Inorganic Chemical Technology
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Lecture - 20
Phosphorus Industries - Phosphates

Welcome to the MOOCs course Inorganic Chemical Technology, the title of today's lecture is Phosphorus Industries - Phosphates. Recapitulation of previous two lectures we started discussions on phosphorus industries.

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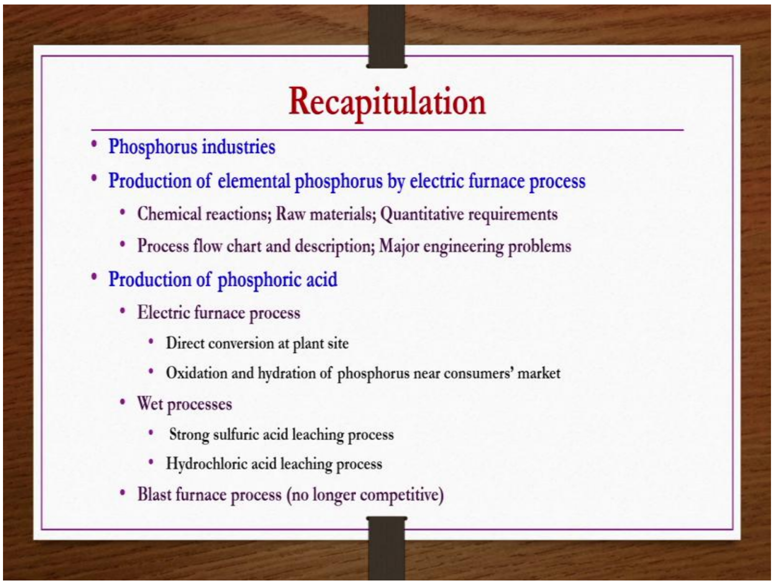

Recapitulation

- Phosphorus industries
- 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)

How it compares with nitrogen industry etcetera. Then we started discussion on production of elemental Phosphorus by electric furnace process under which we discussed its chemical reactions, raw materials, quantitative requirements, process flow chart and description, major engineering problems, economics and uses etcetera. Those things we have discussed.

Then we started our discussion on production of phosphoric acid, we realized three categories. The first category is electric furnace process under which we had discussed two processes: direct conversion at plant site and oxidation and hydration of phosphorus near consumers' market. In the second category we had wet processes where we discussed two methods: strong acid leaching process and then hydrochloric acid leaching process for the production of phosphoric acid.

Third category of blast furnace process which is no more competitive so, that we have not discussed. In this lecture we conclude the phosphorus industries by discussing about different types of phosphates ok. Let us start with calcium phosphates.

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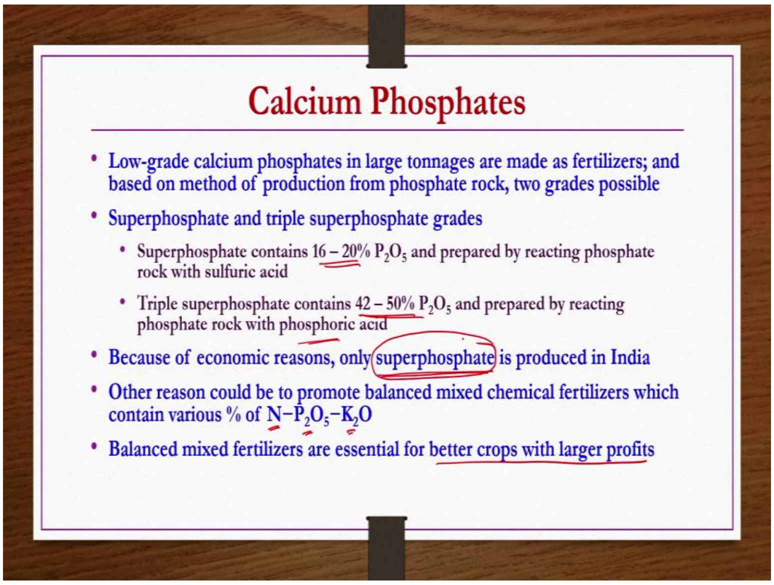

Calcium Phosphates

- Low-grade calcium phosphates in large tonnages are made as fertilizers; and based on method of production from phosphate rock, two grades possible
- Superphosphate and triple superphosphate grades
  - Superphosphate contains 16 – 20% P_2O_5 and prepared by reacting phosphate rock with sulfuric acid
  - Triple superphosphate contains 42 – 50% P_2O_5 and prepared by reacting phosphate rock with phosphoric acid
- Because of economic reasons, only superphosphate is produced in India
- Other reason could be to promote balanced mixed chemical fertilizers which contain various % of $N-P_2O_5-K_2O$
- Balanced mixed fertilizers are essential for better crops with larger profits

Low grade calcium phosphates are produced in large tonnages so as to use as fertilizers and based on the method of production from phosphate rock there are two types or two grades of calcium phosphates are possible. Methods of production in the sense method is same, but the basic acid that is we are using to produce this calcium phosphate is different.

If you are reacting phosphate rock with sulfuric acid then you get a super phosphate, right. If you react phosphate rock with phosphoric acid then you get a triple super phosphate. These are the two grades possible. Actually, they are differ not by the acid that has been used for the reaction with phosphate rock, but also with what is the percentage of P 2 O 5 that is present in this phosphate.

So, super phosphate and triple super phosphate are two grades possible. Super phosphate contains 16 to 20 percent of P 2 O 5 and prepared by reacting phosphate rock with sulfuric acid whereas, the triple super phosphate contains 40 to 50 percent P 2 O 5 which is very high and it is prepared by reacting phosphate rock with phosphoric acid, ok. However, in India because of economic reasons we produce only super phosphates.

This is not the only reason the other reason is that in order to have a balanced mixed fertilizers with appropriate percentage of N, P, K it is essential to produce phosphates as well, right. So, why balanced mixed chemical fertilizers are important? Because they are very essential for better crops with larger profits so, these are the reason that in general mostly in India we prepare super phosphates not the triple super phosphate.

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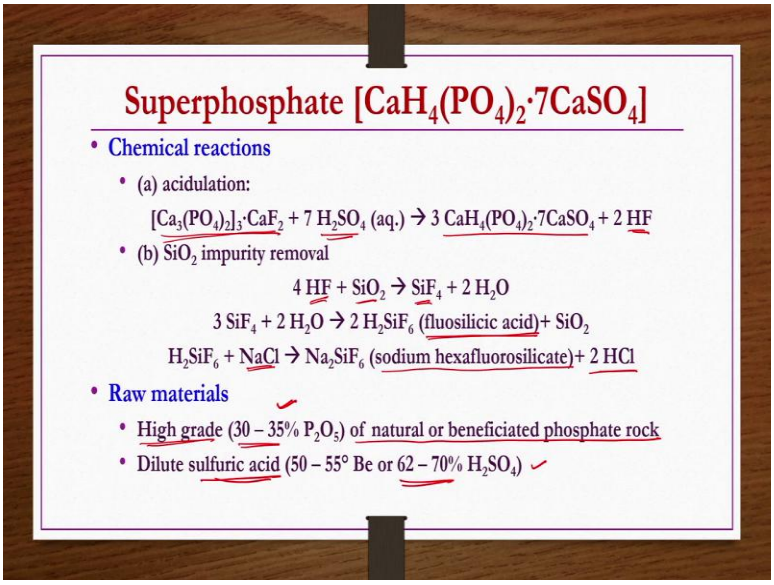

Superphosphate $[CaH_4(PO_4)_2 \cdot 7CaSO_4]$

- Chemical reactions
  - (a) acidulation:

$$[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 7\ H_2SO_4\ (aq.) \rightarrow 3\ CaH_4(PO_4)_2 \cdot 7CaSO_4 + 2\ HF$$

  - (b) SiO_2 impurity removal

$$4\ HF + SiO_2 \rightarrow SiF_4 + 2\ H_2O$$

$$3\ SiF_4 + 2\ H_2O \rightarrow 2\ H_2SiF_6\ \text{(fluosilicic acid)} + SiO_2$$

$$H_2SiF_6 + NaCl \rightarrow Na_2SiF_6\ \text{(sodium hexafluorosilicate)} + 2\ HCl$$

- Raw materials
  - High grade (30 – 35% P_2O_5) of natural or beneficiated phosphate rock
  - Dilute sulfuric acid (50 – 55° Be or 62 – 70% H_2SO_4)

Now, we start discussion on super phosphate its reactions, raw materials, production method, engineering problems, etcetera that we are going to discuss now. Chemical reactions two reactions are there one is the acidulation reaction another one is the impurity removal reaction. Under the acidulation reaction whatever the fluorapatite mineral of phosphate rock is there that react with the sulfuric acid to give super phosphate and then hydrogen fluoride.

Second reaction SiO 2 impurity removal it is done by reacting SiO 2 with HF to get silicates and water. The silicates again react with water to produce fluosilicic acid, fluosilicic acid is produced by this reaction which further react with sodium chloride to produce sodium hexafluorosilicate ok, along with the HCl, right. Raw materials; obviously, low grade phosphate is not suitable because these are the super phosphate.

So, then P 2 O 5 has to be in higher content, ok. So, you need high grade of natural or beneficiated phosphate rock which is containing 30 to 35 percent P 2 O 5 plus dilute sulfuric acid 60 to 70 percent 60 to 70 percent pure sulfuric acid is sufficient. But phosphate rock has to be high grade having 30 to 35 percent P 2 O 5. Because the name itself they contain super phosphate; that means, whatever this P 2 O 5 that is going to be present in the final fertilizer that you produce is going to be high.

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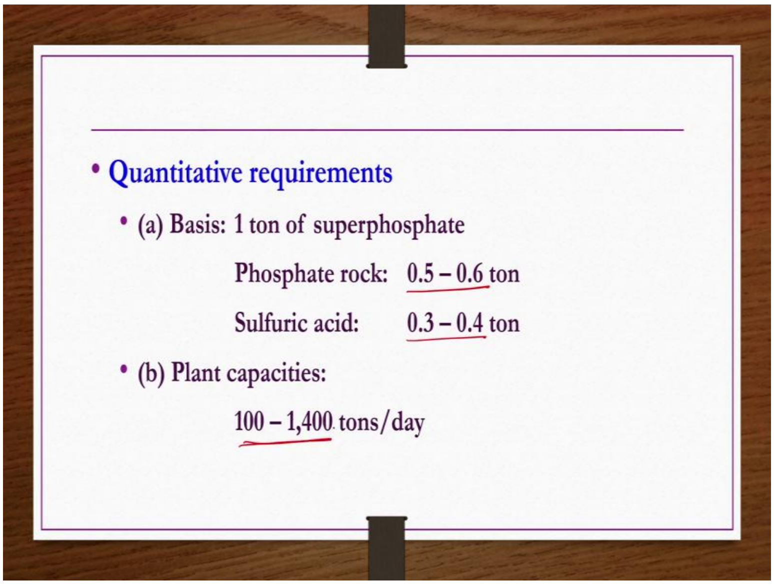

- **Quantitative requirements**
  - (a) Basis: 1 ton of superphosphate
    Phosphate rock: 0.5 – 0.6 ton
    Sulfuric acid: 0.3 – 0.4 ton
  - (b) Plant capacities:
    100 – 1,400 tons/day

Quantitative requirements basis 1 ton of super phosphate production, if you wanted to do then you need to have phosphate rock 0.5 to 0.6 tons and then sulfuric acid 0.3 to 0.4 tons. Plant capacities usually vary between 100 to 1400 tons per day.

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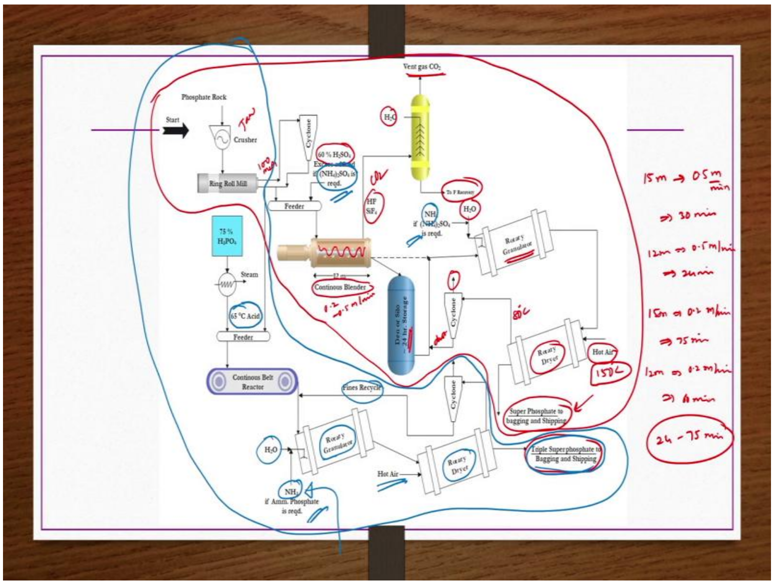

Now, here we have a flow chart in which we are discussing production of super phosphate as well as the triple super phosphate. First, we concentrate on the super phosphate. So, you concentrate on this part of the flow chart as of now, ok. Whatever the phosphate rock is there that you crush in a jaw crusher and then whatever the material is there that you further ground in ring roll mill or hammer mill to a size of 100 mesh, it is very essential ok.

So, when you crush and ground it to 100 mesh that material you take it to the cyclone to remove the fines and then you get back you know those fines to the feeder. To this feeder 60 percent H 2 SO 4 is supplied, right. This 60 percent H 2 SO 4 and then this 100 mesh size or phosphate rock mineral you take into a feeder mixer and then you take into a continuous blender which is approximately 12 to 15 meters length.

This feeder when it comes into the reactor it reaction takes place completely almost completely because it is 12 to 15 meters length and then this reactor is having a shaft to which a blade is provided. So, then when the shaft rotates the rotation of the material takes place. So, whatever the material is coming here the product that is gradually taken towards the other end.

By the material comes to other end the reaction is almost complete because this rod whatever is there which is having a blade that is moving at a speed of 0.2 to 0.5 meters per minute. Let us say you have a 15 meters blender and then you are feeding the speed is at approximately 0.5 meters per minute so, then approximately 30 minutes it takes for the material to pass through the entire reactor.

Let us say if you have a reactor of 12 meters and then it is moving at 0.5 meter per minute then approximately 24 minutes it takes, ok. Let us say you have a 15 meters reactor, but you are moving it only smaller velocity 0.2 meters per minute then approximately 75 minutes it will be there. And then let us say if you take 12 meters and then it moves at 0.2 meters per minute velocity then approximately 60 minutes.

So, a minimum of 24 to maximum of 75 minutes residence time is possible depending on the speed at which you are rotating in this one. And then this time itself is sufficient for the you know mixture to complete the reaction. That means almost all reaction would be complete by the moment mixture enter the entry of the reactor and then leaves the reactor.

This continuous blender is nothing but the reactor here in this one only reaction is taking place, right. So, that product you can directly take to a rotary granulator which is a cylindrical drum. So, which is rotating and then to this drum H 2 O water is sprayed so, that the granules will takes place.

When this drum rotates you know whatever the mixture is that forms that takes in a granular form. Those granules are taken to the rotary dryer, right. So, this rotary dryer again a kind of cylindrical drum which rotates and then to this drum hot air approximately at 150 degree centigrades is provided.

So, that you know what happens the granules whatever coming from the rotary granular they will be dried in this rotary dryer and then moisture content would be less than 0.5 or less than 1 percent of moisture content. So, almost dry super phosphate is taken as a product here from the rotary dryer.

Whatever the aid that is hot air is circulated for the material to dry. So, that will be going out with certain temperature like 80 degree centigrade or something, but it may be also containing the dust of the whatever the phosphate that you are taking right, super phosphate you have produced.

So, what you do you take that gas hot gas to the cyclone separator where dust you collect from the bottom and then mix with the product mixture and then send back to the rotary granulator again for the makeup of the size whereas, the clean air you can take off approximately, right.

So, older methods you know reaction was not completing within the prescribed time of 24 to 75 minutes in general. So, then the mixture is in general stored in den or silo for approximately 24 hours to complete the reaction. And then that mixture is again taken to the rotary granulator either way. But however, nowadays having sophisticated blender.

So, then reaction completes within the prescribed time of less than 1 and of 2 hours, ok. In this mixture blender the reaction when it goes on flourides and then CO 2 would be forming. So, there those gases are taken to a scrubber where they are scrubbed with water to recover the flow rates and then vent gas CO 2 is taken from the top, ok.

So, this is the process the triple phosphate process is also here. So, we can discuss here itself because it is almost similar, right. So, the triple super phosphate production is shown here. Here now you have to concentrate on this part of the flow chart, right. So, whatever the phosphate rock is there that you crush in a jaw crusher, then take it to the ring roll mill or a hammer mill to reduce the material to 100 mesh size.

That material along with a preheated phosphoric acid, phosphoric acid is preheated to the 65 degree centigrade and then the preheated phosphoric acid and then this size reduced ground phosphate rock is taken to a feeder continuous feeder and then that is taken to the continuous belt reactor where the reaction completes, alright.

So, when the reaction completes by the end of the belt of the reactor you know you get the products those product is nothing but the wet triple phosphate along with the some impurities, right. So, then what you do? Mostly the impurities you can remove by the subsequent processes otherwise you know in most of the impurities are taken off from the reactor in the similar way like by using the scrubber method etcetera, right.

The product what you do the slurry mixture you can take to a rotary granulator which is rotating. So, because of the rotation of the drum whatever the mixture is there in the reactor that gets granulated because of the you know water that is being sprayed and then rotation action.

So, then it forms the granules, these granules are taken to a rotary dryer to which hot air is supplied. So, that these granules can be dried and then moisture content reduces to approximately less than 1 or 0.5 percent something like that. So, almost dry super phosphate you can take as a product from here.

So, when you dry this one because of the hot air some of the fines may also be going out along with the air which is slightly cool you know 80 degree something like that inlet air is at 150 degree centigrade something like that. So, this air hot air along with the dust is taken to the cyclones operator where the clean air is taken from the top whereas, the fines are recycled to the granulator for the size makeup of in the rotary granulator again.

Now, in either of the process in the sense the super phosphate as well as the triple super phosphate ammonia is being added to the rotary granulator. This option is there if you wanted to produce a complete mixed fertilizer having both N and P then only you have to do. Otherwise, if you want only super phosphates then you do not need to add this ammonia to the granulator.

In the case of super phosphates not only ammonia ammonium sulfate is also added to the feeder along with the sulfuric acid and then phosphate rock if you wanted to produce balanced nitrogen phosphorous fertilizer rather than individual phosphate itself. So, these things are optional if you wanted to increase the N content in the mixed N P fertilizer, ok. So, both super phosphate and triple super phosphate manufacturing we have seen in the flow chart here.

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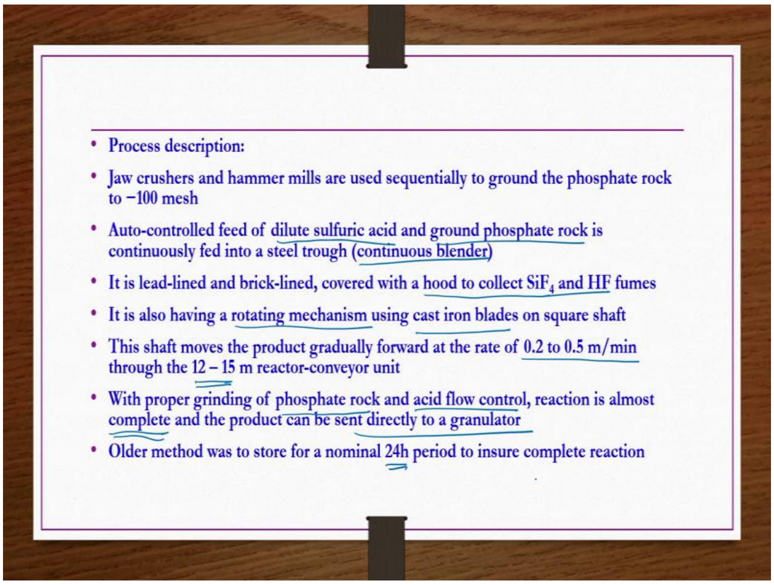

- Process description:
- Jaw crushers and hammer mills are used sequentially to ground the phosphate rock to −100 mesh
- Auto-controlled feed of dilute sulfuric acid and ground phosphate rock is continuously fed into a steel trough (continuous blender)
- It is lead-lined and brick-lined, covered with a hood to collect SiF_4 and HF fumes
- It is also having a rotating mechanism using cast iron blades on square shaft
- This shaft moves the product gradually forward at the rate of 0.2 to 0.5 m/min through the 12 – 15 m reactor-conveyor unit
- With proper grinding of phosphate rock and acid flow control, reaction is almost complete and the product can be sent directly to a granulator
- Older method was to store for a nominal 24h period to insure complete reaction

Now, these details we are going to discuss in a process description part as well. Jaw crushers and hammer mills are roll ring mills are used sequentially to ground the phosphate rock to - 100 mesh size. Auto controlled feed of dilute sulfuric acid and then ground phosphate rock is continuously fed into a steel trough which is nothing but continuous blender. It is lead lined and brick lined covered with hood to collect SiF 4 and HF fumes along with the CO 2.

It is also having a rotating mechanism using a cast iron blade on a square shaft. This shaft moves the product gradually forward at the rate of 0.2 to 0.5 meters per minute through the 12 to 15 meter reactor conveyor unit. With proper grinding of phosphate rock and then acid flow reaction is almost complete in this continuous blender itself and then product can be sent directly to a granulator. Older method was to store for a nominal 24 hours period to ensure complete reaction, but nowadays it is not required.

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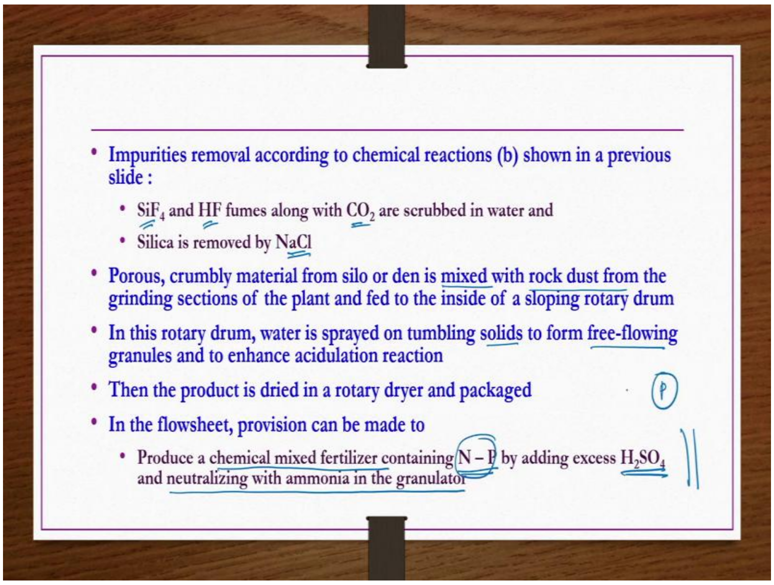

- Impurities removal according to chemical reactions (b) shown in a previous slide :
  - SiF_4 and HF fumes along with CO_2 are scrubbed in water and
  - Silica is removed by NaCl
- Porous, crumbly material from silo or den is mixed with rock dust from the grinding sections of the plant and fed to the inside of a sloping rotary drum
- In this rotary drum, water is sprayed on tumbling solids to form free-flowing granules and to enhance acidulation reaction
- Then the product is dried in a rotary dryer and packaged
- In the flowsheet, provision can be made to
  - Produce a chemical mixed fertilizer containing N – P by adding excess H_2SO_4 and neutralizing with ammonia in the granulator

Now, second part is impurities removal according to chemical reaction shown in a previous slide that reaction we have seen that is Si O 2 reacting with HF to give Si F 4 etcetera those reactions. So, this Si F 4 and then HF fumes along with CO 2 are scrubbed in water whereas, the silica is removed by sodium chloride.

Porous, crumbly material from silo or den is mixed with rock dust from the grinding section of the plant and fed to the inside of the sloping rotary drum. In this rotary drum water is sprayed on tumbling solids to form free flowing granules and to enhance acidulation reaction. Then the product is dried in a rotary dryer and packaged.

In the flowchart provision can be made to produce chemical mixed fertilizer containing N-P by adding excess sulfuric acid and neutralizing with ammonia in the granulator, right. This is the optional and if you wanted to have a mixed chemical fertilizer having both N and P. If you are happy with only P then it is not required.

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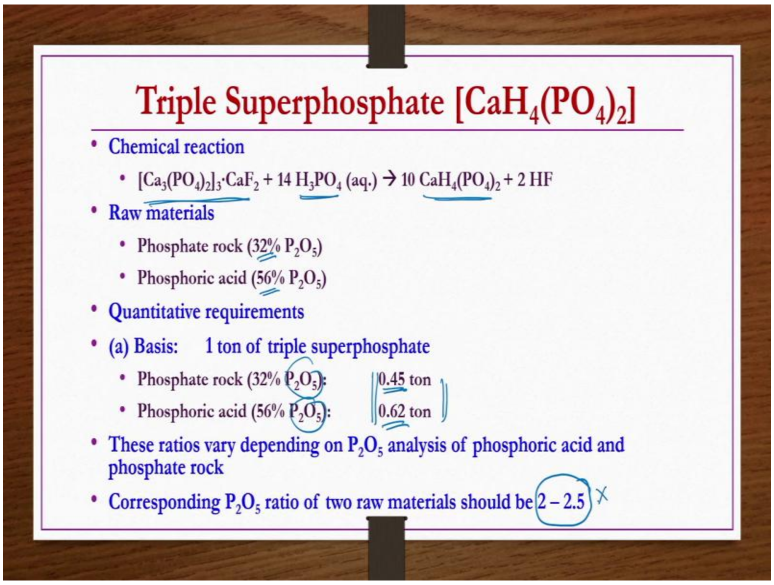

Triple Superphosphate $[CaH_4(PO_4)_2]$

- Chemical reaction
  - $[Ca_3(PO_4)_2]_3 \cdot CaF_2 + 14\ H_3PO_4\ (aq.) \rightarrow 10\ CaH_4(PO_4)_2 + 2\ HF$
- Raw materials
  - Phosphate rock (32% P_2O_5)
  - Phosphoric acid (56% P_2O_5)
- Quantitative requirements
- (a) Basis: 1 ton of triple superphosphate
  - Phosphate rock (32% P_2O_5): 0.45 ton
  - Phosphoric acid (56% P_2O_5): 0.62 ton
- These ratios vary depending on P_2O_5 analysis of phosphoric acid and phosphate rock
- Corresponding P_2O_5 ratio of two raw materials should be 2 – 2.5

Next one is triple superphosphate. Here also the reaction is similar only thing that whatever the fluorapatite mineral of the phosphate rock is there that is reacting with the phosphoric acid rather than sulfuric acid, right. When this fluorapatite react with phosphoric acid it gives triple superphosphate.

Raw materials phosphate rock 32 percent P 2 O 5, phosphoric acid 56 percent P 2 O 5 are required. Quantitative requirements to produce 1 ton of triple superphosphate phosphate rock 0.45 tons and then phosphoric acid 0.62 tons are required. And these ratios vary depending on how much P 2 O 5 that is present in the raw material.

If you have 32 and 56 percent respectively in phosphate rock and phosphoric acid then these quantities are fine. Otherwise, you have to appropriately calculate and then take the quantities of phosphate rock and then phosphoric acid. However, the ratio between 2 raw materials is proposed to have between 2 and 2.5 for a better conversion of the raw materials.

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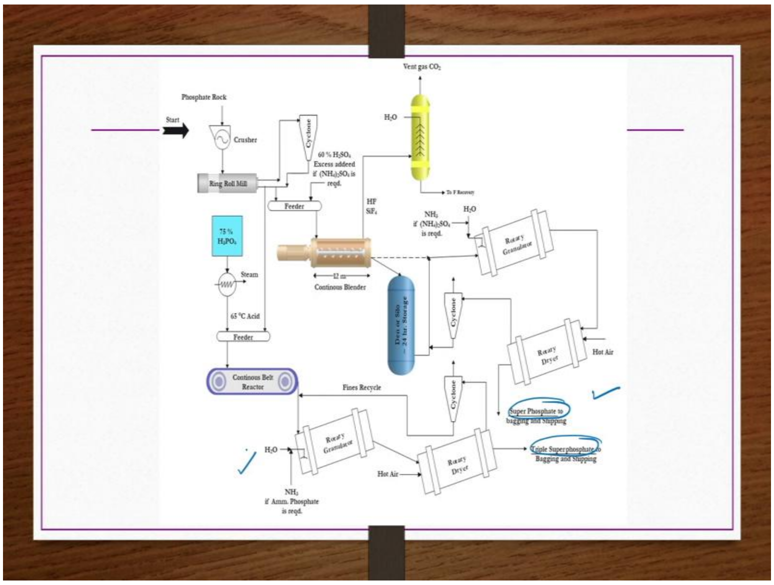

Flow chart is shown here for the production of superphosphate and triple superphosphate again. So, both of them we have already discussed.

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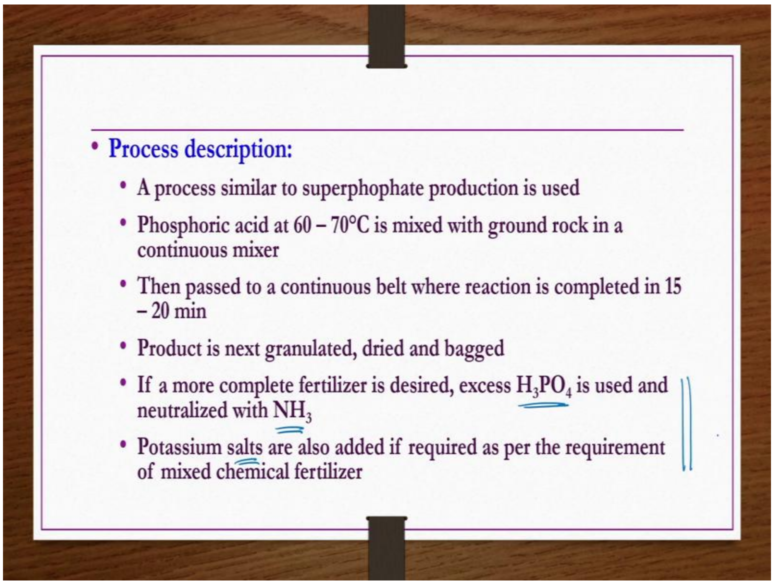

- **Process description:**
  - A process similar to superphophate production is used
  - Phosphoric acid at 60 – 70°C is mixed with ground rock in a continuous mixer
  - Then passed to a continuous belt where reaction is completed in 15 – 20 min
  - Product is next granulated, dried and bagged
  - If a more complete fertilizer is desired, excess H_3PO_4 is used and neutralized with NH_3
  - Potassium salts are also added if required as per the requirement of mixed chemical fertilizer

So, then we can go to the process description of triple superphosphate production. It is very similar to superphosphate production. Phosphoric acid at 60 to 75 degree centigrade is mixed with ground rock in a continuous mixer. Then pass to a continuous belt where reaction is completed in 15 to 20 minutes. Product is next granulated, dried and bagged.

If a more complete fertilizer is desired excess phosphoric acid is used and neutralized with ammonia as has been done in the case of superphosphate. The same thing can be done here in the case of triple superphosphate as well. Potassium salts can also be added if required as per the requirement of mixed chemical fertilizers. And then these two are options in production of both superphosphates as well as the triple superphosphates.

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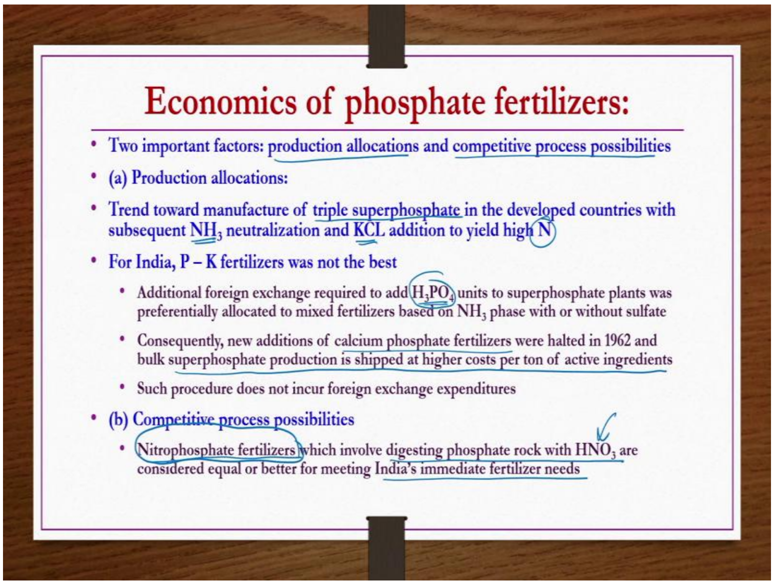

Economics of phosphate fertilizers:

- Two important factors: production allocations and competitive process possibilities
- (a) Production allocations:
- Trend toward manufacture of triple superphosphate in the developed countries with subsequent NH_3 neutralization and KCL addition to yield high N
- For India, P – K fertilizers was not the best
    - Additional foreign exchange required to add H_3PO_4 units to superphosphate plants was preferentially allocated to mixed fertilizers based on NH_3 phase with or without sulfate
    - Consequently, new additions of calcium phosphate fertilizers were halted in 1962 and bulk superphosphate production is shipped at higher costs per ton of active ingredients
    - Such procedure does not incur foreign exchange expenditures
- (b) Competitive process possibilities
    - Nitrophosphate fertilizers which involve digesting phosphate rock with HNO_3 are considered equal or better for meeting India's immediate fertilizer needs

Economics of phosphate fertilizers, two important factors are production allocations and competitive process possibilities we have to see. Under production allocations if you see the trends are towards manufacture of triple superphosphates in the developed countries with subsequent ammonia neutralization and KCL additions to yield high nitrogen fertilizers is there.

But; however, for India, P-K fertilizers phosphorous potassium fertilizers was not the best option because these raw materials for phosphorus and potassium are not indigenous for us we are importing them. So, additional foreign exchange required to add H 3 PO 4 units to superphosphate plants was preferentially allocated to mixed fertilizers based on ammonia phase with or without sulfate.

Then; obviously, because of this one, additions of calcium phosphate fertilizers were halted in around 1960s and then bulk superphosphate production is shipped at higher cost per ton of active ingredients and this does not require any foreign exchange expenditures. Competitive process possibilities nitro phosphate fertilizers which involve digesting phosphate rock with HNO 3 are considered equal or better for meeting India's immediate fertilizer needs rather going for this superphosphate and triple superphosphate where you need strong phosphoric acid etcetera for which you need to depend on the foreign exchange.

But now this nitro phosphate fertilizers are easy to make because we have HNO 3 sources and then phosphate rocks you can react easily that in fact we are going to discuss in the subsequent slide, how to produce this nitro phosphate fertilizers. So, you find production of nitro phosphate is much easier and economical compared to the production of superphosphates and triple superphosphates.

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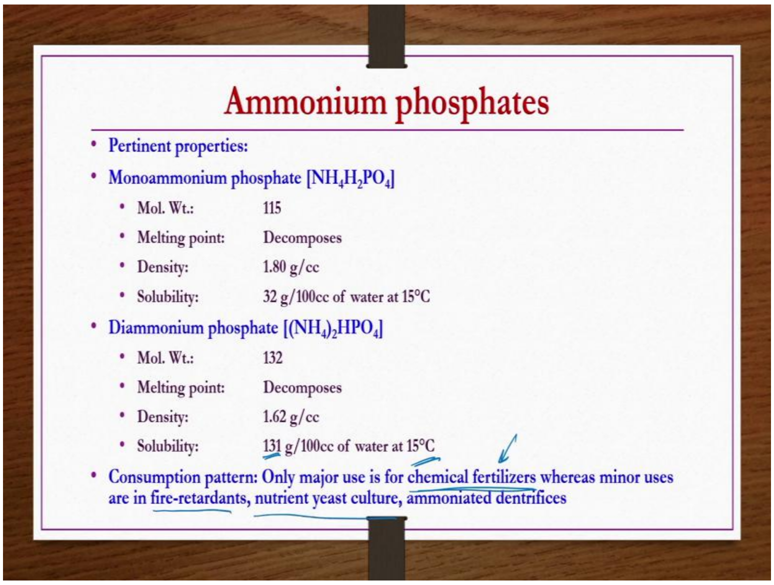

Ammonium phosphates

- Pertinent properties:
- Monoammonium phosphate [$NH_4H_2PO_4$]
    - Mol. Wt.: 115
    - Melting point: Decomposes
    - Density: 1.80 g/cc
    - Solubility: 32 g/100cc of water at 15°C
- Diammonium phosphate [$(NH_4)_2HPO_4$]
    - Mol. Wt.: 132
    - Melting point: Decomposes
    - Density: 1.62 g/cc
    - Solubility: 131 g/100cc of water at 15°C
- Consumption pattern: Only major use is for chemical fertilizers whereas minor uses are in fire-retardants, nutrient yeast culture, ammoniated dentrifices

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So, now we discuss ammonium phosphates before going into the nitro phosphates. Pertinent properties of ammonium phosphates monoammonium phosphate if you want to produce, what should be done and then diammonium phosphate if you want to produce, what should be done that is what we are going to see. But now we see their properties.

Pertinent properties of monoammonium phosphate molecular weight 115, melting point it decomposes on heating density 1.8 gram per cc, solubility 32 grams per 100 cc of water at 15 degree centigrade.

Whereas diammonium phosphate if you take its molecular weight is 132 it also decomposes on heating. So, there is no melting point, density is lower than the monoammonium phosphate here it is 1.62 gram per cc, but the solubility is very high compared to the monoammonium phosphate in water. Here it is diammonium phosphate solubility is 131 grams per 100 cc of water at 15 degree centigrades.

Consumption pattern only major use is chemical fertilizers, mixed chemical fertilizers for that purpose only it is used whereas, minor uses are in fire retardants nutrient yeast culture etcetera. Production of ammonium phosphate as chemical fertilizer we see now here ammonium phosphate in the sense both nitrogens and then phosphates are presence N and P 2 O 5 both are present in that one, how? That is what we are going to see now.

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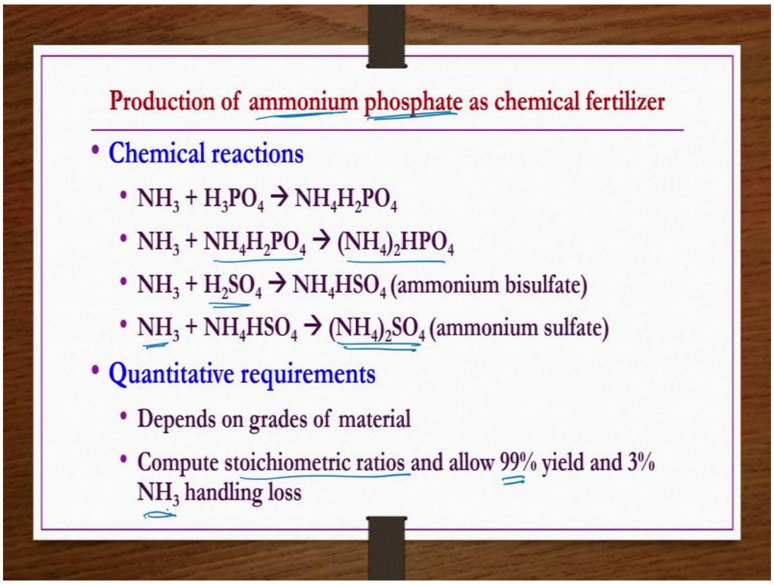

Production of ammonium phosphate as chemical fertilizer

- Chemical reactions
  - $NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4$
  - $NH_3 + NH_4H_2PO_4 \rightarrow (NH_4)_2HPO_4$
  - $NH_3 + H_2SO_4 \rightarrow NH_4HSO_4$ (ammonium bisulfate)
  - $NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4$ (ammonium sulfate)
- Quantitative requirements
  - Depends on grades of material
  - Compute stoichiometric ratios and allow 99% yield and 3% NH_3 handling loss

Chemical reaction ammonia react with the phosphoric acid to produce monoammonium phosphate. This monoammonium phosphate reacts with ammonia again to give diammonium phosphate. Ammonia also reacts with the sulfuric acid to give ammonium bisulphate, which further react with ammonia to give ammonium sulfate.

Quantitative requirements; obviously, ammonia and then phosphoric acid sulfuric acids are required, but depends on the grades of material how much pure H 3 PO 4 is there and then what is the percentage of P 2 O 5 etcetera.

All those things are playing role. And then obviously, depending on what grade of ammonia and what grade of phosphoric acid, sulfuric acid are using the quantities are changing. However, you can compute by on stoichiometric ratios basis allow 99 percent of field and 3 percent ammonia handling loss to get the exact required quantities.

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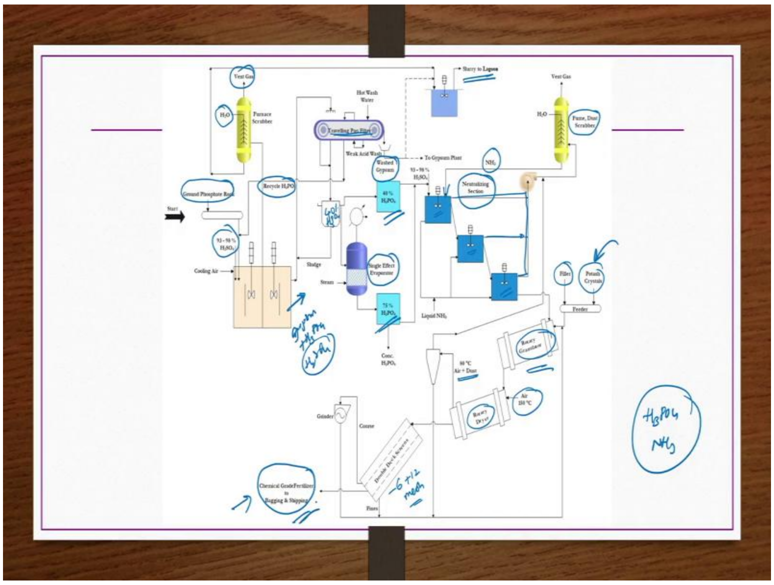

For the production of ammonium phosphate or mixed chemical fertilizer production we have a flow chart here. We have already discussed it in the previous lecture where we were discussing about the production of phosphoric acid, right. So, however, we go through once again it. Whatever the phosphate rock is there that you ground to approximately 200 mesh size.

And this you take it to a batch mixing reactor where baffling or mixing are provided thoroughly. To this reactor sulfuric acid and then recycle phosphoric acid are being added up, right. So, when this reaction takes place some fumes furnace fumes would be there like you know Si F 4, HF etcetera those things are taken to a scrubber to scrub out with water and then take to the whatever the slurry is there that you take to slurry lagoon whereas, the gases you take out vent.

The main product that is coming out of this reactor batch mixing reactor is nothing but a gypsum plus phosphoric acid along with some impurities may be, right. So, this mixture is taken to a travelling pan filter to which weak acid is provided to wash. So, then whatever the filtrate is there of this filter that is taken as a recycle phosphoric acid and then sent to the batch mixing reactor where the main reaction is taking place, right.

So, here in this travelling pan filter by the filtration you can get approximately 40 percent phosphoric acid, right. And then this mixture also contains some amount of a H 2 SO 4, unreacted H 2 SO 4 that actually makes filtration of gypsum easily and then when this slurry product moves to the other end of this travelling filter to the other end you get almost pure gypsum. So, that is washed with wash water if at all traces of phosphoric acid or sulfuric acid are present.

So, the washed gypsum you can collect as a product whereas, the you know weak acid because of washing with hot water is there they are recycle to the reactor again. So, this part we have seen. So, this 40 percent phosphoric acid whatever you are getting from this travelling pan filter is there that you can take it to a single effect evaporator to concentrate it to the higher percentage of phosphoric acid something like more than 50 percent phosphoric acid up to 75 percent etcetera, right.

So, up to this part is phosphoric acid production. Now, this phosphoric acid whether the concentrated one or the weak phosphoric acid along with the sulfuric acid is taken to a series of 3 mixed reactors continuous mixed reactors 1, 2, 3 are there. So, this mixture of phosphoric acid and then sulfuric acid along with the ammonia are taken to the first reactor where the reaction is taking place, to this reactor liquid ammonia is given from the bottom, right.

Product, mixture is whatever is there that is taken to the second reactor to which also liquid ammonia is provided from the bottom and then the product mixture is whatever is there from the second reactor that is taken to this third reactor to which also liquid ammonia is provided from the bottom because this ammonia is neutralizing agent. So, this section whatever is there is known as the neutralizing section, ok. So, the product that is coming from here is almost like pure ammonium phosphate.

Whatever the unreacted or excess ammonia is there that is recovered from the top of each reactor, right. And then sent to a scrubber where you can remove fumes, dust etcetera if at all present using the water, vent gas you can take out and then almost clean ammonia and liquid that you can feed back to the reactor one. This will reduce the ammonia loss; this recycling of ammonia by passing through a scrubber etcetera this process will reduce the ammonia loss because we know ammonia is very expensive, right.

So, then product mixture from the third mixture reactor whatever is there that is nothing but the main product that is taken to a rotary granulator to this rotary granulator if at all some filler or required fillers along with the potash crystals are added if required and then this mixture is rotated in this rotary granulator drum. When it rotates the mixture, you know that gets granulated. Those granules of the product are taken to a rotary dryer to which hot air is supplied at approximately 150 degree centigrade.

So, that drying of this granule takes place and then less hot gases at approximately 80 degree centigrade are collected from the top of the drum rotary dryer you know it may be containing some dust also. So, that mixture is taken to a cyclone separator where the dust, fines etcetera are collected from the bottom and then sent back to the you know rotary granulator here again in this, ok, right.

Whereas, the gases, air, etcetera if at all any products fine products are still there, they are taken to the scrubber in which ammonia scrubbing is done to remove the dust, fumes etcetera to that scrubber they have been taken.

From the rotary dryer whatever the product is there that is pass it through a double deck screens where the products having minus 6 plus 2 mesh size are taken as the required product whereas, the oversize materials are grinded again and then undersized fines are sent back to the granulator to make up the size of the granules again, ok.

So, this is the process here you can see that you know ammonium nitrate chemical fertilizer you can produce within the same plant of phosphoric acid production, ok. So, whatever the raw materials required like H 3 PO 4 and then neutralizing agent ammonia etcetera you know these are you know produced in the plant itself.

If you have a complete fertilizer plant these are produced there itself. Only thing that this potash crystals are not available not produced in the plant itself or have to be imported or taken from the external sources you know if at all you wanted to have them in the mixed chemical fertilizers.

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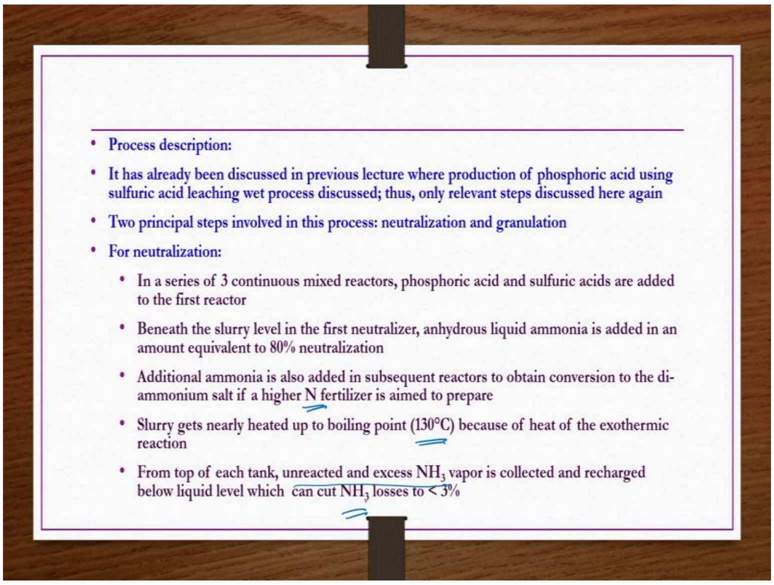

- Process description:
- It has already been discussed in previous lecture where production of phosphoric acid using sulfuric acid leaching wet process discussed; thus, only relevant steps discussed here again
- Two principal steps involved in this process: neutralization and granulation
- For neutralization:
  - In a series of 3 continuous mixed reactors, phosphoric acid and sulfuric acids are added to the first reactor
  - Beneath the slurry level in the first neutralizer, anhydrous liquid ammonia is added in an amount equivalent to 80% neutralization
  - Additional ammonia is also added in subsequent reactors to obtain conversion to the di-ammonium salt if a higher N fertilizer is aimed to prepare
  - Slurry gets nearly heated up to boiling point (130°C) because of heat of the exothermic reaction
  - From top of each tank, unreacted and excess NH_3 vapor is collected and recharged below liquid level which can cut NH_3 losses to < 3%

Same thing whatever we discussed in flowchart are provided as a process description here. This process we have already discussed in the previous lecture where we were discussing you know production of phosphoric acid using weight processes, right. Now, here we discuss once again.

However, we discuss only relevant things. What are the relevant things to the production of ammonium phosphate purpose? One is the neutralization section another one is the granulation section. Those things we are going to discuss here.

For neutralization in a series of 3 continuous mixed reactors phosphoric acid and sulfuric acids are added to the first reactor. Beneath the slurry level in the first neutralizer anhydrous liquid ammonia is added in an amount equivalent to 80 percent neutralization. Additional ammonia is also added in subsequent reactors to obtain conversion to the diammonium salt if higher end fertilizer is aimed to prepare.

Slurry gets nearly heated up to boiling point of 130 degree centigrade because of heat of the exothermic reaction. From top of each tank unreacted excess ammonia vapor is collected and recharged below the liquid level which can cut down the ammonia losses to less than 3 percent.

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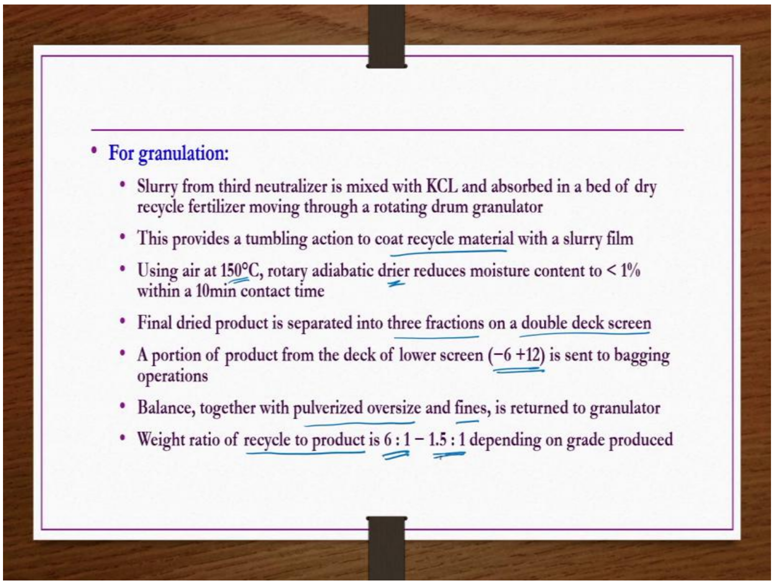

- **For granulation:**
  - Slurry from third neutralizer is mixed with KCL and absorbed in a bed of dry recycle fertilizer moving through a rotating drum granulator
  - This provides a tumbling action to coat recycle material with a slurry film
  - Using air at 150°C, rotary adiabatic drier reduces moisture content to < 1% within a 10min contact time
  - Final dried product is separated into three fractions on a double deck screen
  - A portion of product from the deck of lower screen (−6 +12) is sent to bagging operations
  - Balance, together with pulverized oversize and fines, is returned to granulator
  - Weight ratio of recycle to product is 6 : 1 − 1.5 : 1 depending on grade produced

For the granulation section, slurry from the third neutralizer is mixed with a potash crystals and absorbed in a bed of dry recycle fertilizer moving through a rotating drum granulator. This provides a tumbling action to coat recycle material with a slurry film. Using air at 150 degree centigrades rotary adiabatic dryer reduces moisture content to less than 1 percent within a 10 minutes contact time.

Final dried product is separated into three fractions on a double deck screens. A portion of product from a deck of lower screen having minus 6 plus 12 size is sent to bagging operations. Balance together with a pulverized oversize and fines is written to the granulator. Weight ratio of recycle to product should be maintained 6 is to 1 to 1.5 is to 1, ok.

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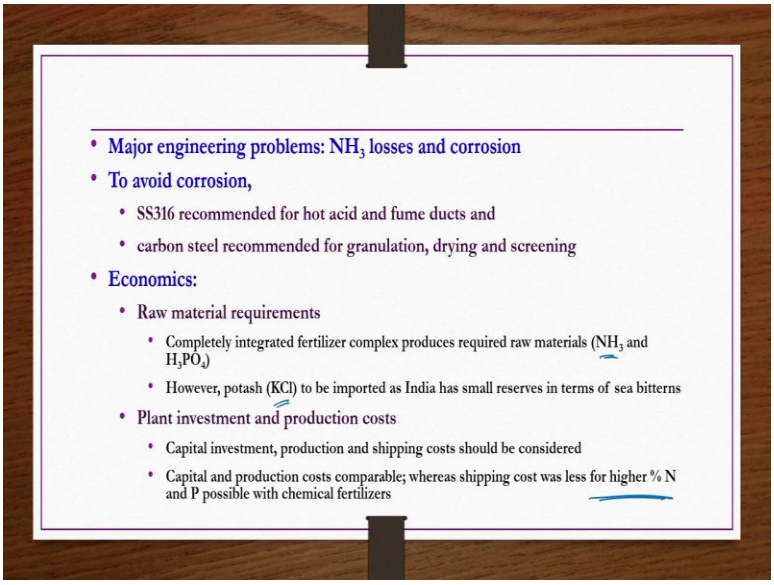

- Major engineering problems: NH_3 losses and corrosion
- To avoid corrosion,
  - SS316 recommended for hot acid and fume ducts and
  - carbon steel recommended for granulation, drying and screening
- Economics:
  - Raw material requirements
    - Completely integrated fertilizer complex produces required raw materials (NH_3 and H_3PO_4)
    - However, potash (KCl) to be imported as India has small reserves in terms of sea bitterns
  - Plant investment and production costs
    - Capital investment, production and shipping costs should be considered
    - Capital and production costs comparable; whereas shipping cost was less for higher % N and P possible with chemical fertilizers

Major engineering problems: ammonia losses is one problem. One has to make sure ammonia recovery has to be properly done and then taken back to the first mixture reactor of a neutralization section, ok. And then another problem is the corrosion, right. To avoid corrosion SS316 recommended for hot acid and fume ducts.

Carbon steel recommended for granulation, drying and screening sections or equipment where granulation drying and screening are being done. Economics, raw materials requirement: completely integrated fertilizer plant if you are having then required raw materials of ammonia phosphoric acids are produced there itself only potash to be imported.

Plant investment and production cost: one has to check capital investment production and shipping cost for the consideration whereas, it has been found at the capital and then production cost are comparable. So, the shipping cost is important and it has been found at shipping cost is less for higher nitrogen and phosphorus fertilizers.

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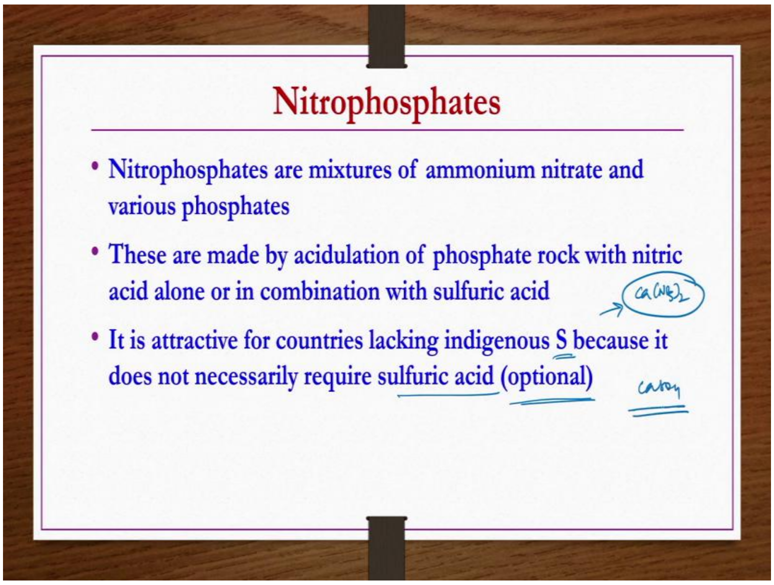

Nitrophosphates

- Nitrophosphates are mixtures of ammonium nitrate and various phosphates
- These are made by acidulation of phosphate rock with nitric acid alone or in combination with sulfuric acid
- It is attractive for countries lacking indigenous S because it does not necessarily require sulfuric acid (optional)

$Ca(NO_3)_2$

$CaSO_4$

Now, we discuss about nitro phosphates. Nitro phosphates can be easily produced by reacting the phosphate rock with nitric acid alone or nitric acid plus sulfuric acid which is known as the mixed acid, ok. Nitro phosphates are mixtures of ammonium nitrate and various phosphates. These are made by acidulation of phosphate rock with nitric acid alone or in combination with sulfuric acid. It is attractive for countries lacking indigenous S because it does not necessarily require sulfuric acid it is optional only, ok.

But however, if you have the sulfuric acid, it is better. Because in the nitric acid plant what happens? This calcium nitrate is forming and this is very difficult to remove from the mixture product mixture. So, you have to do the crystallization etcetera. But if you have this sulfur then what happens? It forms calcium sulphate. So, which is easy to remove ok, those reactions anyway we are going to see here.

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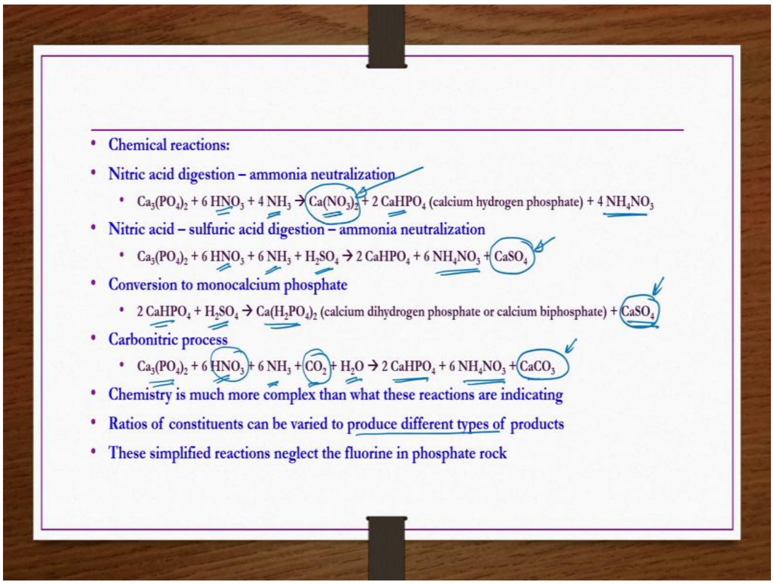

- Chemical reactions:
- Nitric acid digestion – ammonia neutralization
  - $Ca_3(PO_4)_2 + 6\ HNO_3 + 4\ NH_3 \rightarrow Ca(NO_3)_2 + 2\ CaHPO_4$ (calcium hydrogen phosphate) $+ 4\ NH_4NO_3$
- Nitric acid – sulfuric acid digestion – ammonia neutralization
  - $Ca_3(PO_4)_2 + 6\ HNO_3 + 6\ NH_3 + H_2SO_4 \rightarrow 2\ CaHPO_4 + 6\ NH_4NO_3 + CaSO_4$
- Conversion to monocalcium phosphate
  - $2\ CaHPO_4 + H_2SO_4 \rightarrow Ca(H_2PO_4)_2$ (calcium dihydrogen phosphate or calcium biphosphate) $+ CaSO_4$
- Carbonitric process
  - $Ca_3(PO_4)_2 + 6\ HNO_3 + 6\ NH_3 + CO_2 + H_2O \rightarrow 2\ CaHPO_4 + 6\ NH_4NO_3 + CaCO_3$
- Chemistry is much more complex than what these reactions are indicating
- Ratios of constituents can be varied to produce different types of products
- These simplified reactions neglect the fluorine in phosphate rock

First reaction is nitric acid digestion - ammonia neutralization reaction where calcium phosphate react with the nitric acid ammonia to give the calcium nitrate and then calcium hydrogen phosphate along with the ammonium nitrate. Nitric acid - sulfuric acid digestion and ammonia neutralization reaction here calcium phosphate reacts with the nitric acid plus sulfuric acid that is mixed acid along with the ammonia to give the same calcium hydrogen phosphate and then ammonium nitrate, ok.

Now, here you see in this process calcium nitrate is formed, in this process calcium sulfate is formed. Now, conversion to monocalcium phosphate. This calcium hydrogen phosphate whatever is there that further reacts with the sulfuric acid to give calcium biphosphate and then calcium sulfate. Carbonitric process here calcium phosphate react with the nitric acid, ammonia, carbon dioxide and water that is the reason since you have the carbon dioxide also in the reactants it is known as the carbonitric process.

Because both carbon dioxide and nitric acid are there so, when this reaction takes place, you get calcium hydrogen phosphate along with the ammonium nitrate and then calcium carbonate. Now, you see the reactions are very simple, but the chemistry is much more complex than the reaction that are indicating. Because small changes variations in these quantities different reactions may take place.

Ratios of constitutions can be varied to produce different types of products in this process. These simplified reactions neglect the fluorine in phosphate rock. So, now these reactions what you see here calcium sulfate is forming, calcium carbonate is forming. So, these are easy to remove from the process, but calcium nitrate it is not easy to separate. Because it is highly hygroscopic and then product become very lumpy, right so, then in order to remove this one you have to do the crystallization at low temperature.

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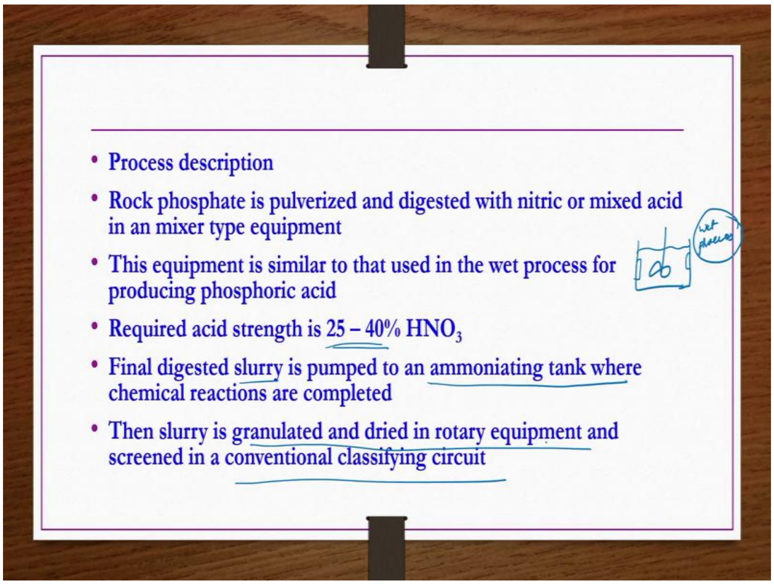

- Process description
- Rock phosphate is pulverized and digested with nitric or mixed acid in an mixer type equipment
- This equipment is similar to that used in the wet process for producing phosphoric acid
- Required acid strength is 25 – 40% HNO_3
- Final digested slurry is pumped to an ammoniating tank where chemical reactions are completed
- Then slurry is granulated and dried in rotary equipment and screened in a conventional classifying circuit

Process description: rock phosphate is pulverized and digested with nitric or mixed acid in an mixer type equipment which is having something like you know batch mixing kind of reactor where you may be having baffles etcetera in order to enhance the mixing such kind of reactors where we have seen in wet processes for the production of phosphoric acid we have used. Same equipment is used here also.

Required acid strength is 25 to 40 percent HNO 3. Final digested slurry is pumped to an ammoniating tank where chemical reactions are completed. Then slurry is granulated and dried in a rotary equipment and screened in a conventional classifying circuit.

So, now what you see the process is quite similar to whatever we have seen in superphosphate and triple superphosphate and then mixed chemical fertilizers like you know ammonium nitrate etcetera those kind of process we have seen it is same like that only. So, that is the reason we are not having flow sheets separately for this one.

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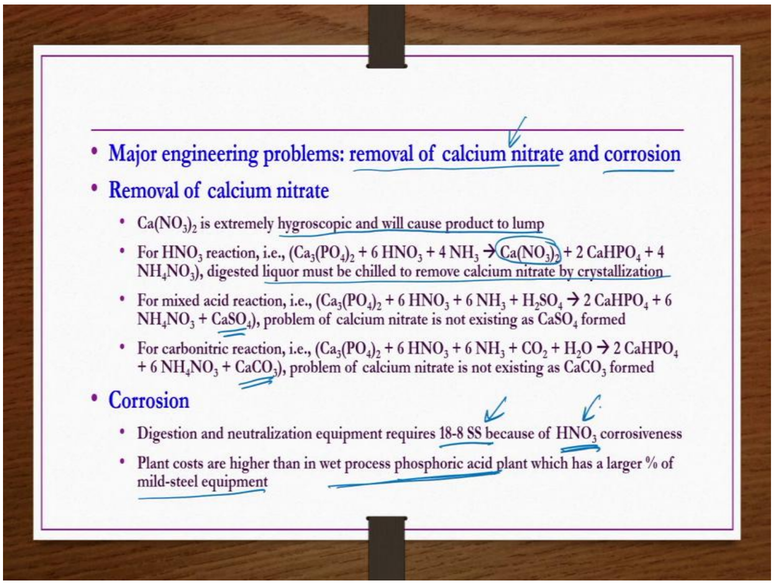

- Major engineering problems: removal of calcium nitrate and corrosion
- Removal of calcium nitrate
  - $Ca(NO_3)_2$ is extremely hygroscopic and will cause product to lump
  - For HNO_3 reaction, i.e., ($Ca_3(PO_4)_2 + 6\,HNO_3 + 4\,NH_3 \rightarrow Ca(NO_3)_2 + 2\,CaHPO_4 + 4\,NH_4NO_3$), digested liquor must be chilled to remove calcium nitrate by crystallization
  - For mixed acid reaction, i.e., ($Ca_3(PO_4)_2 + 6\,HNO_3 + 6\,NH_3 + H_2SO_4 \rightarrow 2\,CaHPO_4 + 6\,NH_4NO_3 + CaSO_4$), problem of calcium nitrate is not existing as $CaSO_4$ formed
  - For carbonitric reaction, i.e., ($Ca_3(PO_4)_2 + 6\,HNO_3 + 6\,NH_3 + CO_2 + H_2O \rightarrow 2\,CaHPO_4 + 6\,NH_4NO_3 + CaCO_3$), problem of calcium nitrate is not existing as $CaCO_3$ formed
- Corrosion
  - Digestion and neutralization equipment requires 18-8 SS because of HNO_3 corrosiveness
  - Plant costs are higher than in wet process phosphoric acid plant which has a larger % of mild-steel equipment

Major engineering problems are removal of calcium nitrate and then corrosion. Then calcium nitrate is very hygroscopic and will cause product to lump. So, this calcium nitrate has to be removed from the product. So, the digested liquor must be chilled to remove calcium nitrate by crystallization.

Whereas, this problem is not existing in other two reactions where calcium sulfate and then calcium carbonate are forming which are easy to remove. Corrosion digestion and neutralization equipment requires 18-8 SS because of nitric acid corrosiveness. Plant costs are higher than in wet process phosphoric acid plant which has a larger percentage of mild steel equipment, ok.

So, mild steel equipment are used in the wet process phosphoric acid plant so, then you know the cost whatever the plant cost is less there, but here you need to have the SS. So, then plant cost is going to be slightly higher. You need it here because here HNO 3 is there which is highly corrosive.

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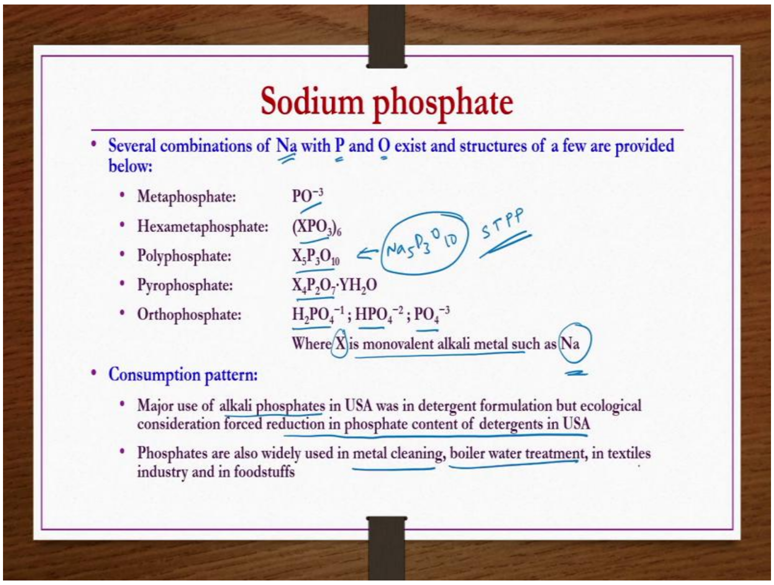

Sodium phosphate

- Several combinations of Na with P and O exist and structures of a few are provided below:
  - Metaphosphate: PO^{-3}
  - Hexametaphosphate: $(XPO_3)_6$
  - Polyphosphate: $X_5P_3O_{10}$ ← $Na_5P_3O_{10}$ STPP
  - Pyrophosphate: $X_4P_2O_7 \cdot YH_2O$
  - Orthophosphate: $H_2PO_4^{-1}$; HPO_4^{-2} ; PO_4^{-3}

    Where X is monovalent alkali metal such as Na
- Consumption pattern:
  - Major use of alkali phosphates in USA was in detergent formulation but ecological consideration forced reduction in phosphate content of detergents in USA
  - Phosphates are also widely used in metal cleaning, boiler water treatment, in textiles industry and in foodstuffs

Now, sodium phosphates several combinations of sodium with phosphorus and oxygen exist and structures of few are provided below, n number of other we are having a few. One is the metaphosphate, another one is the hexametaphosphate, polyphosphate, then pyrophosphate, then orthophosphates these are all orthophosphates where here X is there that is monovalent alkali metal such as sodium.

Now, let us say here it is Na 5 P 3 O 10 is nothing but STPP sodium tri polyphosphate. Here also like that you know different products are there ok, X stands for monovalent alkali metal such as sodium here. Consumption pattern most of the alkali phosphates produced in USA are used for the detergent formulation, but because of ecological consideration force reduction in phosphate content of detergents in USA.

However, these phosphates are also widely used in metal cleaning, boiler water treatment in textile industries, in food stuffs etcetera.

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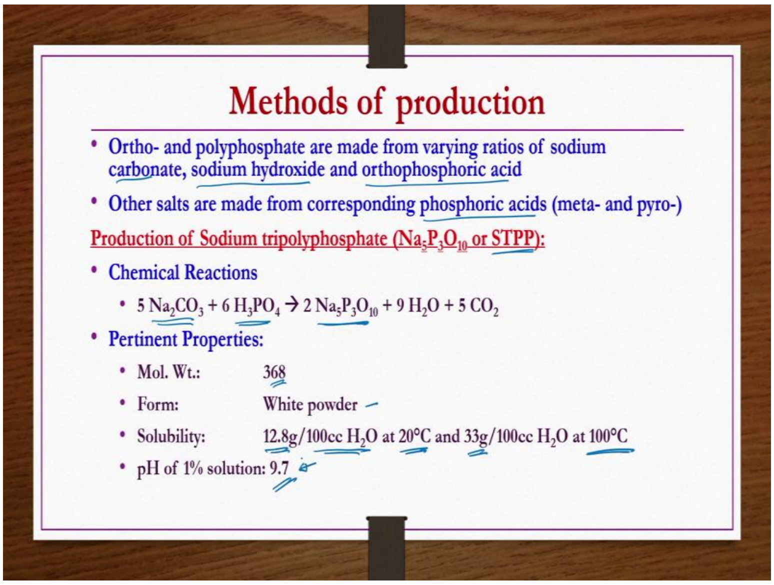

Methods of production

- Ortho- and polyphosphate are made from varying ratios of sodium carbonate, sodium hydroxide and orthophosphoric acid
- Other salts are made from corresponding phosphoric acids (meta- and pyro-)

Production of Sodium tripolyphosphate ($Na_5P_3O_{10}$ or STPP):

- Chemical Reactions
  - $5\ Na_2CO_3 + 6\ H_3PO_4 \rightarrow 2\ Na_5P_3O_{10} + 9\ H_2O + 5\ CO_2$
- Pertinent Properties:
  - Mol. Wt.: 368
  - Form: White powder
  - Solubility: 12.8g/100cc H_2O at 20°C and 33g/100cc H_2O at 100°C
  - pH of 1% solution: 9.7

Now, methods of production we see. Ortho and polyphosphates are made from varying ratios of sodium carbonate, sodium hydroxide and orthophosphoric acid, ok. Other salts are made from corresponding phosphoric acids meta and pyrophosphoric acids etcetera. Now, we see only one type of sodium phosphate that is sodium tripolyphosphate production that is nothing but Na 5 P 3 O 10 which is also known as STPP sodium tripolyphosphate.

Chemical reactions sodium carbonate react with the phosphoric acid to give sodium tripolyphosphates that is STPP water and CO 2. Pertinent properties molecular weight is 368, it is white powder in physical state if you see it is white powder, solubility is 12.8 grams per 100 cc of water at 20 degree centigrade and then its solubility increases to 33 grams in 100 cc of water if you increase the temperature to 100 degree centigrades.

pH of 1 percent of this sodium tripolyphosphate is 9.7. Because it is a powder you take it in water you make 1 percent solution that solution is having 9.7 pH.

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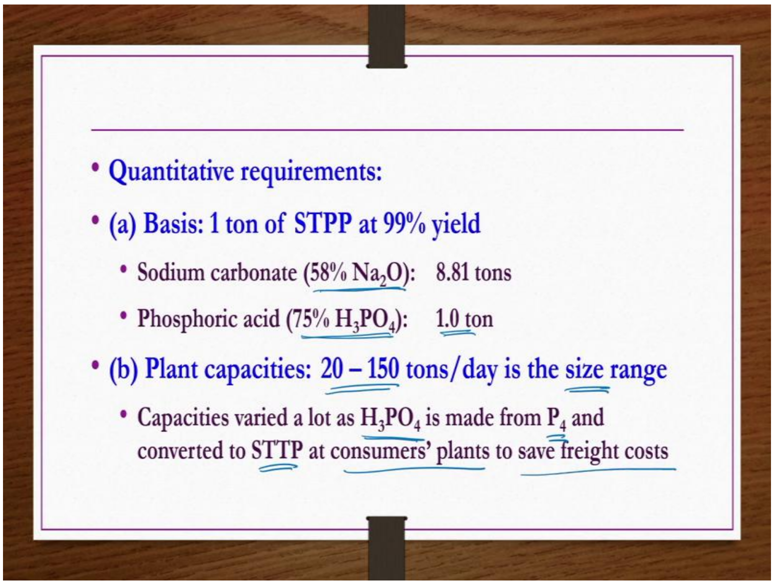

- **Quantitative requirements:**
- **(a) Basis: 1 ton of STPP at 99% yield**
  - Sodium carbonate (58% Na_2O): 8.81 tons
  - Phosphoric acid (75% H_3PO_4): 1.0 ton
- **(b) Plant capacities: 20 – 150 tons/day is the size range**
  - Capacities varied a lot as H_3PO_4 is made from P_4 and converted to STTP at consumers' plants to save freight costs

Quantitative requirements basis for one ton of sodium tripolyphosphate production at 99 percent yield, how much sodium carbonate you required 8.81 tons which is having 58 percent Na 2 O and then phosphoric acid having 75 percent H 3 PO 4 you required 1 ton, ok.

Plant capacities usually 20 to 150 tons a day is the size range in general, ok. Size range in the sense they are not producing the plant, but these are you know varied a lot as H 3 PO 4 is made from P 4 and converted to STTP it consumers plants to save freight costs etcetera. They are produced on demand kind of thing.

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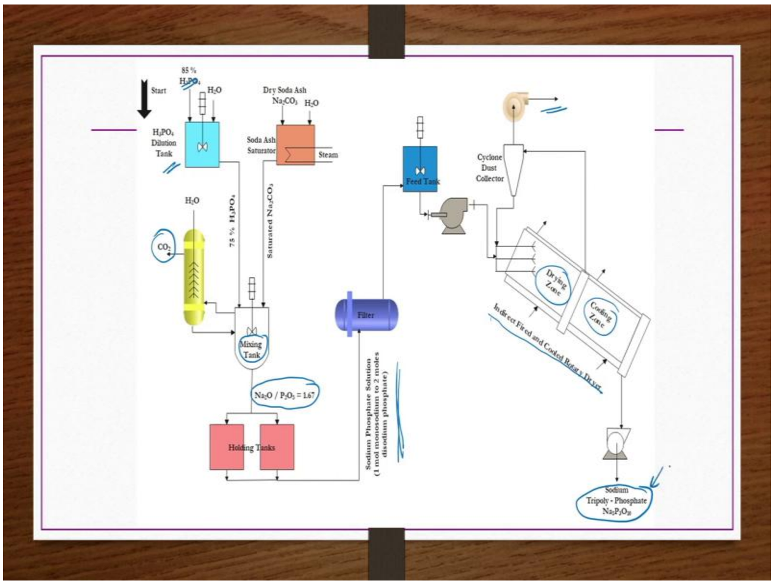

Flow chart for the production of sodium tripolyphosphate is provided here whatever phosphoric acid is there that is diluted in a dilution tank and then dry soda ash whatever is there that is saturated in a mixture by adding with the water soda ash saturator and then dilute acid or taken to a mixing tank, right. From here whatever the gases are revolving they are scrubbed with water to remove CO 2 whereas, the remaining solutions are taken back to the mixing tank.

Here mixing tank the Na 2 O divided by P 2 O 5 ratio is maintained 1.67 and then the mixture is taken to the holding tanks which is primarily containing sodium phosphate solution 1 mole of monosodium 2, 2 moles of disodium phosphates these are taken to the filter and then to the feed tank followed by cyclone dust collector to remove the dust etcetera, ok.

The product that is coming from the feed tank after reaction that is pumped to a drying indirect fried and cooled rotary dryer where 2 zones are there is a drying zone and then cooling zone. Both of them are present in the same in this one in one single unit operations.

And this is done by the hot air here. So, whatever the gases are coming out from the rotary dryer. So, they are taken to the cyclone separator to collect the dust and then feed back to the rotary dryer again whereas, the clean gases taken out from the vent as a top.

The dried granules whatever are there they are taken as a sodium tripolyphosphate products from the bottom here.

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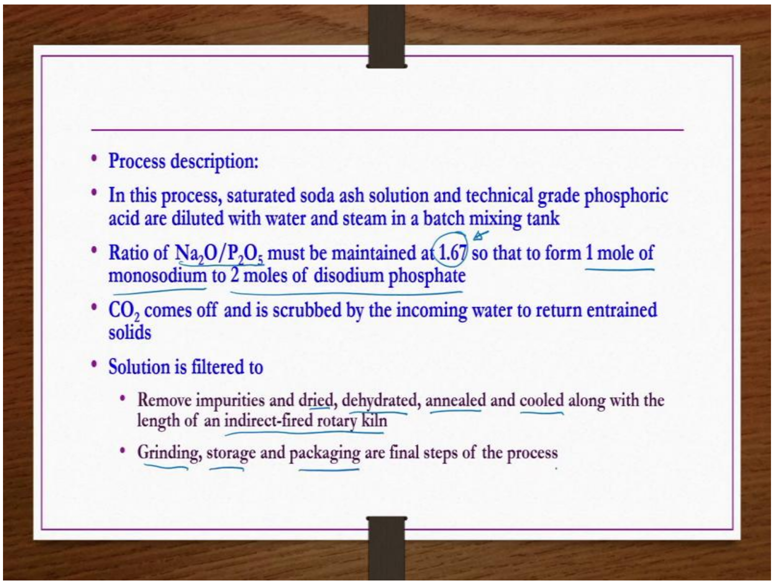

- Process description:
- In this process, saturated soda ash solution and technical grade phosphoric acid are diluted with water and steam in a batch mixing tank
- Ratio of Na_2O/P_2O_5 must be maintained at 1.67 so that to form 1 mole of monosodium to 2 moles of disodium phosphate
- CO_2 comes off and is scrubbed by the incoming water to return entrained solids
- Solution is filtered to
  - Remove impurities and dried, dehydrated, annealed and cooled along with the length of an indirect-fired rotary kiln
  - Grinding, storage and packaging are final steps of the process

Process description in this process saturated soda ash solution and technical grade phosphoric acids are diluted with water and steam in batch mixing tanks. Ratios of Na 2 O divided by P 2 O 5 must be maintained at 1.67. So, that to form 1 mole of monosodium to 2 moles of disodium phosphate this mole ratio is important to produce these products.

CO 2 comes off and is scrubbed by the incoming water to a return entrained solids. Solution is filtered then to remove impurities then dried, dehydrated, annealed and cooled along with the length of an indirect fired rotary kiln. Then finally, grinding storage and packaging of the product is done.

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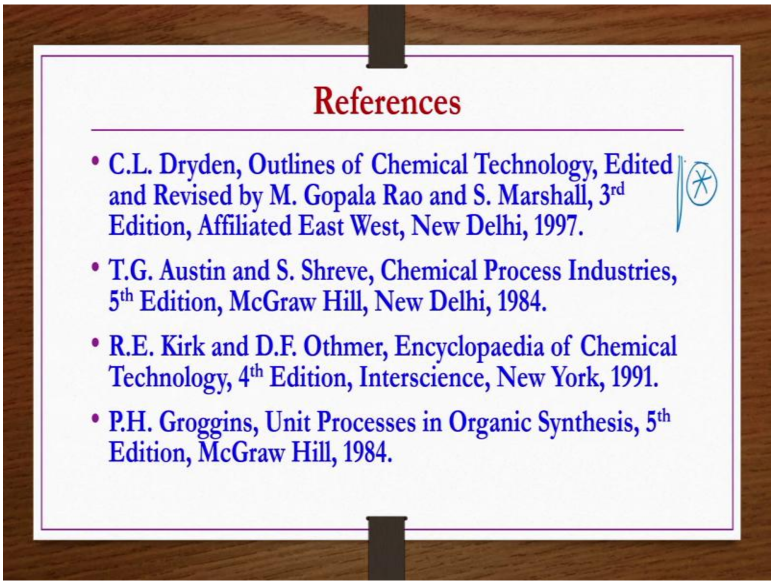

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References for this lecture are provided here. But however, the entire lecture is prepared from this reference book.

Thank you.