Inorganic Chemical Technology
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Lecture - 19
Phosphorus Industries - Phosphoric Acid Production by Wet Processes

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Phosphorus Industries, Phosphoric Acid Production by Wet Processes. Before going into the details of today's lecture, we will have a recapitulation of what we have discussed in the previous lecture.

In the previous lecture, we started discussion on Phosphorus Industries, how it compares with nitrogen industry, especially with respect to the growth, how it has grown, etcetera, those things we have seen.

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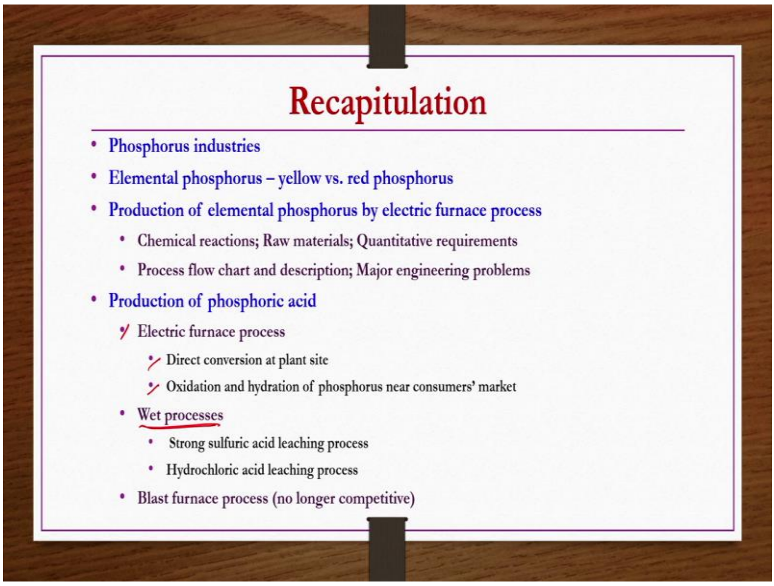

Recapitulation

- Phosphorus industries
- Elemental phosphorus – yellow vs. red phosphorus
- Production of elemental phosphorus by electric furnace process
    - Chemical reactions; Raw materials; Quantitative requirements
    - Process flow chart and description; Major engineering problems
- Production of phosphoric acid
    - Electric furnace process
        - Direct conversion at plant site
        - Oxidation and hydration of phosphorus near consumers' market
    - Wet processes
        - Strong sulfuric acid leaching process
        - Hydrochloric acid leaching process
    - Blast furnace process (no longer competitive)

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Then we started discussions on elemental phosphorus, that is, yellow versus red phosphorus, their properties, the differences, etcetera, we have seen. Then we started discussion on production of elemental phosphorus by electric furnace process, under which we have discussed the reactions, raw materials, quantitative requirements, process flowchart and description, major engineering problems, etcetera, we have seen.

Then we started discussions on production of phosphoric acid. We realized that there are three important methods are there. One of them is electric furnace process, under which two different options are there, direct conversion at plant site and then oxidation and hydration of phosphorus near consumers market.

The second method for the production of phosphoric acid is wet process. Under the wet process, again two options are there, strong sulfuric acid leaching process and then hydrochloric acid leaching process. Third one is blast furnace process, which is no longer competitive.

So, for the production of phosphoric acid, in the previous lecture, we have discussed you know phosphoric acid production using the electric furnace process that we have seen, under which both direct conversion as well as the oxidation and hydration of phosphorus near consumers market, we have already seen.

In today's lecture, we are going to discuss about production of phosphoric acid using wet processes. We start with strong sulfuric acid leaching process. Ok.

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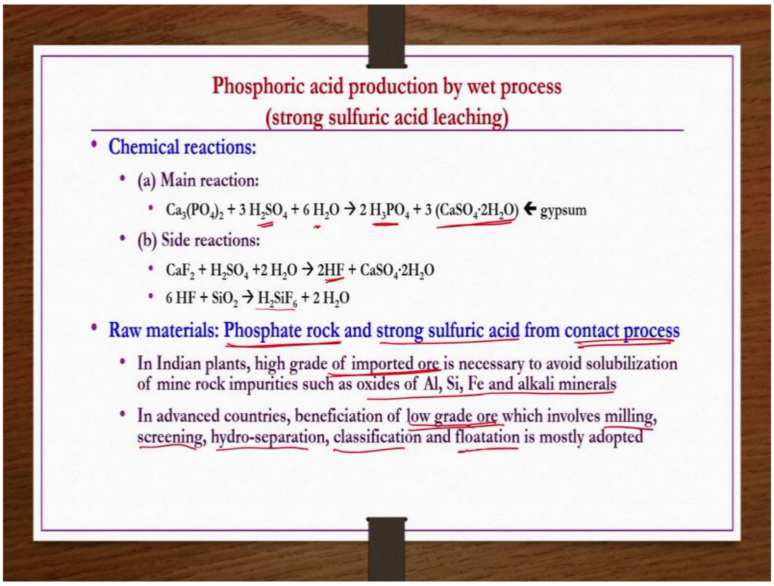

Phosphoric acid production by wet process
(strong sulfuric acid leaching)

- Chemical reactions:
  - (a) Main reaction:
    - $Ca_3(PO_4)_2 + 3\,H_2SO_4 + 6\,H_2O \rightarrow 2\,H_3PO_4 + 3\,(CaSO_4{\cdot}2H_2O)$ ← gypsum
  - (b) Side reactions:
    - $CaF_2 + H_2SO_4 + 2\,H_2O \rightarrow 2HF + CaSO_4{\cdot}2H_2O$
    - $6\,HF + SiO_2 \rightarrow H_2SiF_6 + 2\,H_2O$
- Raw materials: Phosphate rock and strong sulfuric acid from contact process
  - In Indian plants, high grade of imported ore is necessary to avoid solubilization of mine rock impurities such as oxides of Al, Si, Fe and alkali minerals
  - In advanced countries, beneficiation of low grade ore which involves milling, screening, hydro-separation, classification and floatation is mostly adopted

Chemical reactions; main reaction is that calcium phosphate react with the strong sulfuric acid and water to give the phosphoric acid and gypsum. Side reaction is that calcium fluoride react with the sulfuric acid and water to give the hydrogen fluoride and gypsum. This hydrogen fluoride reacts with silica to give H 2 Si F 6.

Raw materials: Phosphate rock obviously. We are taking as initial point and then strong sulfuric acid from contact process. From contact process, we can get sulfuric acid up to 93, 98 percent purity. So, that acid directly we can use here in this process.

In Indian plants, what happens you know, we need high grade imported ore because we understand, we realize that you know phosphorus resources are not available in India. So, we are dependent on the import. So, since we are doing importing, it is better to take the high grade imported ore because there is a possibility.

If you have a low grade ore, then you know, mine rock impurities such as oxides of alumina silica, iron and alkali minerals may take place. Solubilization of these mine rock impurities may take place with the ore and then that is going to hamper the process and decrease the yield. So, better to go for high grade imported phosphate rocks for the processes for the plants in India.

In advanced countries, what they do? They take even a low grade ore and then further improve its purity by going through several beneficiation processes which includes milling, screening, hydro-separation, classification and floatation. Ok.

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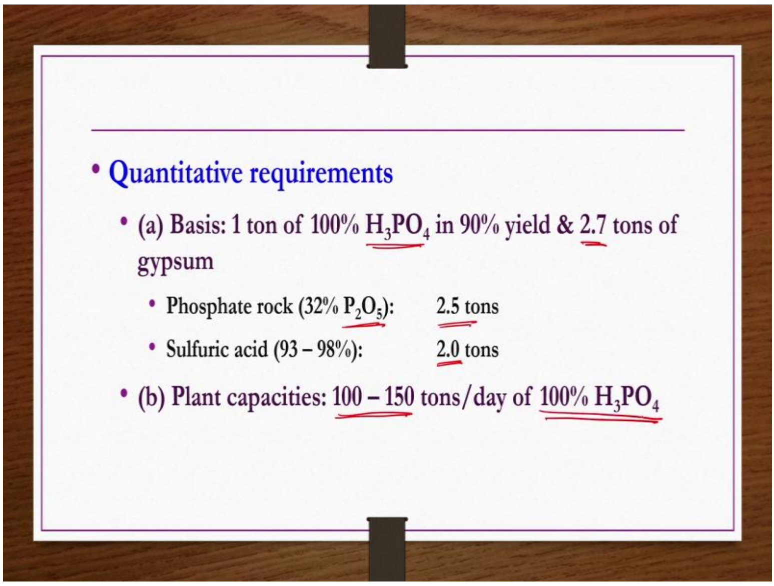

- Quantitative requirements
  - (a) Basis: 1 ton of 100% H_3PO_4 in 90% yield & 2.7 tons of gypsum
    - Phosphate rock (32% P_2O_5): 2.5 tons
    - Sulfuric acid (93 – 98%): 2.0 tons
  - (b) Plant capacities: 100 – 150 tons/day of 100% H_3PO_4

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Quantitative requirements for this process if you see, if you wanted to produce 1 ton of 100 percent phosphoric acid in 90 percent yield and 2.7 tons of a gypsum because in this process you get both phosphoric acid as well as gypsum and then gypsum quantity is much higher compared to the phosphoric acid quantity in this plant.

So, accordingly the raw material requirements are phosphate rock having 32 percent P 2 O 5, unit 2.5 tons, sulfuric acid 93 to 98 percent purity unit 2 tons. Plant capacities usually 100 to 150 tons per day of 100 percent H 3 PO 4.

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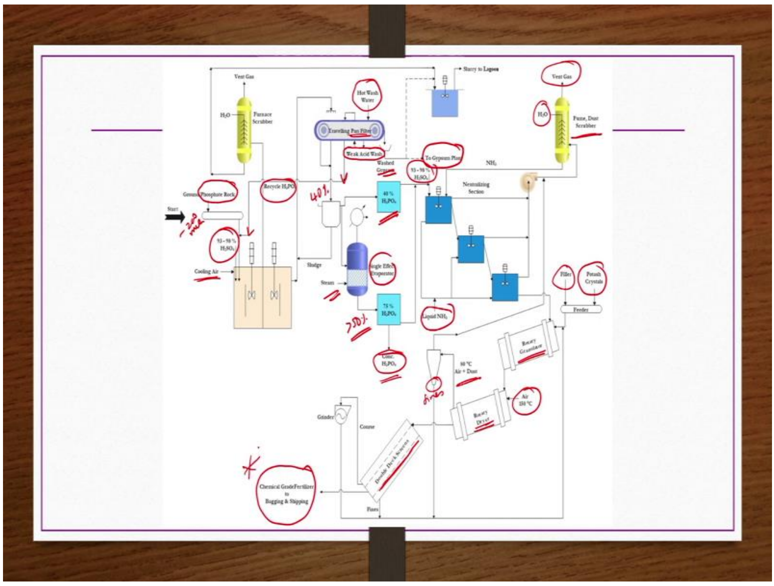

Now, we see the flow sheet here how to obtain the phosphoric acid concentrated phosphoric acid using the wet process where strong sulfuric acid leaching is taking place ok So, here the phosphate rock whatever is there that you ground to 200 mesh and then take to a reactor to which strong sulfuric acid 93 to 98 percent pure H 2 SO 4 along with the recycle phosphoric acid is taken right. So, this recycle phosphoric acid helps this material to get into the reactor comfortably.

To this reactor the concentrated sulfuric acid is allowed using a automatic control because you know the ratio between rock and then sulfuric acid has to be properly maintained, has to be properly maintained and then that is very much essential because you are producing low cost phosphoric acid and then using you know strong sulfuric acid.

So, it has to be meticulously utilized as well as it has to be recovered later again. After the production of the process when you do the purification of the products etcetera it should also be recovered as much as possible otherwise it has to be used for production of some other chemicals there in the plant itself.

Otherwise, this process is not going to be economically feasible if you are not you know meticulously using this H 2 SO 4 for the process as well as recovery if not recovery utilizing for some other chemicals fertilizer productions right.

So, now here the reaction when reaction takes place whatever the heat of the reaction is there so, that has to be controlled. So, for that cooling air is being circulated to the reactor. Now, the output of the reaction is nothing, but what we understand from the reactions is primarily phosphoric acid and gypsum of course, there are other kind of impurities are also there as per the reaction, but primarily it is phosphoric acid and gypsum.

So, this mixture is taken to the travelling pan filter where we are using weak acid for washing, weak acid is used for washing and then whatever the filtrate of this filter is there that is nothing, but weak phosphoric acid that has been taken as a kind of recycle here to this you know reactor again ok.

So, here what you do in this process almost 40 percent of phosphoric acid you get it by this filtration process right, 40 percent of phosphoric acid you get it and then you further concentrate it in a single effective evaporator as shown here to increase its concentration more than 50 percent anything up to 75 80 percent as per your requirement and then store it right.

So, here after that you know because this is a travelling pan filter. So, the other end what you get, a gypsum and then for washing of the acids etcetera whether it is unreacted sulfuric acid or you know weak phosphoric acid whatever it present, you have to wash it for that purpose you use hot water wash at the end of the or at the other side of the you know travelling pan filter that is just before the collection of the washed gypsum.

Before collecting the gypsum, you use the hot water for the washing of the slurry. So, that to wash out the acids ok, and then take the almost pure washed gypsum as a product here. This you can take to gypsum plants for making of paints etcetera or whatever the other products that you can make from the gypsum for that purpose you can take it by drying etcetera ok.

Now, see the other option is that now you are getting you know from here travelling pan filter you are getting 40 percent H 3 PO 4 you can take it as it is if it is sufficient for your purpose otherwise you can concentrate in single effective operator using this steam right. So, concentrated phosphoric acid you can get from this single effective operator right.

So, but now what happens there is a problem of you know economy right if you only do this much then if you do not recover or utilize properly the H 2 SO 4 etcetera then it is not going to be economical process. So, then what we do in general this phosphoric acid is neutralized whether it is weak acid or strong acid.

It will be neutralized using the liquid ammonia and then make up sulfuric acid you know solution right and there will be series of neutralizers would be there this entire you know it depends on the how much how many sections are required in a plant that depends on the quantities 2 to 3 neutralizing sections would be there.

After this neutralizing section what you get from the bottom of the last neutralization section you get a chemical fertilizersy like you know ammonium phosphate, ammonium sulfate etcetera those kind of mixed chemical fertilizers you get, that slurry what you do, you take it to a rotary granulator to this rotary granulator you can also add potash crystals and then filler if anything are required.

So, when this slurry which is nothing, but mixed chemical fertilizer something like you know ammonium phosphate and then ammonium sulfate etcetera these kind of thing alright. So, these this slurry along with the filler and potash are taken to the rotary granulator where the granulation of this mixture is takes place, these granules are taken to the rotary dryer to which air at 150 degrees centigrade is supplied for the drying purpose.

So, this dried granules what you do, you take it to double deck screens where you see the size requirement if the granules are of sufficient size, then you can take them as a product for the bagging. So, here the granules which are bigger than the desired size they are re-grinded and then sent back for the screening again whereas, the fines are taken back to the rotary granulator along with the filler and potash crystals for the further makeup of the size alright.

So, where whereas, the air from the rotary dryer that would be approximately at 80 degrees centigrade that may also be containing some dust of this you know chemical fertilizer. So, you cannot leave this air to the atmosphere as it is. So, then what you do, you take it to the cyclone separator from there you try to remove the dust from the air and then that air is sent is sent through a fume dust scrubber if at all some more scrub dust is remaining that would be scrubbed using the water and then clean air sent as a vent gas.

Whereas from the bottom of the cyclone separator if any fines are there you know fine granules are there. So, they will be collected and sent back to the granulator along with the filler and potash crystal for the makeup of a granular size right. So, this way you can make use of a sulfuric acid without any wastage because you are getting weak acid as well as the concentrated phosphoric acid plus in addition to that one you are able to produce the mixed chemical fertilizers as well ok.

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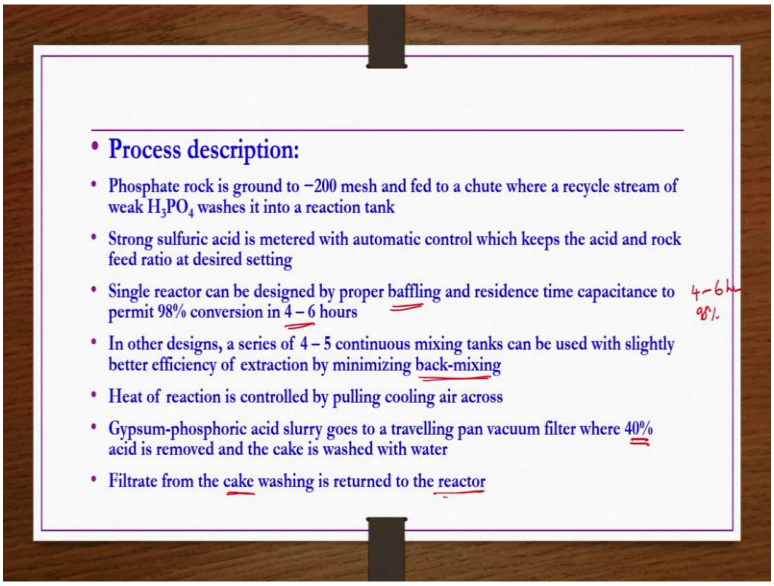

- Process description:
- Phosphate rock is ground to −200 mesh and fed to a chute where a recycle stream of weak H_3PO_4 washes it into a reaction tank
- Strong sulfuric acid is metered with automatic control which keeps the acid and rock feed ratio at desired setting
- Single reactor can be designed by proper baffling and residence time capacitance to permit 98% conversion in 4 – 6 hours
- In other designs, a series of 4 – 5 continuous mixing tanks can be used with slightly better efficiency of extraction by minimizing back-mixing
- Heat of reaction is controlled by pulling cooling air across
- Gypsum-phosphoric acid slurry goes to a travelling pan vacuum filter where 40% acid is removed and the cake is washed with water
- Filtrate from the cake washing is returned to the reactor

4-6 h
98%

So, the same description is given here phosphate rock is ground to 200 mesh and fed to a chute where a recycle stream of weak phosphoric acid washes it into a reaction tank. Strong sulfuric acid is metered with automatic control which keeps the acid and rock feed ratio at desired setting.

So, single reactor can be designed by proper baffling and residence time capacitance permit 98 percent conversion in 4 to 6 hours. If you have a single reactors you have to react it you have to do the reaction for 4 to 6 hours right and then proper baffling etcetera should be provided or mixing thorough mixing has to be provided in the reactor. So, here you can get up to 98 percent of conversion.

Some designs what happens you know you can have multiple reactors right you know 4 to 5 continuous mixing tanks can be used with slightly better efficiency of extraction by minimizing back mixing. The heat of reaction is controlled by pulling cooling air across the reactors.

Gypsum phosphoric acid slurry goes to a traveling pan vacuum filter where 40 percent acid is removed and the cake is washed with water. Filtrate from the cake washing is returned to the reactor as weak phosphoric acid recycle.

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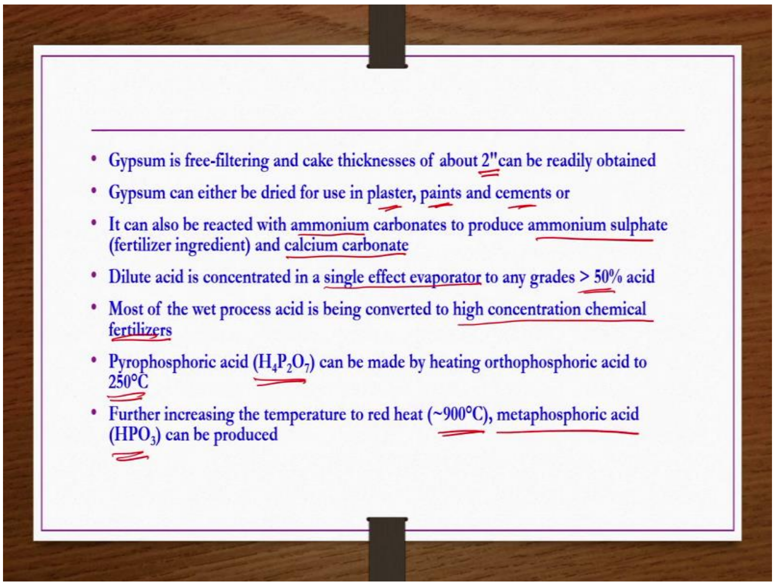.

- Gypsum is free-filtering and cake thicknesses of about 2"can be readily obtained
- Gypsum can either be dried for use in plaster, paints and cements or
- It can also be reacted with ammonium carbonates to produce ammonium sulphate (fertilizer ingredient) and calcium carbonate
- Dilute acid is concentrated in a single effect evaporator to any grades > 50% acid
- Most of the wet process acid is being converted to high concentration chemical fertilizers
- Pyrophosphoric acid ($H_4P_2O_7$) can be made by heating orthophosphoric acid to 250°C
- Further increasing the temperature to red heat (~900°C), metaphosphoric acid (HPO_3) can be produced

Gypsum is free filtering and cake thicknesses of about 2 inches can be readily obtained. Gypsum can either be dried for use in plaster, paints and cements or it can also be reacted with ammonium carbonates to produce ammonium sulphate which is a fertilizer and calcium carbonate. Either way it can be used.

Dilute acid is concentrated in a single effect evaporator to any grades more than 50 percent acid. Most of the wet process acid is being converted to high concentration chemical fertilizers as discussed in the flow chart. Pyrophosphoric acid can be obtained by heating orthophosphoric acid to 250 degrees centigrade.

If you heat the orthophosphoric acid to very high temperature like 900 degrees centigrade then you can get metaphosphoric acid as well Ok.

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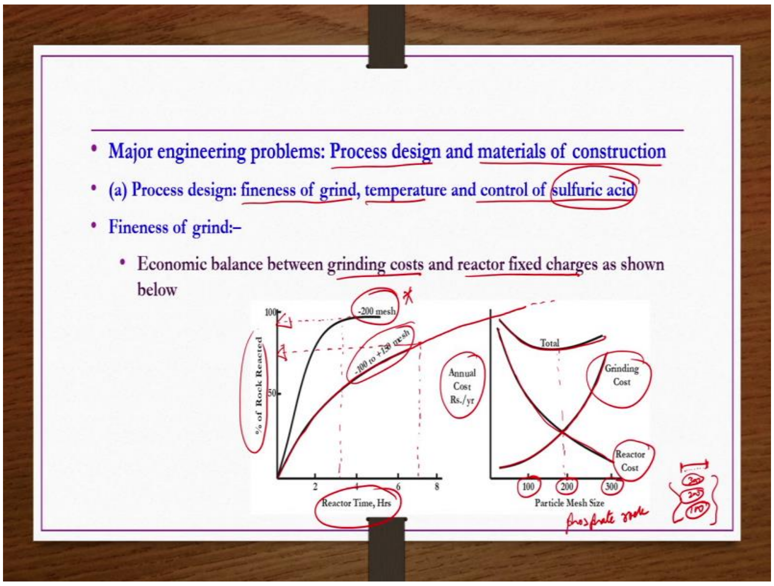

- Major engineering problems: Process design and materials of construction
- (a) Process design: fineness of grind, temperature and control of sulfuric acid
- Fineness of grind:–
  - Economic balance between grinding costs and reactor fixed charges as shown below

Engineering problems; process design and then materials of construction these are the two important parameters that one should be careful while designing this plant as well as operating this plant.

Under the process design, fineness of grind, temperature and then control of sulfuric acid is important because you are producing a phosphoric acid which is less expensive compared to the concentrated sulfuric acid. Using a expensive sulfuric acid you are producing a cheaper phosphoric acid. So, then it has to be properly mitigated right. The sulfuric acid utilization has to be done properly.

So, that is again one of the important engineering process you know engineering problem in such phosphoric acid production plants. Fineness of grinding, grinding as we mentioned that you know size of the rock phosphate after crushing whatever you say that is very essential right. So, if it is bigger size the complete conversion or you know sufficient conversion may not take place. So, it has to be fine enough right.

If you do the fine enough then grinding cost increases and then we know grinding efficiency, efficiency of any size reduction equipment for that matter is very poor. It is less than 20, 25 percent in general right. Why? Because most of the power supplied for the grinding of this ores is utilized for the operation running of the size reduction equipment itself rather than you know size reducing the this rocks ok. So, if you go for getting finer and finer mineral ore from the big rocks then you know your grinding cost will increase ok.

So, accordingly you have to make a judicious you know selection. So, that you do not cross economic cost balance and then you produce financially you know economically feasible products by the plant. For that economic balance between grinding cost and then reactor fixed charges are very essential. And then we can see here if you take annual cost per year.

So, the grinding cost increases you know rather increasing exponentially increasing as you are going for a finer particle. Increasing mesh size in; that means, you are getting finer and finer particles right. This mesh size is nothing, but within one linear inch of you know screen how many openings are there. So, 300 openings are there or 200 openings are there 100 openings are there. If 100 openings are there; that means, it is a bigger opening, 200 intermediate, 300 smallest opening compared to amongst these three right.

So, if you are going for a finest particles so, then you know grinding cost exponentially increasing though if you have the finer particle reactor cost decreasing actually it is a good thing right. So, but grinding cost is very much higher and then grinding is least energy efficient process. So, better what you do you combine them and then total you see and then optimum one you consider.

That is the reason here for this plant we have selected the materials are ground to 200 mesh size, whatever the phosphate rock is there that have been ground to 200 mesh size because based on this consideration. But is it the only one, the reactivity is also important factor. If you take the percentage of rock reacted versus the reaction time if you have a let us say 200 mesh particle. So, then almost complete conversion takes place you know by 3 hours or 2 to 3 hours approximately within that time ok.

You can see here, now most of the conversion takes place you know when the reaction time is approximately 3 hours or slightly more than 3 hours if you have a 200 mesh size particles. But if you have slightly coarser particles not much coarser slightly coarser minus 100 to plus 150 mesh right. And what does it means, by minus 100 and then plus

150 minus 100; that means, particle is retaining on this one and then passing through 150 in between average size this one.

So, then under such condition you can see if you wanted to get the higher conversion more than 90-95 percent you know the reaction time you know it is going on if you extrapolate you know it may be several hours it will take.

But here itself if you take you know to double the time let us say you do you know up to 7 hours you do the reaction then you are not even getting 80 percent conversion you are getting up to approximately 70-75 percent conversion by this size particle.

So, accordingly you have to select this one not only the cost one, but you know reaction time is also important ok. Because size reduction from 150 mesh to 200 mesh is not going to become increase the grinding cost much, but the reactivity is increasing drastically. So, then better you go for this 200 mesh ok. This is the another reason that phosphate rock are ground to 200 mesh if you are using strong sulfuric acid leaching process for production of phosphoric acid from this you know phosphate rock.

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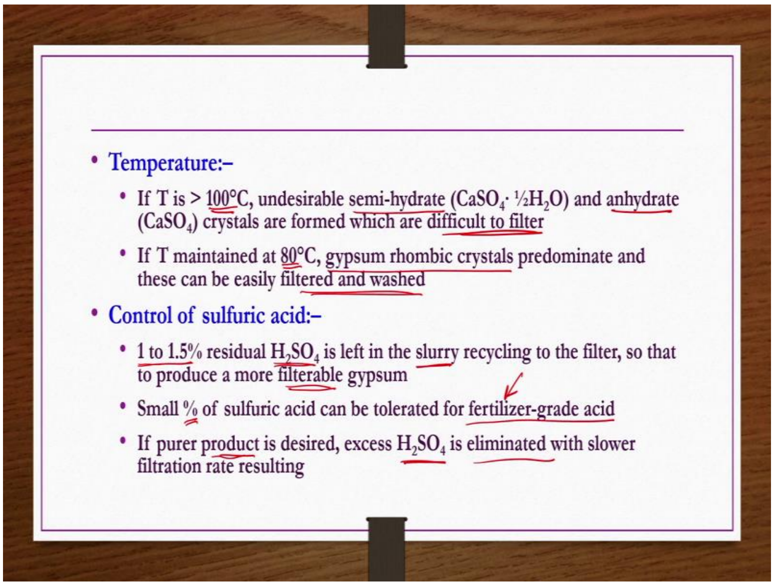

- Temperature:–
  - If T is > 100°C, undesirable semi-hydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) and anhydrate ($CaSO_4$) crystals are formed which are difficult to filter
  - If T maintained at 80°C, gypsum rhombic crystals predominate and these can be easily filtered and washed
- Control of sulfuric acid:–
  - 1 to 1.5% residual H_2SO_4 is left in the slurry recycling to the filter, so that to produce a more filterable gypsum
  - Small % of sulfuric acid can be tolerated for fertilizer-grade acid
  - If purer product is desired, excess H_2SO_4 is eliminated with slower filtration rate resulting

Second one is the temperature if the temperature is more than 100 degree centigrade undesirable semi hydrates of calcium sulfate and then anhydrate calcium sulfate crystals are formed and these are very difficult to filter out. Gypsum can be easily filter out, but these semi hydrates and then an anhydrate calcium sulfate crystals are very difficult to be filtered out to get the acid from the slurry mixture.

If the temperature is maintained to 80 degree centigrade gypsum rhombic crystals formation is predominant and then these are easily filtered and then washed as we have discussed in the flow sheet easily right.

Control of sulfuric acid: Actually, if you have 1 to 1.5 percent sulfuric acid in this slurry so, it is going to be good for the filtration process that has been found. If you have a 1 to 1.5 percent sulfuric acid unreacted sulfuric acid in the slurry of a phosphoric acid and gypsum. So, it is going to be advantageous, how it is going to be advantageous? It makes filtration of gypsum easier.

Further small percentage of sulfuric acid can be tolerated for fertilizer grade acid also because whatever unreacted sulfuric acid or recovered sulfuric acid in the process is there if you are not using for the chemical fertilizer production as we have discussed in the process flow chart you can sell it to the fertilizer industries they can use it for production of fertilizers where small percentage of sulfuric acid is sufficient enough you do not need to have 98 percent sulfuric acid in general.

If purer product is desired then excess H 2 SO 4 is eliminated with a slower filtration rate becoming the result.

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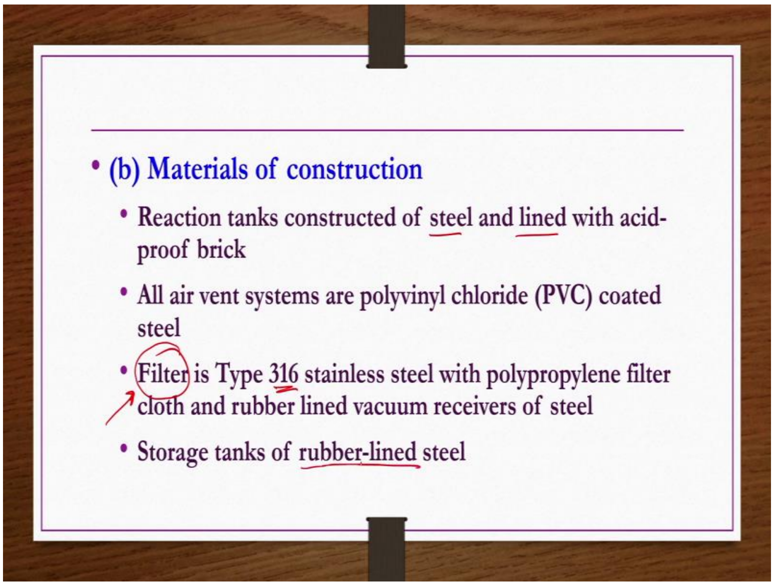

- (b) Materials of construction
  - Reaction tanks constructed of steel and lined with acid-proof brick
  - All air vent systems are polyvinyl chloride (PVC) coated steel
  - Filter is Type 316 stainless steel with polypropylene filter cloth and rubber lined vacuum receivers of steel
  - Storage tanks of rubber-lined steel

Next materials of construction, this is again important parameter because wherever acids are there materials of construction becomes very important. Reaction tanks constructed of steel and then lined with acid proof brick. All air vent systems are PVC coated with steel, filter because now the filter is playing very important role here, the filter is separating the phosphoric acid and then gypsum from it then only you are able to use the phosphoric acid and then gypsum separately for different products.

So, this is again very important and then since this slurry phosphoric acid is also there and then some amount of unreacted sulfuric acid is also there. So, because of that one the material of construction for this filter is also very essential very important for this type 316 stainless steel that is SS316 with polypropylene filter cloth and rubber lined vacuum receivers of steel are provided. Storage tanks are usually rubber-lined steel tanks are used.

Now, we see phosphoric acid production by wet process which is the second one hydrochloric acid leaching. Ok.

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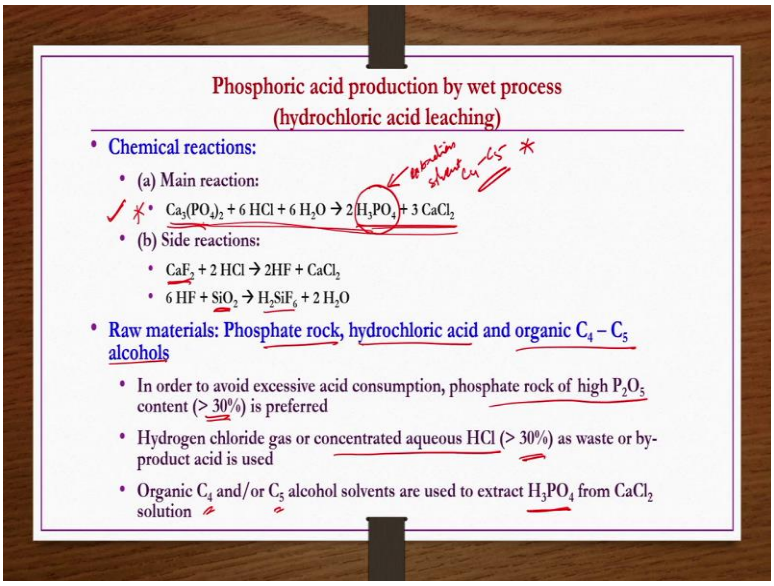

Phosphoric acid production by wet process
(hydrochloric acid leaching)

- Chemical reactions:
  - (a) Main reaction:
    - $Ca_3(PO_4)_2 + 6\,HCl + 6\,H_2O \rightarrow 2\,H_3PO_4 + 3\,CaCl_2$
  - (b) Side reactions:
    - $CaF_2 + 2\,HCl \rightarrow 2HF + CaCl_2$
    - $6\,HF + SiO_2 \rightarrow H_2SiF_6 + 2\,H_2O$
- Raw materials: Phosphate rock, hydrochloric acid and organic $C_4 - C_5$ alcohols
  - In order to avoid excessive acid consumption, phosphate rock of high P_2O_5 content (> 30%) is preferred
  - Hydrogen chloride gas or concentrated aqueous HCl (> 30%) as waste or by-product acid is used
  - Organic C_4 and/or C_5 alcohol solvents are used to extract H_3PO_4 from $CaCl_2$ solution

extraction solvent $C_4 - C_5$

Here the reactions if you take calcium phosphate react with the hydrochloric acid and water to give a mixture of phosphoric acid and then calcium chloride solution. It is a solution and then its mixture there. So, then from this mixture you have to extract phosphoric acid.

So, extraction has to be done. So, some solvent is required and then for this purpose butyl or amyl alcohols are used as solvents. So, now these are again expensive solvents to be frank and then you are you know producing cheaper phosphoric acid. So, then recovery of the solvent is again important that we are going to see in the process anyway.

Side reactions; calcium fluoride react with the hydrochloric acid to give hydrogen fluoride and then this react with silicon to give this H 2 SiF 6 and then water right. See; these all these things are you know present in the rock because we are taking the rock. Phosphate rock when you take actually it is a fluorapatite you know mineral.

It is also having the fluoride. So, all these reactions are possible, but primarily this is the reaction that you should concentrate and then you should make sure that this reaction progress at a better pace compared to the other reactions.

So, according the process operation in terms of the control of the flow rates of the acids etcetera, temperature etcetera, temperature etcetera has to be done. So, that this reaction predominates.

Raw materials; obviously, phosphate rock and then hydrochloric acid and then organic C 4 to C 5 alcohols which act as a solvents for the extraction of this phosphoric acid from the solution of phosphoric acid and calcium chloride. In order to avoid excessive acid consumption phosphate rock of high P 2 O 5 content more than 30 percent is preferred.

Hydrogen chloride gas or concentrated aqueous hydrogen chloride more than 30 percent purity as waste or byproduct acid is used for this process and then organic C 4 and or C 5 alcohol solvents are used to extract phosphoric acid from calcium chloride solution.

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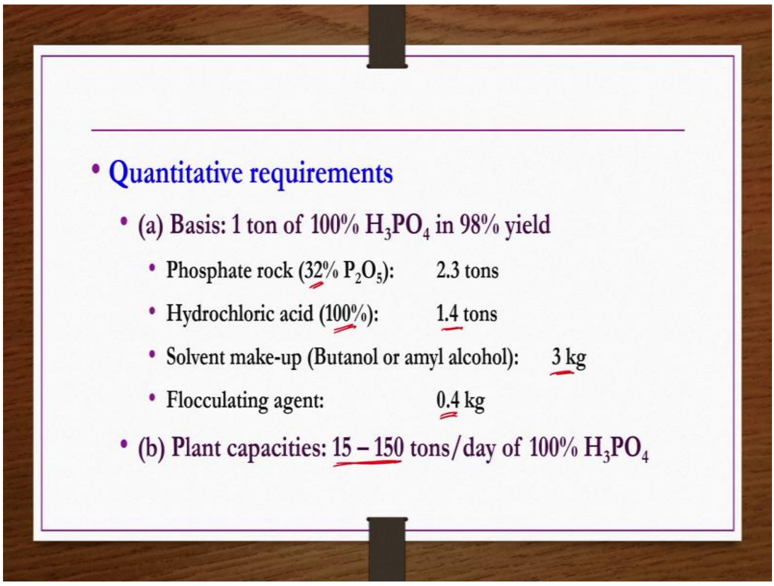

- Quantitative requirements
  - (a) Basis: 1 ton of 100% H_3PO_4 in 98% yield
    - Phosphate rock (32% P_2O_5): 2.3 tons
    - Hydrochloric acid (100%): 1.4 tons
    - Solvent make-up (Butanol or amyl alcohol): 3 kg
    - Flocculating agent: 0.4 kg
  - (b) Plant capacities: 15 – 150 tons/day of 100% H_3PO_4

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Quantitative requirements if you see basis 1 ton of 100 percent pure phosphoric acid in 98 percent yield if you wanted to produce phosphate rock more than 30 percent that is 32 percent P 2 O 5 if you are using 2.3 tons required. Hydrochloric acid if you are using 100 percent pure then 1.4 tons of hydrochloric acid is required. Solvent makeup solvent butanol or amyl alcohol 3 kgs are required. Flocculating agent 0.4 kgs required. Plant capacities: 15 to 150 tons per day for the production of 100 percent pure phosphoric acid.

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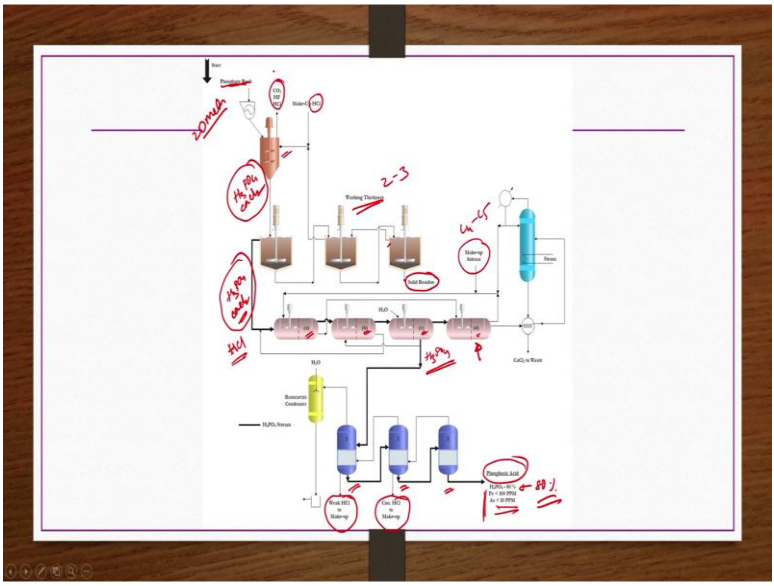

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Now, flow sheet we discuss first then we go to the process description which is the description of this flow sheet itself. Here in this process whatever the phosphate rock is there that is ground to 20 mesh size and then sent to a dissolver where makeup HCl along with the makeup water etcetera are provided for the proper mixing right.

So, in the mixer whatever the reaction takes place right and then you get a H 3 PO 4 and then CaCl 2 phosphoric acid and then calcium chloride solution along with the impurities you get here. So, this mixture what you do you take a series of a washing thickness 2 to 3 thickness are there right. So, in that one you take and then do the processing.

Right here what you do, the mixture when you take to the first thickener overflow whatever is there that is primarily having H 3 PO 4 and then calcium chloride primarily. That overflow is taken to a series of extract extractors, where the extraction of a phosphoric acid is taking place using the makeup solvent that is C 4 or C 5 alcohols ok.

Whatever the solids from the bottom of first thickener is there that is taken to the second thickener right, whatever the overflow from the second thickener is there that is having mostly HCl acid or some traces of H 3 PO 4 CaCl 2 may also be there. They are all taken as a makeup and then sent back to the mixer. Then the slurry or the solids from the bottom of the second thickener is taken to the third thickener right.

So, whatever the overflow of the third thickener is there. So, that is going to the second thickener right and then solid residue is collected from the bottom of the third thickener ok. Overflow of the first thickener is primarily having phosphoric acid and calcium chloride solution mixture. So, that is taken to the extraction unit a series of extractors whereas, the underflows from the thickeners are primarily having the solids with a some traces of some minor amount of a HCl.

So, those things are taken to the subsequent second and third washing thickeners. There may be some plants there are only two thickeners some plants more than three thickeners are also there right. Overflows from these thickness are you know from the third thickener overflow is taken to the second one and then from the second thickener whatever the overflow is there that is taken as a make up HCl and then sent back to the mixer ok.

Now, whatever the overflow of the first thickener is there that is taken to a extractor number a right. There are batteries or series of extractors are there a, b, c and then d are the designations we have given. This overflow from the first thickener is primarily having and the solution of calcium chloride with H 3 PO 4 mixed in. So, that solution is taken here and then to this extractor a this make up solvent butyl or amyl alcohol solvent is provided from the top right.

So, from here first extractor whatever the raffinate is there that is taken to the last extractor d whereas, the whatever extractant is there that is taken to the second extractor right. From here whatever the raffinate is there that is taken back to the first extractor along with the calcium chloride and H 3 PO 4 solution.

Whereas, the extractant from the second extractor is going to the third extractor as feed, from the third extractor primarily you get you know almost pure H 3 PO 4 solution as a you know product and then that is taken to a triple effective operator because it may also be containing some amount of HCl.

We are saying that calcium chloride H 3 PO 4 solution, but some amount of HCl and other impurities may also be there that we are clearly understand it ok. So, that here after this third extractor whatever the solution that you are getting H 3 PO 4 is the primary content and in some traces of HCl may be there so, those traces are the minor impurities of HCl are removed in triple effective operator right.

So, in the first effective operator weak HCl is recovered and sent as a makeup solvent to the mixer. From the second effective operator concentrated HCl you get that again you take it as a kind of a makeup for the mixer and from the third effective operator bottom you will be getting phosphoric acid. So, these H 3 PO 4 you get here is having 80 percent purity ok. Iron and arsenic kind of impurities whatever possible because of the rock they are also in limited quantities like in few PPMs ok as shown here right.

So, here from the fourth extractor whatever the solution is there that is primarily calcium chloride solution along with the solvent that is taken to a steam stripper where solvent is recovered and then sent back to the first extractor for the continuation of the process as shown in the flow sheet ok. This is the process for the production of phosphoric acid concentrated phosphoric acid using hydrogen chloride leaching process.

Now, we see the description of the process here.

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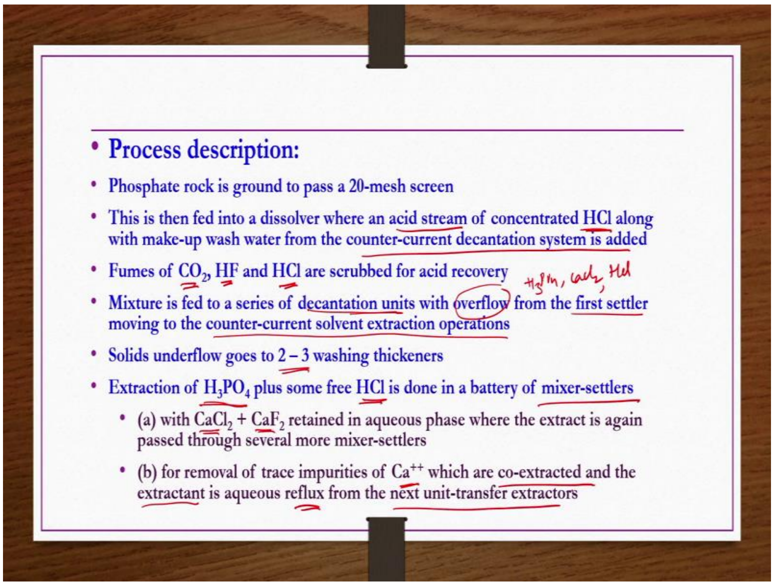

- **Process description:**
- Phosphate rock is ground to pass a 20-mesh screen
- This is then fed into a dissolver where an acid stream of concentrated HCl along with make-up wash water from the counter-current decantation system is added
- Fumes of CO_2, HF and HCl are scrubbed for acid recovery
- Mixture is fed to a series of decantation units with overflow from the first settler moving to the counter-current solvent extraction operations
- Solids underflow goes to 2 – 3 washing thickeners
- Extraction of H_3PO_4 plus some free HCl is done in a battery of mixer-settlers
  - (a) with $CaCl_2$ + CaF_2 retained in aqueous phase where the extract is again passed through several more mixer-settlers
  - (b) for removal of trace impurities of Ca^{++} which are co-extracted and the extractant is aqueous reflux from the next unit-transfer extractors

H_3PO_4, $CaCl_2$, HCl

Phosphate rock is ground to pass it 20-mesh screen. This is then fed into a dissolver where an acid stream of concentrated HCl along with make-up wash water from the counter current decantation system is added. Fumes of CO 2, HF and HCl are scrubbed for acid recovery that is shown here whatever the fumes of HCl, HF and CO 2 are there they are taken to the acid recovery for the recovery of acid.

Then mixture is fed to a series of decantation or thickener units with overflow from the first settler moving to the counter current solvent extraction operation. This overflow contains primarily H 3 PO 4, CaCl 2 and then HCl ok. Solids underflow goes to 2 to 3 washing thickness. Extraction of H 3 PO 4 plus some free HCl is done in a battery of mixer settlers.

In the first one calcium chloride and then calcium fluoride retained in aqueous phase where the extract is again passed through several more mixer settlers b and c as we have seen in this flow chart. In the b extractor it is for removal it is for removal of traces impurities of calcium fluoride or calcium chloride or whatever are present which are co extracted and the extractant is aqueous reflux from the next unit transfer extractors.

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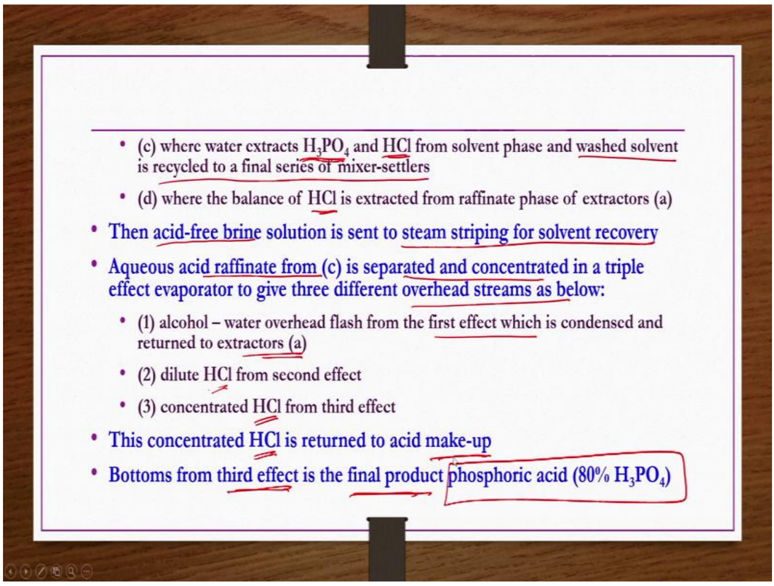
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- (c) where water extracts H_3PO_4 and HCl from solvent phase and washed solvent is recycled to a final series of mixer-settlers
- (d) where the balance of HCl is extracted from raffinate phase of extractors (a)

- Then acid-free brine solution is sent to steam striping for solvent recovery
- Aqueous acid raffinate from (c) is separated and concentrated in a triple effect evaporator to give three different overhead streams as below:
  - (1) alcohol – water overhead flash from the first effect which is condensed and returned to extractors (a)
  - (2) dilute HCl from second effect
  - (3) concentrated HCl from third effect
- This concentrated HCl is returned to acid make-up
- Bottoms from third effect is the final product phosphoric acid (80% H_3PO_4)

C, extractor is the one where water extracts H 3 PO 4 and HCl from solvent phase and washed solvent is recycled to a final series of mixer settlers where the balance of HCl is extracted from the raffinate phase of extractors a. This acid free brine solution is sent to steam stripping for solvent recovery. So, that solvent can be used in the first thickener again for the extraction process and then cycle continues.

Aqueous acid raffinate from c is separated and concentrated in a triple effect evaporator to give three different overhead streams as below. First one alcohol water overhead flash and from the first effect which is condensed and written to the extractors a. Dilute HCl from second effect and then concentrated HCl from the third effect you can get and then this concentrated HCl is returned to acid makeup.

Bottoms from the third effect is the final product which is nothing, but phosphoric acid 80 percent purity.

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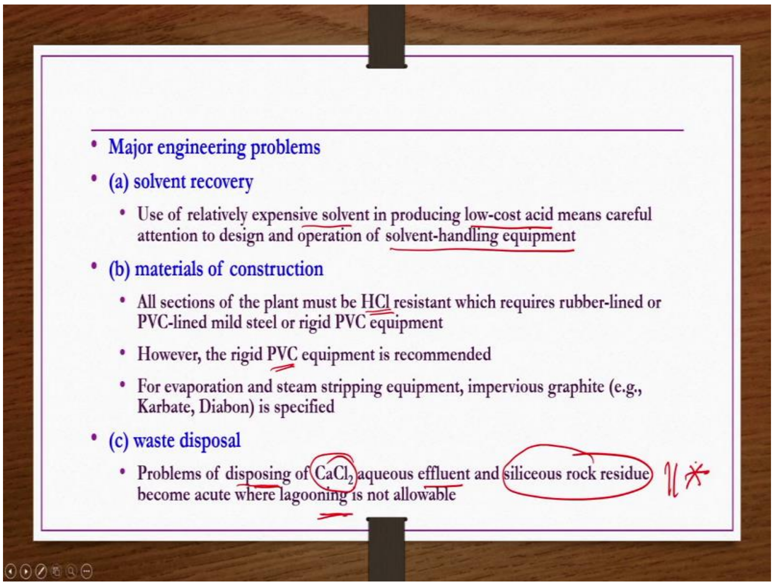

- Major engineering problems
- (a) solvent recovery
  - Use of relatively expensive solvent in producing low-cost acid means careful attention to design and operation of solvent-handling equipment
- (b) materials of construction
  - All sections of the plant must be HCl resistant which requires rubber-lined or PVC-lined mild steel or rigid PVC equipment
  - However, the rigid PVC equipment is recommended
  - For evaporation and steam stripping equipment, impervious graphite (e.g., Karbate, Diabon) is specified
- (c) waste disposal
  - Problems of disposing of $CaCl_2$ aqueous effluent and siliceous rock residue become acute where lagooning is not allowable

Major engineering problems if you see some of them like you know solvent recovery as we mentioned you are using expensive solvent to produce low cost acid. So, the recovery of solvent is very much essential.

Then materials of construction wherever the acids especially strong acid like you know concentrated sulfuric acid is there, then material of construction is another important factor to be considered, then waste disposal. Lot of solids is being generated how are you disposing these are the problems in addition to the other engineering problems.

Like you know under solvent recovery use of relatively expensive solvent in producing low cost acid means careful attention to design and operation of solvent handling equipment is required.

Materials of construction all sections of the plant must be HCl resistant which require rubbers rubber lined or PVC lined mild steam or rigid PVC equipment. However, rigid PVC equipment is recommended. For evaporation and steam stripping equipment, impervious graphite is specified.

Waste disposable problems of disposing of calcium chlorides, aqueous effluent and then siliceous rock residue become acute where lagooning is not allowable. So, this is another problem one should carefully consider how are you disposing this liquid effluents and then solid wastage.

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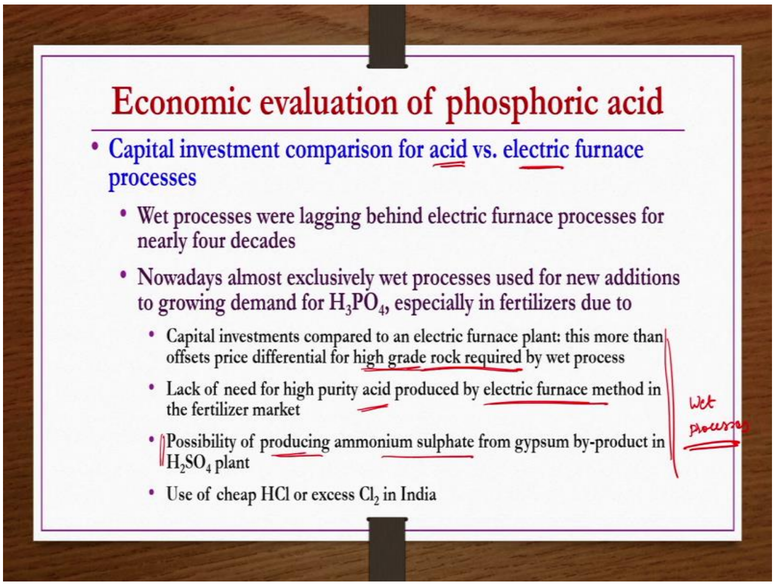

Economic evaluation of phosphoric acid

- Capital investment comparison for acid vs. electric furnace processes
  - Wet processes were lagging behind electric furnace processes for nearly four decades
  - Nowadays almost exclusively wet processes used for new additions to growing demand for H_3PO_4, especially in fertilizers due to
    - Capital investments compared to an electric furnace plant: this more than offsets price differential for high grade rock required by wet process
    - Lack of need for high purity acid produced by electric furnace method in the fertilizer market
    - Possibility of producing ammonium sulphate from gypsum by-product in H_2SO_4 plant
    - Use of cheap HCl or excess Cl_2 in India

Wet process

Now, coming to the economic evaluation of phosphoric acid different factors one should consider. Capital investment comparison acid versus electric furnace processes which one should you use, three processes were there blast furnace processes no more competitive, now you have two processes electric furnace processes and wet processes which one should you use that is very essential right.

Although almost for 4 decades or 5 decades this electric furnace process dominated over the wet process. However, nowadays whatever the plants that are available for the production of phosphoric acid they are primarily based on the wet processes, this is because capital investment compared to electric furnace plant, the wet process plants you know they required less capital investment.

So, that money probably you can make use for high grade rock you know required by the wet process. Then lack of need for high purity acid because whatever the phosphoric acid you produce primarily more than 90 percent of it is being used for the fertilizer production and then for fertilizer production you do not need such high purity acids actually.

Whereas, this electric furnace method it produce produces very high purity acid ok, that much high purity acid is not at all required if at all if you are using this acid for the fertilizer production. So, this is another reason that it is better to go for wet process.

Then possibility of producing ammonium sulphate from gypsum by product in H 2 SO 4 plant is there which is missing in the electric furnace plant. So, that is one. So, this is a wet process or acid process versus electric furnace process now you realize that because of these factors wet processes where leaching of you know strong and weak acids are possibilities are there.

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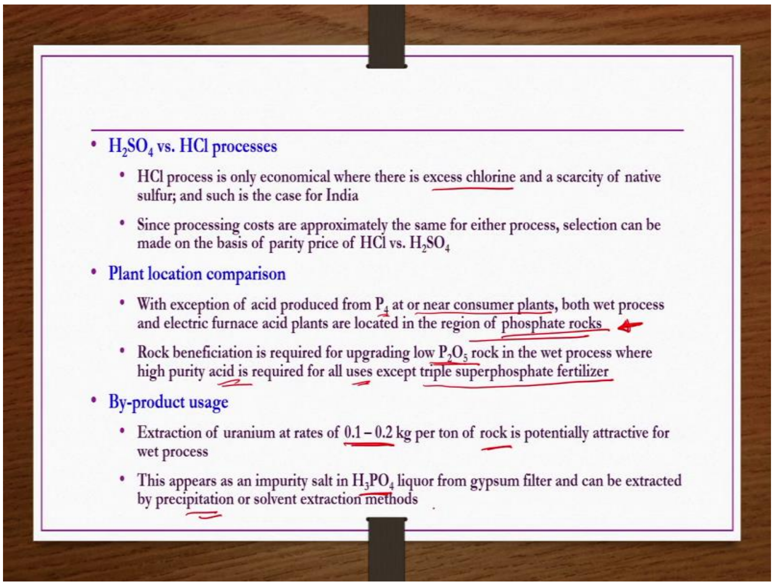

- H_2SO_4 vs. HCl processes
  - HCl process is only economical where there is excess chlorine and a scarcity of native sulfur; and such is the case for India
  - Since processing costs are approximately the same for either process, selection can be made on the basis of parity price of HCl vs. H_2SO_4
- Plant location comparison
  - With exception of acid produced from P_4 at or near consumer plants, both wet process and electric furnace acid plants are located in the region of phosphate rocks
  - Rock beneficiation is required for upgrading low P_2O_5 rock in the wet process where high purity acid is required for all uses except triple superphosphate fertilizer
- By-product usage
  - Extraction of uranium at rates of 0.1 – 0.2 kg per ton of rock is potentially attractive for wet process
  - This appears as an impurity salt in H_3PO_4 liquor from gypsum filter and can be extracted by precipitation or solvent extraction methods

So, now, within the wet process which one you use right whether you go for H 2 SO 4 process or HCl process, HCl process is only economical where there is excess chlorine and a scarcity of native sulfur. So; obviously, in India that is the issue. So, then we can go for HCl process.

So, if that is at all not a problem for a given plant you know if they are already having you know H 2 SO 4 from the other sources other plants. So, then selection has to be done based on the cost how much are you how at what cost are you know getting this H 2 SO 4 or HCl for the production of a phosphoric acid. So, that based on that parity price of these two you have to select otherwise you know both of them are almost same.

Plant location comparison, with exception of acid produced from phosphorus, 8 or near consumer plant both wet processes as well as electric furnace processes are located in the region of phosphate rocks because we understand this you know phosphate rock as well as you know phosphorus these things are very poisonous.

And then often the technicians labour working in the plant they get ill because of inhaling this ah phosphorus you know vapors that are present in the gases though they are present in the minute near the plant you cannot avoid them anyway . So, because of such reasons these are located at the phosphate rocks.

Rock beneficiation is required for upgrading low P 2 O 5 rock in the wet process where high purity acid is required for all uses except the triple super phosphate fertilizer production that we are going to discuss in the next lecture.

By-product usage what happens in calcium chloride effluent whatever you are getting it is it has been found at some amount of uranium is present. So, extraction of uranium at rates of 0.1 to 0.2 kg per ton of rock is potentially attractive for wet processes this appears as an impurity salt in H 3 PO 4 liquor from gypsum filter and can be extracted by precipitation or solvent extraction method.

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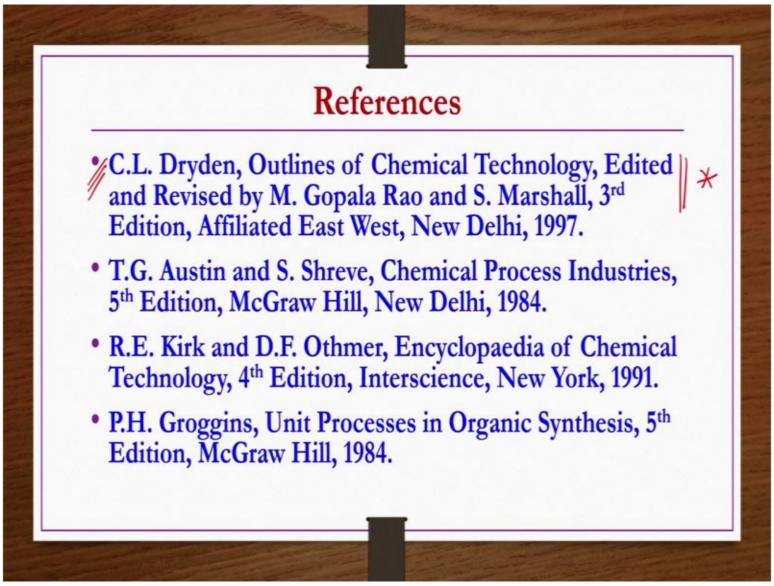

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References for this lecture the references are provided here, but the entire lecture is prepared from this reference book C.L. Dryden that is outlines of chemical technology edited by Gopala Rao and Marshall third edition, all the details presented in this lecture can be found in this reference book.

Thank you.