coarse material are bigger than the size opening of the screen they will be taken to the impact crusher further. Likewise, the first screen also whatever the bigger size or the material having the size more than the opening of the screen will be taken to the impact crusher where further the size reduction will be taken place. And then the size reduced to material would again come to the second screen to check its size again.

So, whatever since those material have undergone again size reduction here their size would be smaller here ok their size would be smaller and then the fines again will be collected to the fines bin and then this process continues until all the materials you know crushed to the required fine ore size, ok This fine ore along with the brine is taken to a leaching tank where carnallite is leached out and then remaining NaCl whatever are there they will be passed through different screens to separate out the coarse as well as the fine.

Here in this one whatever this one is there this is having both coarse as well as the fine NaCl, KCls are there they will be passed through different you know units to separate out. So, let us say whatever the finers of the first screen are there they will be taken to a hydrocyclone to remove any water etcetera are there and then fine KCl, NaCl are there they will be taken to the filter right.

So, from the top of the hydrocyclone whatever the water etcetera going out that may also contain some amount of NaCl, KCl. So, those would be separated in a hydro separator here then after separating that moisture etcetera whatever the NaCl, KCl are there they will also be taken to the filter from the hydro separators whatever the solutions etcetera

are there in which you know slims would be there those slims will be taken as a tails for the disposal.

Whatever the over size of the screens are there you know they will be having you know bigger coarse or KCl and NaCl crystals they will be taken to another screen further to do separation and then fines are taken along with the filter it is taken to this case and to this filtered fine now here we get the fines here you get the coarse coarse NaCl, KCl and then here fine KCl, NaCl you get to these tanks what you are doing you are adding amine and then starch.

Then whatever this coarse and fine NaCl are there they are again come mixed together in a flotation feed tank. So, what is the point of this one if you are mixed again. So, the primary aim is following this step here in between is to leach out the carnallite and then to take of the slims or tails which are nothing but mud etcetera to disposal. So, this is the primary aim.

So, after the size reduction what we have done we removed, removed carnallite this is one and then removed mud etcetera as a tailing this is two then whatever the NaCl KCls are there they are mixed together in a flotation tank. Now, in the flotation tanks different stages of flotation should be there you can have 3 stages 5 stages as per your requirement.

So, that is may be like you know in the first flotation cell whatever the product is there the froth is there for example, it is supposed to have only NaCl, but it may also have some KCl in the first flotation cell. So, then what you do this you will take to the second flotation cell and then you try to reduce the KCl in froth as much as possible you try to reduce like that you know as per your requirement you try to make sure that there should not be any KCl in froths only NaCl should be there accordingly as per your design calculation those many number of flotation cells you need it.

So, here whatever the pure KCl is there so, that is dried in a rotary dryer, right. Now, it may be this dried product coming out from here it may be having you know various size you know fine intermediate course and then irregular shapes of this things would be there. So, if that is itself is your product.

So, no problem if you wanted to make some kind of tablets or you know proper size of this KCl's or pellets etcetera then this kind of this subsequent process has to be gone through. What we are doing here dried KCl from the rotary dryers you know screened, screened you know in order to get intermediate fines and then coarse ones right.

Intermediates ones of the or the product of the are the underflow of the first screen is taken to the second screen to further do the separation and then overflow of this second screen is taken to the bins as a intermediate storage bin right. So, overflow of the first screen is taken to a impact crusher.

So, that to crush that material again and then sent back to the first screen again here to this one right. So, intermediate storage bins they will be taken as it is a product if it is fine for you or otherwise if you wanted to make pellets etcetera then they will be taken to the compactor to make a size enlargement of a proper briquette size or something like that.

So, when you do this process, it is possible that there may be some flakes formation. So, those flakes are taken to the flake breaker which is again a size reduction kind of equipment right. So, here after breaking this flakes you do the size analysis again right though required size ones you can take to the pug mills and then you do the drying etcetera whereas, the oversize particles are there.

So, they will be again crushed in a roll crusher this process continues until the all particles are of almost uniform size if not exactly uniform size almost uniform size or within the range of your requirements and then further drying, granulation, bins etcetera all that if required they should be done, ok.

So, now this is the process. So, now what we have in this process first step is mining and size reduction is the step 1, second step is that leaching out carnallite and mud etcetera then concentrating KCl in floatation units or floatation cells and then size reduction or size enlargement to make KCl pellets etcetera. So, these are the steps involved in this process, ok.

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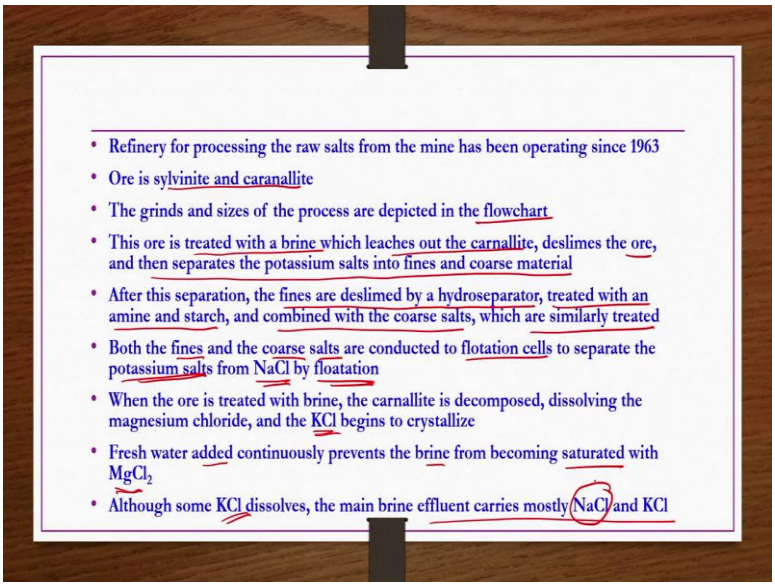

So, now the details we see in descriptive text form here refinery for processing the raw salts from the mine has been operating since 1963 ore is sylvinite and carnallite. The grinds and sizes of the process are depicted in the flowchart as discussed in the previous slide. This ore is treated with a brine which leaches out the carnallite, deslimes the ore then separates the potassium salts into fines and coarse material using the screens.

After the separation the fines are de-slimed by hydro separator treated with an amine and starch and combined with the coarse salts, which are similarly treated and then both the fines and coarse salts are conducted to floatation cells to separate out potassium salts from NaCl by floatation, ok.

When the ore is treated with brine the carnallite is decomposed dissolving the magnesium chloride because carnallite is having MgCl2 as well in its molecular structure. So, then carnallite when it decomposed it is possible that the magnesium chloride would be released. So, the carnallite is decomposed dissolving the magnesium chloride and the KCl begins to crystallize.

Fresh water added continuously to prevent the brine from forming or from becoming saturated with magnesium chloride. Although some KCl dissolves the main brine effluent carries mostly NaCl and KCl, ok. Primarily NaCl would be there then some amount of KCl would also be there in the brine effluent.

Until now what we have seen how to get KCl by different processes that is what we have seen because it is very much essential important component of potassium. But there are also many other potassium salts etcetera are there which are very essential from application point of view. We cannot go into the float sheeting and then description of each and every product formation. But; however, we see some simple reactions that you can do and then get these products. Primarily these are very simple.

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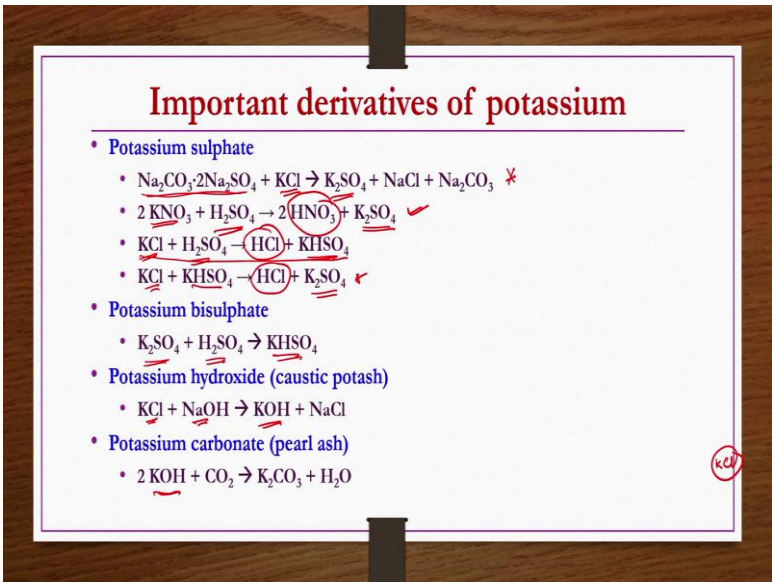

For example, some of the important derivatives of potassium under this category if you take potassium sulphate you take a burkeite that is mineral Na 2 CO 3 2Na 2 SO 4 and then react with KCl you can get potassium sulphate sodium chloride and sodium carbonate. This is one possible way, but there are other possible ways also. Let us say if you take potassium nitride and then react with sulfuric acid then also you can get potassium sulphate.

Other approach is that if you take KCl and then react with H 2 SO 4 then you get potassium bisulphate which further reacts with KCl to give potassium sulphate. Now, here in this process where you are getting K 2 SO 4 potassium sulphate you are getting nitric acid whereas, here in this process you are getting sulfuric acid.

So, separating out and then proper purification of the product may become slightly difficult if you have the acid. So, appropriately you have to choose a process. So, this seems to be better and easier one. Potassium bisulphate K 2 SO 4 if you take as a

reactant and then react with the sulfuric acid then you can get the potassium bisulphate or otherwise here also sulfuric acid and then KCl if you react then you can get potassium bisulphate, ok. Potassium hydroxide, caustic potash KCl if you react with NaOH then you get KOH and NaCl. Potassium carbonate which is also known as the pearl ash that you can get by reacting potassium hydroxide or caustic potash with carbon dioxide to get it K 2 CO 3.

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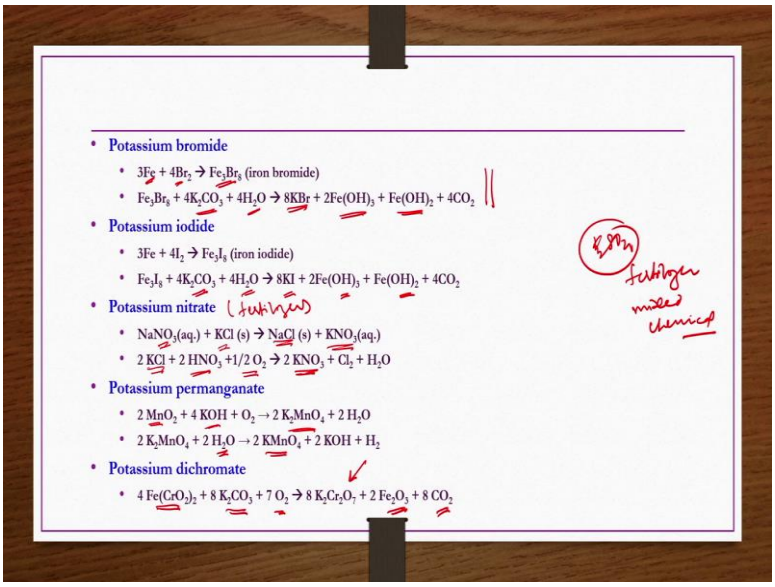

Potassium bromide if you want it to do it is a two-step process. Iron reacts with the bromine to give iron bromide which further reacts with the potassium carbonate and water to give potassium bromide and then hydroxide of iron ok along with the carbon dioxide.

If you wanted to do the potassium iodide production it is same reactions are same like the potassium bromide case where iron reacts with the iodine to give iron iodide which reacts with the potassium carbonate and water to give potassium iodide and then iron hydrates along with the carbon dioxide.

Potassium nitrate if you wanted to produce let us say sodium nitrate if you react with KCl you can get the sodium chloride and then potassium nitrate. This potassium nitrate you can directly use as a fertilizer many a times or it is used in mixed fertilizer production. Even potassium sulphate also used in fertilizers mixed chemical fertilizers, ok.

So, other possible way of getting potassium nitrate is that KCl if you react with the nitric acid and then in the presence of oxygen you get potassium nitrate. Potassium permanganate if you want to produce manganese dioxide if you react with the caustic potash then you get potassium manganate. This potassium manganate further reacts with water to give potassium permanganate and then potassium hydroxide plus hydrogen.

Potassium dichromate if you wanted to produce iron chromate if you react with potassium carbonate and then oxygen you get potassium dichromate and then iron oxide and carbon dioxide. Most of these processes are very simple reaction mostly you can do in a batch kind of mode easily.

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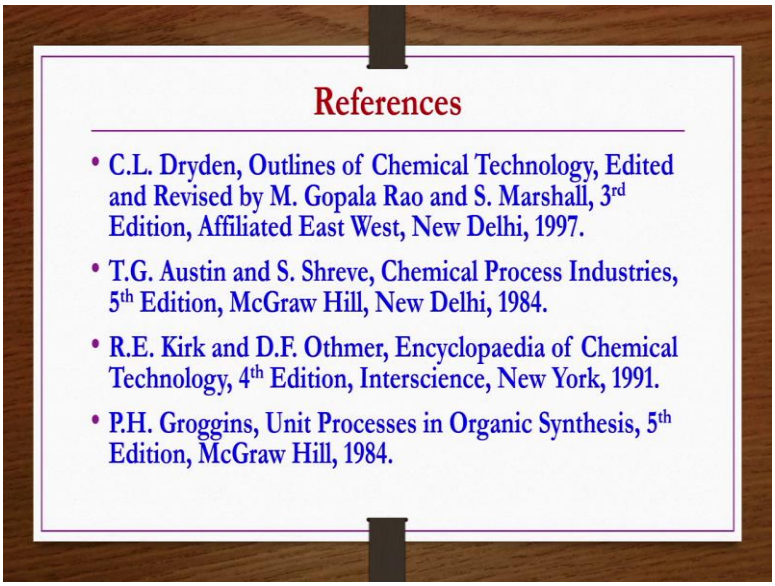

References for this lecture are presented here. Outlines of Chemical Technology by Dryden edited and revised by Gopal Rao and Marshall, 3rd edition and then Chemical Process Industry is by Austin and Shreve 5th edition. Other reference books are Encyclopaedia of Chemical Technology, 4th edition by Kirk and Othmer and then Unit Processes in Organic Synthesis by Groggins 5th edition.

Thank you.