Inorganic Chemical Technology
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Lecture - 18
Phosphorus Industries - Phosphorus and Phosphoric Acid Production

Welcome to the MOOCs course Inorganic Chemical Technology. The title of today's lecture is Phosphorus Industries, Phosphorus and Phosphoric Acid Production. In the previous lecture, we discussed about nitrogen industries and in production of different types of nitrogen fertilizers.

In this week, we will be discussing about phosphorus Industries, where we will be discussing about the production of elemental phosphorus, then several derived components like phosphoric acid, P 2 O 5 etcetera, those things we are going to discuss. So, phosphorus industries, basic raw material is, phosphate rock right.

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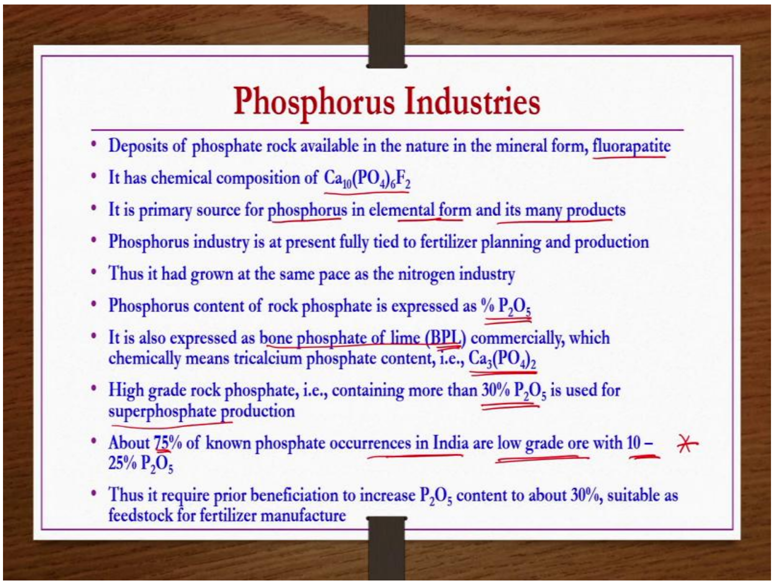

Phosphorus Industries

- Deposits of phosphate rock available in the nature in the mineral form, fluorapatite
- It has chemical composition of $Ca_{10}(PO_4)_6F_2$
- It is primary source for phosphorus in elemental form and its many products
- Phosphorus industry is at present fully tied to fertilizer planning and production
- Thus it had grown at the same pace as the nitrogen industry
- Phosphorus content of rock phosphate is expressed as % P_2O_5
- It is also expressed as bone phosphate of lime (BPL) commercially, which chemically means tricalcium phosphate content, i.e., $Ca_3(PO_4)_2$
- High grade rock phosphate, i.e., containing more than 30% P_2O_5 is used for superphosphate production
- About 75% of known phosphate occurrences in India are low grade ore with 10 – 25% P_2O_5
- Thus it require prior beneficiation to increase P_2O_5 content to about 30%, suitable as feedstock for fertilizer manufacture

This phosphate rock available in the nature in the mineral form, which is known as fluorapatite. This is having chemical structure Ca 10, PO 4 6, F 2. It is primary source for phosphorus in elemental form and its many products as well, whatever the phosphoric acid, P 2 O 5 etcetera or any other mixed chemical fertilizers, where phosphorus is also used.

So, this phosphorus is a source for the phosphorus derived materials like you know phosphoric acid etcetera. At present, whatever the phosphorus industry is there, it is primarily associated or connected to the fertilizer, planning and production because whatever the phosphorus is produced, it is intern again utilized for the production of phosphoric acid or other kind of a fertilizers, phosphorus fertilizers.

That is the reason primarily phosphorus industry at present is fully tied to fertilizer planning and production especially in India. Thus, it had grown at the same pace as the nitrogen industry. Actually, we have seen that nitrogen is indigenous for any country because we are getting it from the air. But phosphorus and then potassium are not available in many of the countries including India.

So, mostly for phosphorus and potassium, we are depending on the imports right. Despite of that one, you know this phosphorus industry has grown at the same pace as the nitrogen industry because of its importance in the fertilizers plants, fertilizer manufacturing which is going to be utilized for the growth of different types of plants.

Phosphorus content of rock phosphate is expressed as percentage P 2 O 5. Like in nitrogen industries or nitrogen fertilizers, what we see? How much nitrogen that is total, N is present in the fertilizer that is taken as a basis to grade a nitrogen fertilizer, right. So, here also phosphorus content of a rock phosphate is expressed as percentage of P 2 O 5. So, if it is more than 30 percent P 2 O 5 instead then we can say that you know it is a high grade rock phosphate.

And then if it is having less than 20 or 25 percent P 2 O 5 that is phosphorus pentoxide, if it is less than 20, 25 percent then we can say it is a low grade rock. It is also expressed as bone phosphate of lime especially commercially which is BPL right. If you see the chemical name it is tricalcium phosphate content that is Ca 3 PO 4 twice.

High grade rock phosphate that is containing more than 30 percent P 2 O 5 is used for super phosphate production. Super phosphate is one of the important fertilizers that is been used in general. About 75 percent of known phosphate occurrence in India, we don’t have phosphate or we don’t have phosphate rocks in nature.

Very few are there whatever they are there out of which also 75 percent are having low grade that is they are having 10 to 25 percent P 2 O 5, 10 percent is very less. Actually, if you have anything less than 30 percent P 2 O 5 then what you have to do? That ore whatever you take you have to do the beneficiation etcetera to increase its concentration. So, that whatever the percentages of P 2 O 5 is required that reaches 30 percent or more. So, that it can be utilized for a fertilizer production ok.

If you have a low grade ore then what you have to do? You have to do beneficiation so, that you can increase the content of P 2 O 5 up to 30 percent and then use it for a fertilizer manufacture.

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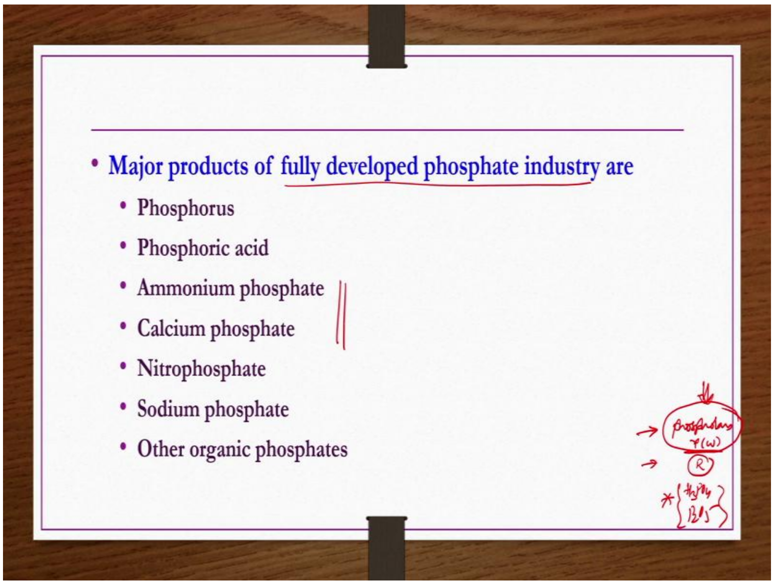

- Major products of fully developed phosphate industry are
  - Phosphorus
  - Phosphoric acid
  - Ammonium phosphate
  - Calcium phosphate
  - Nitrophosphate
  - Sodium phosphate
  - Other organic phosphates

Major products of fully developed phosphate industry. Phosphate industry fully developed phosphate industry why we are specifying? Because we understand or we are going to see phosphorus whatever is there it is having in two form yellow or white form and then red form. This yellow or white form it is very reactive when it come in interaction with air that is it ignites or combusts or burns immediately when it comes in contact with the air right.

So, its reactiveness which is very high. So, then; obviously, safety wise it is very dangerous. So, one has to be careful. So; obviously, even if you are producing phosphorus in white or yellow form you do not want to preserve in that form because of its high reactiveness. So; obviously, what you try to do? You try to convert into the red phosphorus or you know phosphoric acid or phosphorus pentoxide and so on.

So, different types of chemicals you try to produce because that is what having the major market because whatever the yellow phosphorus or red phosphorus that you are producing that again you are converting to the other required you know chemicals ok. So, all these things are done in one plant actually if not all majority of them at least three of them are produced in one plant that's the reason fully developed phosphate industry terminology has been used.

So, often you do not find any phosphorus industries where you may be producing only yellow or white phosphorus ok in addition to that one you may be producing red phosphorus, phosphoric acid, phosphorous pentoxide etcetera. These kind of chemicals also.

So, some of them if you see elemental phosphorus is anyway one of the product then phosphoric acid, then ammonium phosphate, calcium phosphate, nitro phosphate, sodium phosphate and several types of other kinds of organic phosphates are also possible. So, we know that this ammonium phosphate, calcium phosphates etcetera are also known as the mixed chemical fertilizers.

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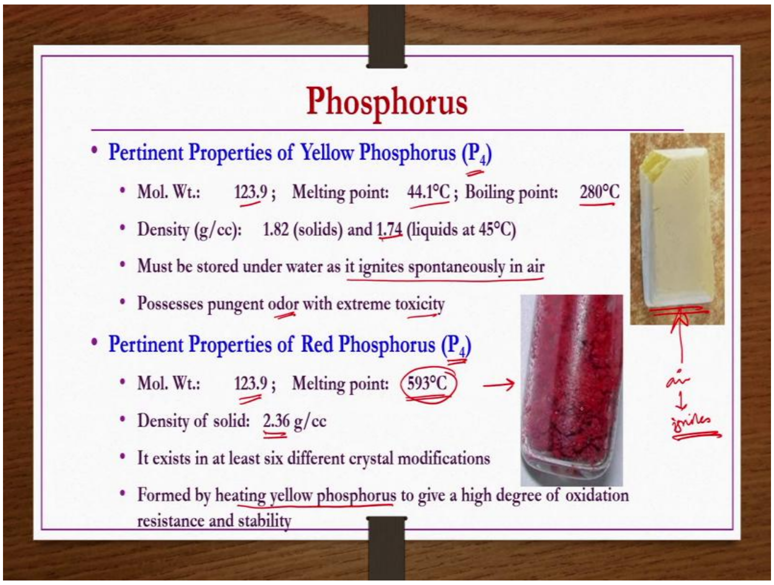

Phosphorus

- Pertinent Properties of Yellow Phosphorus (P_4)
  - Mol. Wt.: 123.9 ; Melting point: 44.1°C ; Boiling point: 280°C
  - Density (g/cc): 1.82 (solids) and 1.74 (liquids at 45°C)
  - Must be stored under water as it ignites spontaneously in air
  - Possesses pungent odor with extreme toxicity
- Pertinent Properties of Red Phosphorus (P_4)
  - Mol. Wt.: 123.9 ; Melting point: 593°C →
  - Density of solid: 2.36 g/cc
  - It exists in at least six different crystal modifications
  - Formed by heating yellow phosphorus to give a high degree of oxidation resistance and stability

Now, we start discussing about the phosphorus its properties and production process. Pertinent properties of yellow phosphorus P 4. P 4 in the sense its having tetrahedral structure that is sp3 hybridization. It is actually having white color, but when it come in contact with the light what happens? It turns into the yellow.

Its a waxy soft solid which you can cut using knife right, but when it comes into contact with air it immediately ignites. Its molecular weight is 123.9, melting point is 44.1 degree centigrades, boiling point is 280 degree centigrades. Density in solid form 1.82 gram per cc in liquid form at 45 degree centigrade it is 1.74.

It must be stored underwater as it ignites spontaneously in the air. It possesses pungent odor like garlic kind of order with extreme toxicity. So, these are the properties of yellow phosphorus. Some of the properties there may be n number of properties we are taking a few physical properties here.

So, if you see the pertinent properties of red phosphorus which is also having tetrahedral structure, but it gets polymerized that is one tetrahedral structure of P 4 another connects with the other one and then it forms a kind of polymer. So, then it is a red hard crystalline kind of material right.

So, how you can get? If you heat this white or yellow phosphorus at temperature something like 250 to 450 degree centigrade for longer hours, then you can get this red phosphorus which is crystalline and very hard material ok. Actually, it is also having tetrahedral structure, but it gets polymerized with different P 4 molecules ok whereas, yellow phosphorus does not get polymerized.

Molecular weight of red phosphorus is also same 123.9, melting point is very high 593 degree centigrade whereas, for the yellow phosphorus it is just 44.1 degree centigrade. This increase in melting point because this red phosphorus get polymerized and forms a crystalline hard crystalline kind of material and then density of this one is also high compared to the yellow phosphorus it is 2.36 gram per cc.

It exists in at least 6 different crystal modifications formed by heating yellow phosphorus to give a high degree of oxidation resistance and stability. Actually, what happens? This is immediately gets oxidized by air when it comes into the contact with the air it ignites immediately and oxidize this right.

So, that oxidation resistance can be improved if you heat it at high temperature in inert atmosphere at high temperature for longer hours then you can get a you know a material which is red in color and then it is having high degree of oxidation resistance and stability.

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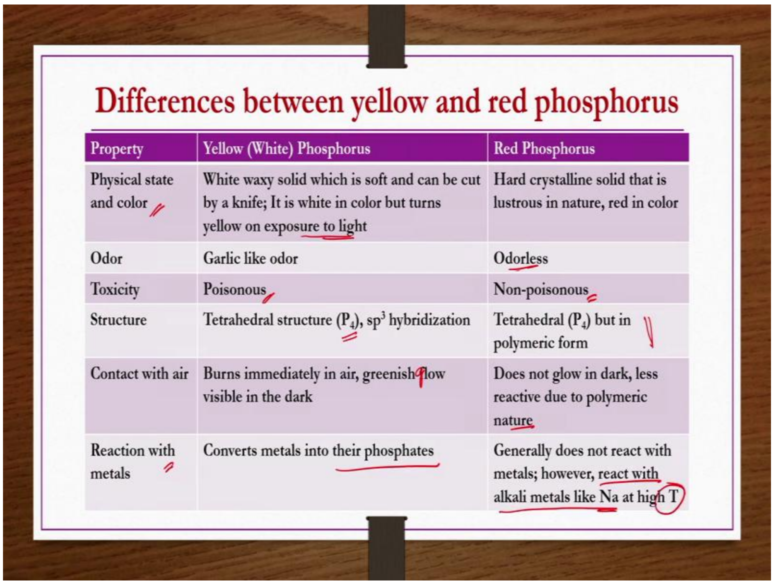

Differences between yellow and red phosphorus

Property	Yellow (White) Phosphorus	Red Phosphorus
Physical state and color	White waxy solid which is soft and can be cut by a knife; It is white in color but turns yellow on exposure to light	Hard crystalline solid that is lustrous in nature, red in color
Odor	Garlic like odor	Odorless
Toxicity	Poisonous	Non-poisonous
Structure	Tetrahedral structure (P_4), sp^3 hybridization	Tetrahedral (P_4) but in polymeric form
Contact with air	Burns immediately in air, greenish glow visible in the dark	Does not glow in dark, less reactive due to polymeric nature
Reaction with metals	Converts metals into their phosphates	Generally does not react with metals; however, react with alkali metals like Na at high T

Now, we see a few basic differences between yellow and red phosphorus. Physical property physical state and color if you see this yellow phosphorus actually which is white in color white waxy solid which is soft and can be cut by knife, but though it is in white in color, but turns into yellow on exposure to light that's the reason it is also known as the yellow phosphorus as well.

Whereas, the red phosphorus is hard crystalline solid that is lustrous in nature and then red in color. Odor is garlic like odor yellow phosphor is having whereas, the red phosphorus is not having any odor. Toxicity yellow phosphorus is highly poisonous whereas, this one is non-poisonous. Structure, yellow phosphorus is having P 4 tetrahedral structure sp 3 hybridization whereas, the red phosphorus is also tetrahedral, but in polymeric form.

Different P 4 molecules are connecting and forming a polymer to give a very hard red crystalline material having very high melting point. When contact with air yellow or white phosphorus burns immediately in air, greenish glow visible in the dark whereas, the red phosphorus does not glow in the dark less reactive due to polymeric nature.

Reaction with metals yellow phosphorus converts metals into their phosphates whereas, the red phosphorus does not react with metals; however, react with alkali metals like sodium, but at high temperatures. These are a few basic you know differences between yellow and red phosphorus.

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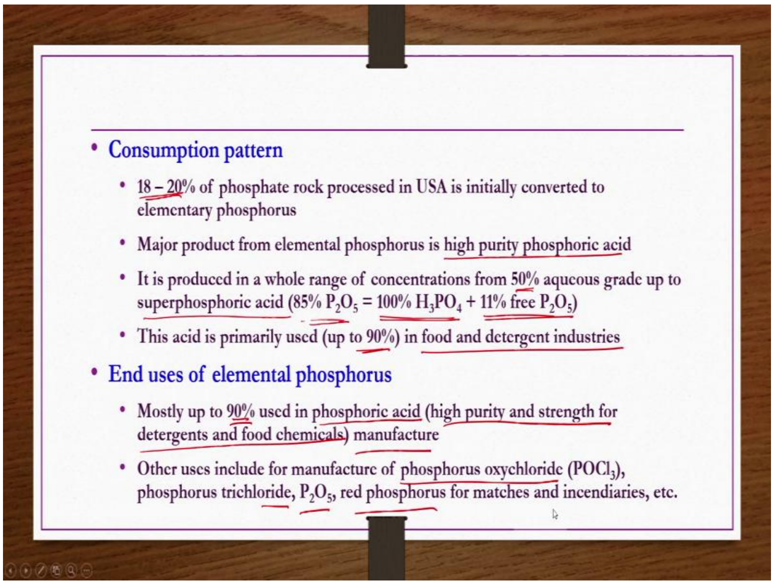

- Consumption pattern
  - 18 – 20% of phosphate rock processed in USA is initially converted to elementary phosphorus
  - Major product from elemental phosphorus is high purity phosphoric acid
  - It is produced in a whole range of concentrations from 50% aqueous grade up to superphosphoric acid (85% P_2O_5 = 100% H_3PO_4 + 11% free P_2O_5)
  - This acid is primarily used (up to 90%) in food and detergent industries
- End uses of elemental phosphorus
  - Mostly up to 90% used in phosphoric acid (high purity and strength for detergents and food chemicals) manufacture
  - Other uses include for manufacture of phosphorus oxychloride ($POCl_3$), phosphorus trichloride, P_2O_5, red phosphorus for matches and incendiaries, etc.

Consumption pattern if you see in USA whatever phosphate rock processed out of which 18 to 20 percent is utilized for converting into elemental phosphorus. Major product from elemental phosphorus is high purity phosphoric acid which is used for different purposes.

It is produced in a whole range of concentration from 50 percent aqueous grade up to super phosphoric acid whereas, in the super phosphoric acid you will be having 85 percent P 2 O 5 which is nothing but 100 percent H 3 PO 4 plus 11 percent free P 2 O 5.

This acid is primarily used in food and detergent industries up to 90 percent end uses of elemental phosphorus if you see in India mostly up to 90 percent used in phosphoric acid manufacture which is high purity and strength for detergents and food chemicals. Other uses include for manufacture of chemicals like phosphorus, oxychloride, POCl 3, phosphorus, trichloride P 2 O 5, red phosphorus, for matches and incendiaries etcetera.

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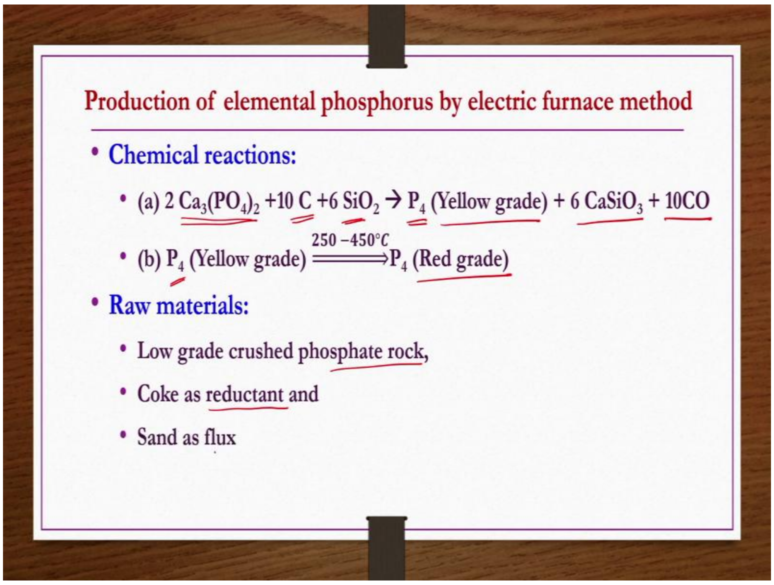

Production of elemental phosphorus by electric furnace method

- Chemical reactions:
  - (a) $2\ Ca_3(PO_4)_2 + 10\ C + 6\ SiO_2 \rightarrow P_4$ (Yellow grade) + $6\ CaSiO_3 + 10CO$
  - (b) P_4 (Yellow grade) $\xrightarrow{250-450°C}$ P_4 (Red grade)
- Raw materials:
  - Low grade crushed phosphate rock,
  - Coke as reductant and
  - Sand as flux

Now, we see production of elemental phosphorus by electric furnace method ok. So, we start with the conventional process of starting with reactions raw materials, basis etcetera. So, chemical reactions whatever the phosphate rock is there fluorapatite that is in the mineral form that reacts with the coke and then silica that is available in the sand we are going to use sand also for this process.

So, this reaction takes place you get P 4, yellow grade and then calcium silicate and then carbon monoxide ok. Other reactions you know if you wanted to get red grade phosphorus what you have to do you have to take this yellow grade phosphorus and then heat it at about 250 to 450 degree centigrade for longer duration of several hours to get this P 4 red grade.

Raw materials, low grade crushed phosphate rock, then coke as reductant because whatever the fluorapatite is there that has to be reduced to P 4 and then calcium silicate and then carbon monoxide. Then sand as flux.

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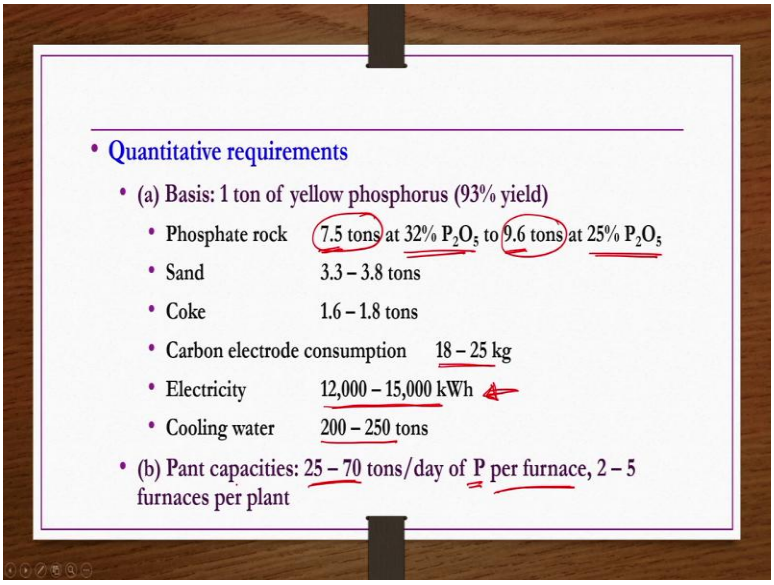

- Quantitative requirements
  - (a) Basis: 1 ton of yellow phosphorus (93% yield)
    - Phosphate rock 7.5 tons at 32% P_2O_5 to 9.6 tons at 25% P_2O_5
    - Sand 3.3 – 3.8 tons
    - Coke 1.6 – 1.8 tons
    - Carbon electrode consumption 18 – 25 kg
    - Electricity 12,000 – 15,000 kWh
    - Cooling water 200 – 250 tons
  - (b) Pant capacities: 25 – 70 tons/day of P per furnace, 2 – 5 furnaces per plant

Quantitative requirements if you see basis 1 ton of yellow phosphorus with 93 percent yield if you wanted to produce phosphate rock you need 7.5 tons at 32 percent P 2 O 5 to 9.6 tons at 25 percent P 2 O 5. So, this number of tons 7.5 to 9.6 that depends on the what is the purity of P 2 O 5 in the raw material phosphate rock that you have taken right.

So, accordingly you have to calculate and select that amount ok. Sand 3.3 to 3.8 tons coke 1.6 to 1.8 tons and then carbon electrode consumption because electric furnace method we are using. So, electrodes; obviously, is required 18 to 25 kgs of carbon electrode consumption is there.

Electricity for this process because its electric furnace method. So, then in the furnace high temperature is there around 1400 to 1500 degree centigrade. So; obviously, in if you wanted to maintain such high temperature in the furnace. So, then you have to give high electricity cooling water 200 to 250 tons required.

Plant capacity is less per furnace in a plant more than one furnace usually there in some plants there may be two furnace there in some plants there may be 5, 6 furnaces may also be there. Per furnace you get 25 to 70 tons per day of phosphorus whereas, 2 to 5 furnaces per plant are possible depending on the capacity of the plant.

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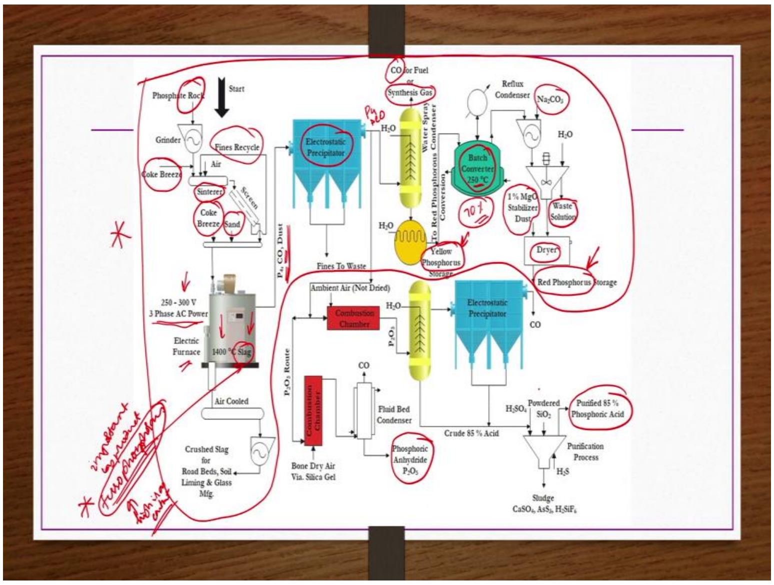

Now, this is the flow chart for the production of a yellow phosphorus, red phosphorus, phosphoric anhydride P 2 O 5 and then purified phosphoric acid right. These many are there in one plant usually it is there. So, we take step by step what we do? We first concentrate on production of yellow and red phosphorus.

So, we take only this part of flow sheet and discuss now. We are going to discuss after discussing this one when we discuss about the phosphoric acid production at the end of the class. So, whatever the phosphate rock is there fluorapatite that you crush in a grinders and then size reduce it and then what you do?

You add Coke Bridge; Coke Bridge is nothing but very fine particles that you get while doing the coking of coal right. So, then that mixture you take that mixture of coke bridge and then crushed or crushed and grounded phosphate rock take it to the sinterer where you do the sintering by adding some amount of air also. Why do we need to do the sintering?

It provides the electrical resistivity also it avoids entrainment of fines because when this material when you take it to the furnace actually without doing sintering also you can directly take it to the furnace and do the desired reduction of fluorapatite to get the phosphorus vapors and then you do the condensation to get the yellow phosphorus etcetera all those that is also possible, but what happens?

We have already seen this phosphorus is very reactive towards the atmosphere. So, whatever the fines are there. So, they should not be going out of the process and then they are also toxic. So, also you know one of the important factor is that you know technicians are labour working in phosphorus industries for longer time they often get a typical disease.

So, that is the reason it is very essential to maintain or doing the sintering so, that to avoid escaping of fines of P 4 from the vapors after the reaction or before the reaction. So, that is the other advantage. So, first advantage is that when you do the sintering it gives the electrical resistivity ok. Also, it will entrainment of fines in release to P 4 and then CO vapors after the reaction in the furnace.

When this material you take here in the furnace and do the reaction. So, what you are going to get? You are going to get PO CO and dust. So, here you do not want lot of entrainments like particles you want to be flowing down along the fused area so, that you know reduction can take place effectively.

You do not want the particles to be suspended on the top of the furnace and then they may not be easily getting reduced to the P 4 ok. So, that is the other advantage. Two advantages are there for doing the sintering and then since you are talking about the escape of the fines etcetera. That you do not want. So, then screening has to be done. So, that the desired size of the sintered material you can take to the furnace right.

After doing the screening any fines are there that you can take it as a fines recycle and send back to the sinterer to proper size enhancement by sintering again ok. Size control is very much essential here ok that is one of the engineering parameter or engineering major engineering problem that we are going to see ok. Size of the particle is one of the essential part here.

Now, depending on the size analysis right are not only based on the size analysis, but also based on the analysis of the phosphate rock that you are having that is how much percentage of P 2 O 5 it is having based on that one appropriate quantities of Coke Bridge and sand are added here along with the sintered material sintered phosphate rock right.

How much quantities of sand, coke etcetera that depends on you know what is the percentage of P 2 O 5 that is present in the phosphate rock. This mixture is then sent to the top shot of the electric furnace which is having you know 250 to 300 volts requirement 3 phase alternative current power electric furnace right.

Here the temperature is maintained around 1400 to 1450 degree centigrades right the feed charge drops gradually into the fused section of the furnace where the reduction to elemental phosphorus takes place so, that you get the P 4 vapors and then CO gas along with that one some dust may also be there right. So, here at the bottom what you may be having?

You may be having the slag right this slag is very important by product because it is often found to have ferro phosphorus. So, it has to be recovered ok. Sometimes it is important because of high iron content may be there based on the sources of the rock whatever the phosphate rock fluorapatite you take sometimes you know iron content may also be there if the iron content is high.

So, then all that comes into the slag the slag that is the reason it is very important not only from the ferro phosphorus point of view, but also from the point of high iron content. So, then you have to recover them carefully and then use them appropriately ok. So, in the downstream of this furnace what you have?

You will be having a vacuum fan kind of thing the furnace is maintained under slight vacuum by fans in downstream end of the plant so, that whatever the P 4 CO and dust are there that can be comfortably removed from the furnace and then can be taken to electrostatic precipitator ok.

Here in the electrostatic precipitator whatever the fines are there they will be collected and then sent to the waste dust fines etcetera are there they will be collected and sent to the waste whereas, the P 4 and then CO are there they will be sent to a condenser where water is being sprayed.

So, here this P 4 whatever is there when it passes through the condenser what happens? It gets cooled and then liquid yellow phosphorus collected as a product and then that is stored under the water because of the safety reasons ok. So, here you are getting yellow phosphorus as a product whereas, the non-condensed CO is there that can be taken as fuel or sent to synthesis gas plant for the production of synthesis gas fine.

So, let us say if you wanted to produce red phosphorus from this yellow phosphorus. What you can do? You can take this yellow phosphorus in a batch converter which is a closed reactor operating at 250 degree centigrade which is having a total reflux condenser as well. So, that to avoid any escape of P 4 from here right.

So, this reactor is provided with a jacketed system to provide cooling water because the reaction itself is exothermic and then that also you are doing at 250 degree centigrade. So, then proper temperature of the reactor has to be maintained. So, then water circulation is been provided to this batch converter its a batch reactor and then it is having total reflux. So, that to avoid going out of any of the P 4 vapors etcetera are there.

So, then they can come back because of the total reflux. So, this reaction occurs at 250 degree centigrade and then it occurs for a longer hours you have to run it for the longer hours 6 to 8 hours or something like that. So, when 70 percent conversion is taken place approximately that is 70 percent of yellow phosphorus is converted into the red phosphorus then this material gets solidified whatever the material that you have taken that gets solidified.

So, after 6 to 8 hours of running approximately 70 percent of conversion takes place once 70 percent of conversion takes place this material gets solidified that you can take it to a subsequent process of cooling, chipping out and washing with the aqueous Na 2 CO 3 solution right followed by washing with water to remove waste solution waste any wastes are there as a waste solution etcetera. That you do it.

And if at all unstable P 4 is there that can also be removed in this one and then that product final product is taken to a dryer where it is stabilized with a 1 percent magnesium oxide stabilizer dust ok. So, that you get the final high oxidation resistant and stable red phosphorus as a product here ok.

So, this is about production of yellow phosphorus and red phosphorus production from phosphate rock using the electric furnace method. So, whatever the description that we have seen through flow sheet the same we are going to see as a text here again before going into the production of phosphoric acid etcetera by the remaining part of the flow chart.

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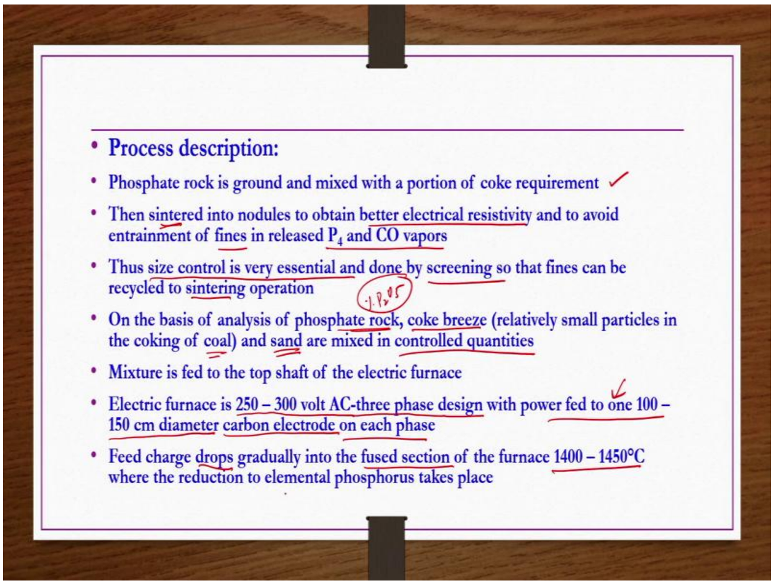

- Process description:
- Phosphate rock is ground and mixed with a portion of coke requirement ✓
- Then sintered into nodules to obtain better electrical resistivity and to avoid entrainment of fines in released P_4 and CO vapors
- Thus size control is very essential and done by screening so that fines can be recycled to sintering operation

% P_2O_5

- On the basis of analysis of phosphate rock, coke breeze (relatively small particles in the coking of coal) and sand are mixed in controlled quantities
- Mixture is fed to the top shaft of the electric furnace
- Electric furnace is 250 – 300 volt AC-three phase design with power fed to ✓ one 100 – 150 cm diameter carbon electrode on each phase
- Feed charge drops gradually into the fused section of the furnace 1400 – 1450°C where the reduction to elemental phosphorus takes place

Phosphate rock is ground and mixed with portion of coke requirement, then sintered into nodules to obtain better electrical resistivity and to avoid entrainment of fines in released P 4 and CO vapors whatever are forming after the reduction reaction in the furnace that is the advantage of sintering essentiality of the sintering.

Thus, size control is very essential and done by screening so, that fines can be recycled to sintering operations after sintering still if any fines are there you do not want to take them into the furnace because they may be entraining in the reaction zone and then may not be undergoing the required reduction.

So, those fines what you do? You take back to the sintering operation for the recycling purpose. On the basis of analysyis of phosphate rock that is how much percentage of P 2 O 5 is there accordingly coke bridge which is nothing but small particles in coking of coal and then sand are mixed in control quantities how much it is required that depends on what is the percentage of P 2 O 5 that is present in the phosphate rock.

Then mixture is fed to the top shaft of the electric furnace. Electric furnace is 250 to 300 volt alternative current three phase design with power fed to 100 to 150 centimeter diameter carbon electrode on each phase this is to one electrode only. Feed charge drops gradually into the fused section of the furnace which is at 1400 to 1450 degree centigrade where the reduction to elemental phosphorus takes place.

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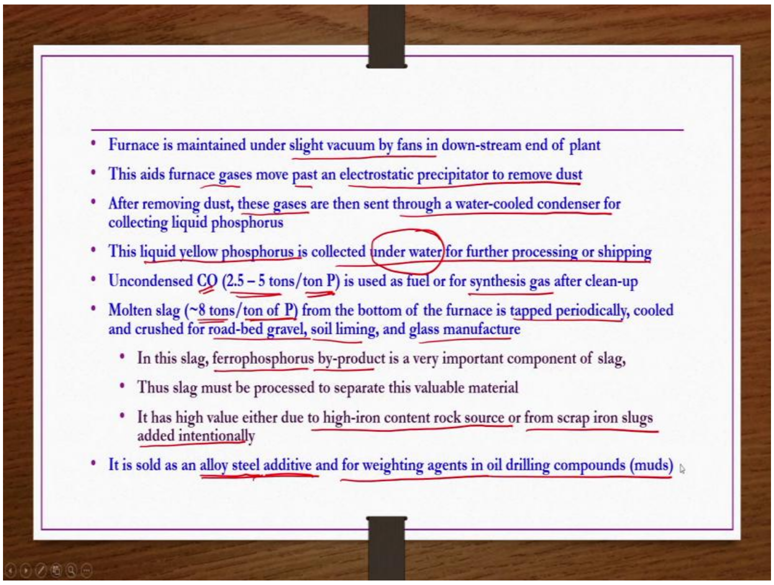

- Furnace is maintained under slight vacuum by fans in down-stream end of plant
- This aids furnace gases move past an electrostatic precipitator to remove dust
- After removing dust, these gases are then sent through a water-cooled condenser for collecting liquid phosphorus
- This liquid yellow phosphorus is collected under water for further processing or shipping
- Uncondensed CO (2.5 – 5 tons/ton P) is used as fuel or for synthesis gas after clean-up
- Molten slag (~8 tons/ton of P) from the bottom of the furnace is tapped periodically, cooled and crushed for road-bed gravel, soil liming, and glass manufacture
    - In this slag, ferrophosphorus by-product is a very important component of slag,
    - Thus slag must be processed to separate this valuable material
    - It has high value either due to high-iron content rock source or from scrap iron slugs added intentionally
- It is sold as an alloy steel additive and for weighting agents in oil drilling compounds (muds)

Furnace is maintained under slight vacuum by fans in downstream end of plant this aids furnace gases move fast an electrostatic precipitator to remove the dust. After removing the dust these gases are then sent through a water cooled condenser for collecting liquid phosphorus product. This liquid yellow phosphorus is collected under water for further processing or shipping under water because of safety concerns because when it comes into contact with air it immediately ignites.

So, one of the engineering problem is that nearby this production plant there should not be any air as well or especially in the zones where this phosphorus formation and condensation is taking place there should not be any air. Whatever, uncondensed CO is there that is in high quantities for example, per ton of phosphorus production you get 2.5 to 5 tons of CO carbon monoxide that can be used for synthesis gas production after clean up or it can be used as it is as fuel.

Molten slag is also high quantity let us say for ton of phosphorus production you get approximately 8 tons of molten slag from the bottom of the furnace is tapped periodically cooled and crushed for roadbed gravel soil liming and glass manufacture. In this slag ferro phosphorus by product is a very important component of the slag.

So, then it has to be recovered properly it is high value either due to high iron content rock source or from scrap iron slags added intentionally. It is sold as alloy steel additive and for waiting agents in oil drilling muds or oil drilling compounds etcetera.

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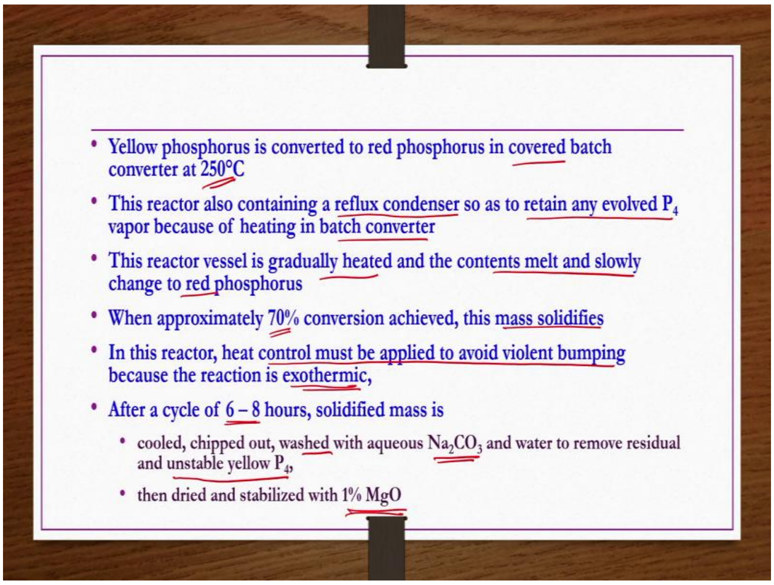

- Yellow phosphorus is converted to red phosphorus in covered batch converter at 250°C
- This reactor also containing a reflux condenser so as to retain any evolved P_4 vapor because of heating in batch converter
- This reactor vessel is gradually heated and the contents melt and slowly change to red phosphorus
- When approximately 70% conversion achieved, this mass solidifies
- In this reactor, heat control must be applied to avoid violent bumping because the reaction is exothermic,
- After a cycle of 6 – 8 hours, solidified mass is
  - cooled, chipped out, washed with aqueous Na_2CO_3 and water to remove residual and unstable yellow P_4,
  - then dried and stabilized with 1% MgO

Yellow phosphorus is converted to the red phosphorus in covered batch converter at 250 degree centigrades. This reactor also containing a reflux condenser so, as to retain any evolved P 4 vapor because of heating in the batch converter. This reactor vessel is gradually heated and contents melt and slowly change to red phosphorus. When approximately 70 percent conversion is achieved this mass gets solidified.

In this reactor heat control must be applied to avoid violent bumping because the reaction is highly exothermic. After a cycle of 6 to 8 hours, the solidified mass is cooled, chipped out washed with aqueous Na 2 CO 3 and water to remove residual and unstable yellow P 4 then dried and stabilized with 1 percent magnesium oxide dust.

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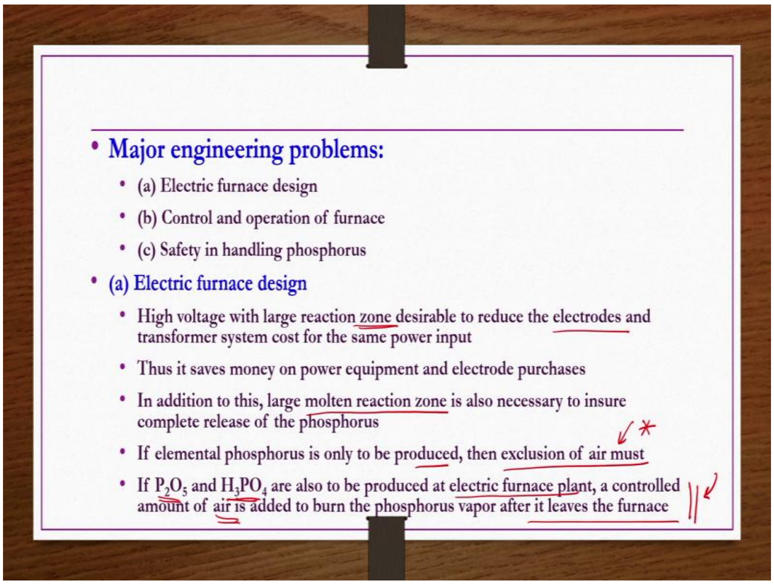

- **Major engineering problems:**
  - (a) Electric furnace design
  - (b) Control and operation of furnace
  - (c) Safety in handling phosphorus
- **(a) Electric furnace design**
  - High voltage with large reaction zone desirable to reduce the electrodes and transformer system cost for the same power input
  - Thus it saves money on power equipment and electrode purchases
  - In addition to this, large molten reaction zone is also necessary to insure complete release of the phosphorus
  - If elemental phosphorus is only to be produced, then exclusion of air must
  - If P_2O_5 and H_3PO_4 are also to be produced at electric furnace plant, a controlled amount of air is added to burn the phosphorus vapor after it leaves the furnace

Now, we see major engineering problems, the electric furnace design must be done very carefully because the process is electric furnace process. So, then whatever the reaction is taking place within the reaction is taking place. So, the reaction zone has to be sufficiently large such kind of problems may be there ok. And then power and then how to save the money by giving how much power saving you can do all those things are also needed to be carefully evaluated.

Then control and operation of the furnace specified quantities of feed has to come because of the percentage of P 2 O 5 present in the phosphate rock. Accordingly, coke and then sand should also be taken and then size of the sintered material is also essential. So, the control and operation of furnace is very essential.

Safety in handling phosphorus because we understand the yellow phosphorus especially it ignites immediately when it comes in contact with the air. So, then proper safety precaution should be taken near the production and then storage of this yellow phosphorus.

So, we see individual details of these three problems. Electric furnace design high voltage with large reaction zone desirable to reduce the electrodes and transformer system cost for the same power unit because it will save the money and then in addition to this large molten reaction zone is also necessary to ensure complete release of the phosphorus by the reduction reaction of fluorapatite within the electric furnace.

If elemental phosphorus is only to be produced then exclusion of air is must. How are you excluding the air from the furnace and near by the zone that is very much essential ok. Otherwise, it will catch up the fire immediately and then explosions may take place. If phosphorus pentoxide or phosphoric acid are also to be produced at electric furnace plant.

A controlled amount of air is added to burn the phosphorus vapor after it leaves the furnace and then this is what we are going to discuss now anyway under the title of production of phosphoric acid.

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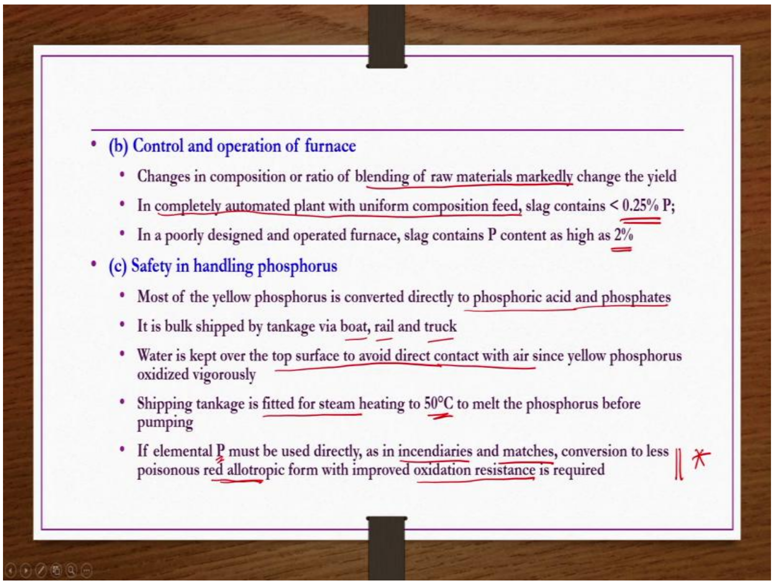

- (b) Control and operation of furnace
  - Changes in composition or ratio of blending of raw materials markedly change the yield
  - In completely automated plant with uniform composition feed, slag contains < 0.25% P;
  - In a poorly designed and operated furnace, slag contains P content as high as 2%
- (c) Safety in handling phosphorus
  - Most of the yellow phosphorus is converted directly to phosphoric acid and phosphates
  - It is bulk shipped by tankage via boat, rail and truck
  - Water is kept over the top surface to avoid direct contact with air since yellow phosphorus oxidized vigorously
  - Shipping tankage is fitted for steam heating to 50°C to melt the phosphorus before pumping
  - If elemental P must be used directly, as in incendiaries and matches, conversion to less poisonous red allotropic form with improved oxidation resistance is required || *

Control and operation of furnace changes in composition or ratio of blending of raw materials markedly change the yield because of the percentage of P 2 O 5 that is present and then because of the size of the sintered phosphate rock. If you have a completely automated plant with uniform composition feed then slag contains less than 0.25 percent P.

If it is not properly designed and operated, then slag contains phosphorus content as high as 2 percent in the slag that is not good that can be taken as a loss. Safety in handling we know that yellow phosphorus is very reactive and immediately ignites when it comes in contact with air. So, then it must be stored properly.

So, most of the yellow phosphorus is converted directly to phosphoric acid and phosphates because of its high reactivity. It is bulk shipped by tankage via boat rail and trucks. Water is kept over the top surface to avoid direct contact with air since yellow phosphorus oxidized vigorously immediately. Shipping tankage is fitted for steam heating to 50 degree centigrade to melt the phosphorus before pumping.

If elemental P must be used directly as in incendiaries and matches conversion to less poisonous red allotropic form with improved oxidation resistance is required if you are producing only elemental phosphorus. Now, we see discuss about the production of phosphoric acid H 3 PO 4.

Pertinent properties of orthophosphoric acid H 3 PO 4 if you see completely miscible with water and forms anhydride phosphoric acid H 3 PO 4 twice H 2 O in water solutions.

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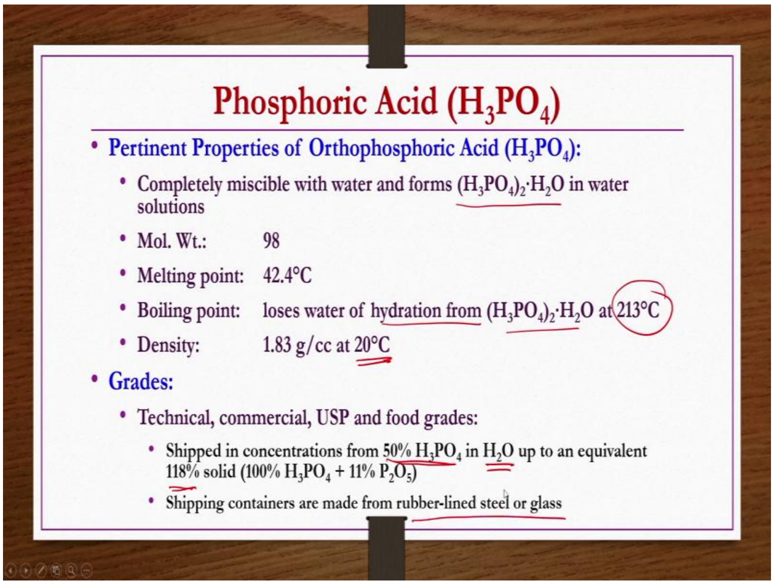

Phosphoric Acid (H_3PO_4)

- **Pertinent Properties of Orthophosphoric Acid (H_3PO_4):**
  - Completely miscible with water and forms $(H_3PO_4)_2 \cdot H_2O$ in water solutions
  - Mol. Wt.: 98
  - Melting point: 42.4°C
  - Boiling point: loses water of hydration from $(H_3PO_4)_2 \cdot H_2O$ at 213°C
  - Density: 1.83 g/cc at 20°C
- **Grades:**
  - Technical, commercial, USP and food grades:
    - Shipped in concentrations from 50% H_3PO_4 in H_2O up to an equivalent 118% solid (100% H_3PO_4 + 11% P_2O_5)
    - Shipping containers are made from rubber-lined steel or glass

Molecular weight is 98, melting point is 42.4 degree centigrade close to the one that yellow phosphorus is having. Yellow phosphorus is approximately 41.4 degree centigrades. Boiling point looses water of hydration from H 3 PO 4 twice H 2 O at 213 degree centigrades. Density at 20 degree centigrade is 1.83 gram per cc. Grades technical commercial USP and food grades are available.

Shipped in concentration from 50 percents phosphoric acid in water up to an equivalent 118 percent solid that is having 100 percent H 3 PO 4 and 11 percent P 2 O 5. Shipping containers are made from rubber line steel or glass from the safety point of view.

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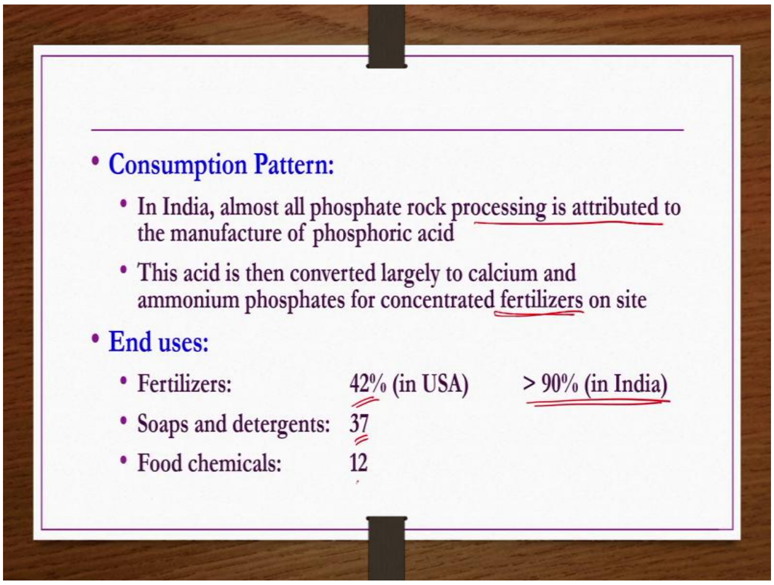

- **Consumption Pattern:**
  - In India, almost all phosphate rock processing is attributed to the manufacture of phosphoric acid
  - This acid is then converted largely to calcium and ammonium phosphates for concentrated fertilizers on site
- **End uses:**
  - Fertilizers: 42% (in USA) > 90% (in India)
  - Soaps and detergents: 37
  - Food chemicals: 12

Consumption pattern in India almost all phosphate rock processing is attributed to the manufacture of phosphoric acid. This acid is then converted largely to calcium and ammonium phosphates for concentrated chemical or mixed fertilizers on site requirement. End uses in India more than 90 percent of phosphoric acid is used for fertilizers production whereas, in US it is only 42 percent for fertilizers, 37 percent for soaps and detergents whereas, the 12 percent for food chemicals.

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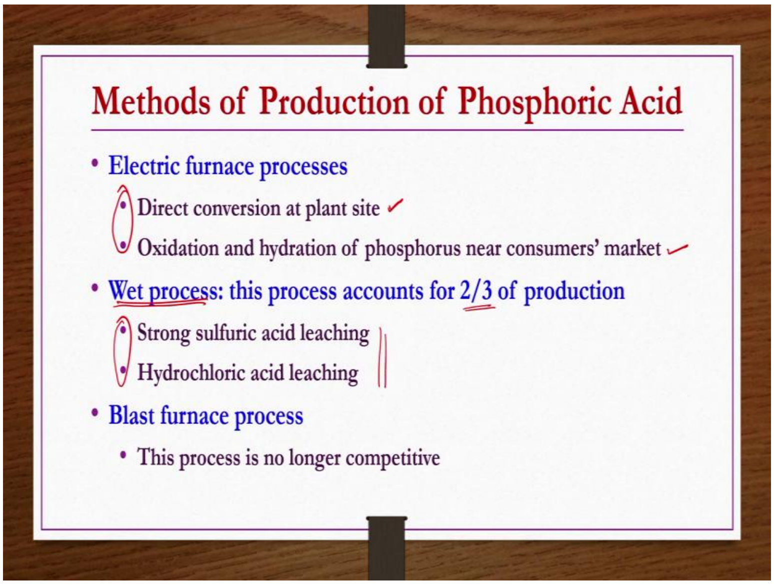

Methods of Production of Phosphoric Acid

- Electric furnace processes
  - Direct conversion at plant site
  - Oxidation and hydration of phosphorus near consumers' market
- Wet process: this process accounts for 2/3 of production
  - Strong sulfuric acid leaching
  - Hydrochloric acid leaching
- Blast furnace process
  - This process is no longer competitive

Methods of production of phosphoric acid there are several methods. We take one by one. The first one is electric furnace method where we have direct conversion at plant site and then oxidation and hydration of phosphorus near consumers market. So, these two methods we are going to discuss now. Then wet process, this process account for two-third of phosphoric acid production.

Whatever the phosphoric acid is available in the market, two-third of that one is produced by this wet process which we are going to discuss in next lecture. Here also wet process is done by two different ways. One is strong sulfuric acid leaching; another one is hydrochloric acid leaching process. Third one is blast furnace process, but it is no longer competitive anymore.

So, we are not going to discuss this one. So, we are going to complete these two things now in today's lecture and then in the next lecture we will be discussing about these two processes.

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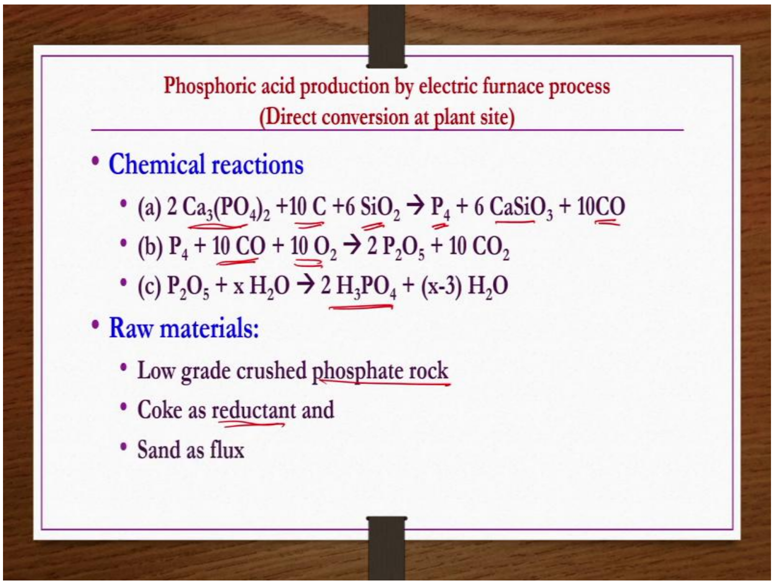

Phosphoric acid production by electric furnace process
(Direct conversion at plant site)

- Chemical reactions
  - (a) $2\ Ca_3(PO_4)_2 + 10\ C + 6\ SiO_2 \rightarrow P_4 + 6\ CaSiO_3 + 10CO$
  - (b) $P_4 + 10\ CO + 10\ O_2 \rightarrow 2\ P_2O_5 + 10\ CO_2$
  - (c) $P_2O_5 + x\ H_2O \rightarrow 2\ H_3PO_4 + (x-3)\ H_2O$
- Raw materials:
  - Low grade crushed phosphate rock
  - Coke as reductant and
  - Sand as flux

Phosphoric acid production by electric furnace process that is direct conversion at plant site. Chemical reactions whatever the fluorapatite mineral is there that is in the phosphate rock that would be reacting with the coke and then silica of the sand to give phosphorus and then calcium silicate and carbon monoxide.

This phosphorus further reacts with the carbon monoxide and then with air oxygen to give phosphorus pentoxide and then carbon dioxide. This P 2 O 5 further reacts with water to give phosphoric acid ok. Raw materials; obviously, phosphate rock, low grade crushed phosphate rock itself is sufficient.

Coke as reductant because when the phosphate rock get reduced to P 4 yellow phosphorus, then only you can get the P 2 O 5 from P 4 then only you can get a H 3 PO 4 by reacting P 2 O 5 and water. Sand as flux.

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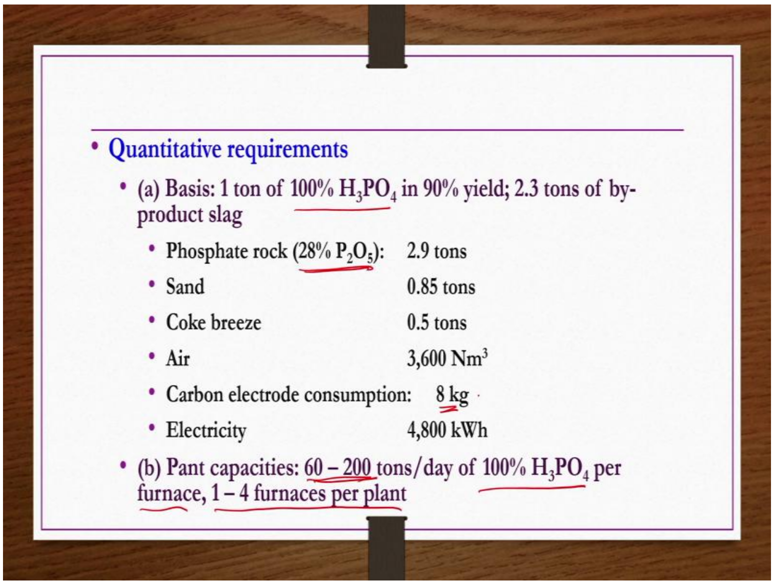

- Quantitative requirements
  - (a) Basis: 1 ton of 100% H_3PO_4 in 90% yield; 2.3 tons of by-product slag
    - Phosphate rock (28% P_2O_5): 2.9 tons
    - Sand 0.85 tons
    - Coke breeze 0.5 tons
    - Air 3,600 Nm^3
    - Carbon electrode consumption: 8 kg
    - Electricity 4,800 kWh
  - (b) Pant capacities: 60 – 200 tons/day of 100% H_3PO_4 per furnace, 1 – 4 furnaces per plant

Quantitative requirements basis 1 ton of 100 percent H 3 PO 4 in 90 percent yield in addition to that 2.3 tons of by-product slack if you wanted to produce. Phosphate rock 28 percent P 2 O 5 you need 2.9 tons, sand 0.85 tons, coke bridge 0.5 tons, air 3600 normal cubic meters, carbon electrode consumption 8 kgs, electricity 4800 kilowatt hour and then plant capacity 60 to 200 tons per day of 100 percent H 3 PO 4 per furnace and then there may be 1 to 4 furnaces per plant.

Now, you can see in this method if you are targeting H 3 PO 4 production rather than the red phosphorous etcetera. Then electrode consumption drastically decreased and then electricity consumption is also drastically decreased compared to the previous process where we discussed about production of yellow and red phosphorous.

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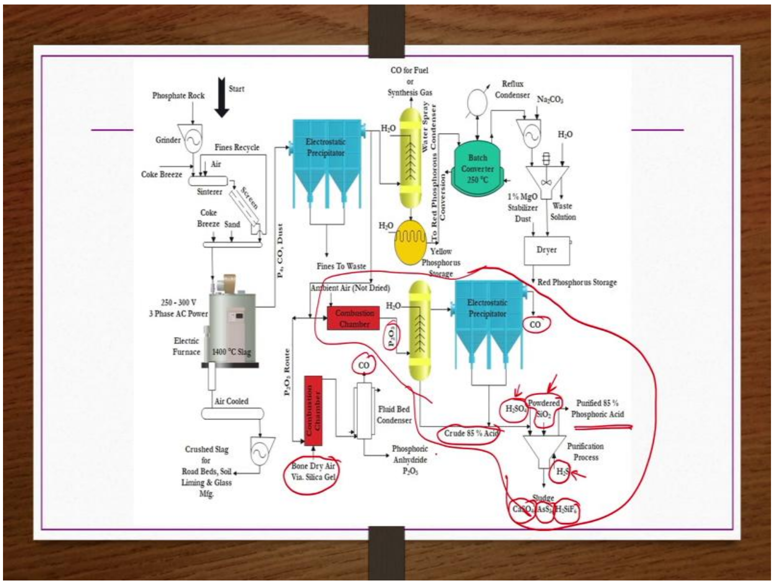

So, now the process is same actually mostly up to the production of these fines whatever from the furnace whatever the P 4 CO are you are producing and then dust etcetera. They are removing the dust from the electrostatic precipitator all that process from up to that point is same.

So, rather now going for the condensation of the vapor to get the liquid P 4 yellow phosphorous what you do you take this approach, right So, now we are not going to repeat the remaining of the process because just now we have seen. So, what you do? Whatever the PO and CO mixture is there after removing the dust from the electrostatic precipitator that you can take to a combustion chamber where ambient air may be added in a controlled manner depending on the composition of P 4 and CO.

Then what happens? This P 4 get converts into the P 2 O 5 and then this P 2 O 5 if you bring in contact with water spray. So, then what you can do? You can remove the acid mix which is approximately 80 percent crude acid. So, then crude 85 percent acid you can get whereas, if you wanted to remove CO.

So, when remaining of the vapors which are not being able to removed by the water spraying. So, they will be sent back to electrostatic precipitator from which you can remove the CO and then here again you get the crude 85 percent acid. This crude acid has to be purified for purification three types of processes are there H 2 SO 4 process if you treat this crude 85 percent acid with H 2 SO 4 then calcium sulphate sludge you can get if arsenic is present in the raw material as impurity.

So, then that would be there in the crude 85 percent acid also. So, then that if you wanted to remove what you can do? You can treat with H 2 S so, that to get arsenic sulphides as a waste material and then if there are fluorides etcetera are there. So, then what you can do? You can use powdered silica material to purify it and then when you react them together this 85 percent acid and then silica.

So, then whatever the fluorides are there in the crude 85 percent acid they will be coming out as a product H 2 SI F 6 ok. All these three are depending individual purification processes treating with H 2 SO 4 powdered SiO 2 and then H 2 S it is shown in one particular unit itself for understanding purpose, but actually it depends on the purity.

Let us say in your crude 85 percent acid there is no arsenic. So, then you do not need to treat with H 2 S you have to selective selectively you have to use them. If all three are then you have to do all three of these treatment process one after other to get the purified 85 percent phosphoric acid ok.

This is one process next process is this one. So, whatever the P 2 O 5 is there that you can take to a combustion chamber where you provide bone dry air via silica gel and then whatever the P 2 O 5 gases etcetera are there. So, they will be sent to a fluidized bed condenser from which CO is removed and then phosphoric anhydride P 2 O 5 is produced this is the other process ok. So, now what we do? We see the descriptive part of the same process ok.

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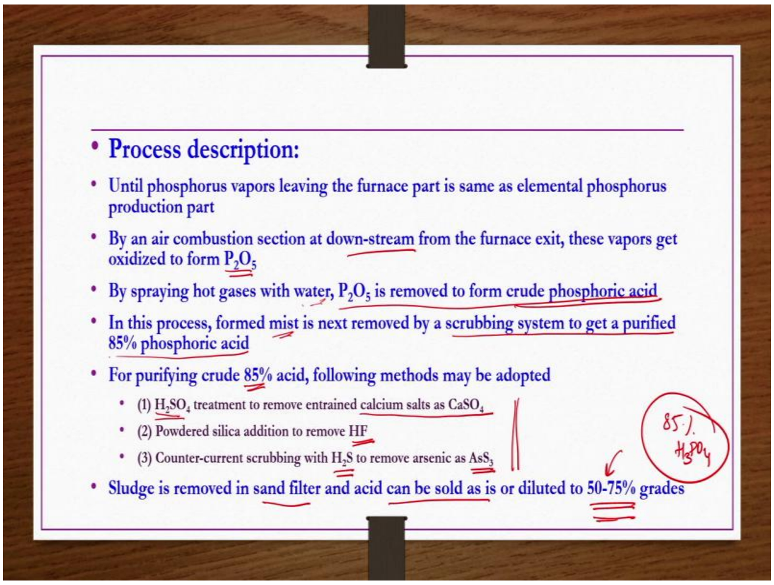

- **Process description:**
- Until phosphorus vapors leaving the furnace part is same as elemental phosphorus production part
- By an air combustion section at down-stream from the furnace exit, these vapors get oxidized to form P_2O_5
- By spraying hot gases with water, P_2O_5 is removed to form crude phosphoric acid
- In this process, formed mist is next removed by a scrubbing system to get a purified 85% phosphoric acid
- For purifying crude 85% acid, following methods may be adopted
  - (1) H_2SO_4 treatment to remove entrained calcium salts as $CaSO_4$
  - (2) Powdered silica addition to remove HF
  - (3) Counter-current scrubbing with H_2S to remove arsenic as AsS_3
- Sludge is removed in sand filter and acid can be sold as is or diluted to 50-75% grades

85% H_3PO_4

Until phosphorous vapors leaving the furnace part is same as elemental phosphorous production part by an air combustion section a downstream from the furnace exists these vapors get oxidized to form P 2 O 5 as we have seen in flow sheet. By spraying hot gases with water P 2 O 5 is removed to form crude phosphoric acid in this process formed mist is next removed by a scrubbing system to get a purified 85 percent phosphoric acid then this purification depends on the nature of impurity that is present in the crude phosphoric acid.

So, for purifying crude 85 percent phosphoric acid following methods are adopted one is treatment with H 2 SO 4 to remove entrained calcium salts as calcium sulphate and then addition of powdered silica to crude 85 percent phosphoric acid to remove HF and then counter current scrubbing of crude phosphoric acid with H 2 S to remove arsenic as arsenic sulphides etcetera.

So, depending on the impurity you have to choose the purification method if all three impurities are there. So, then you have to do all three of them though we have shown them in one unit you have to do sequentially one after other if all three are present. Sludge is removed in sand filter and acid can be sold as is are diluted to 50 to 75 percent grade because 85 percent H 3 PO 4 is very strong actually is very very strong acid ok.

So, rather further improving its purity what you do you dilute it as per the requirements you do not need phosphoric acid more than 85 percent for any of the applications you need diluted ones only. So, then you can dilute as per the requirement of the consumer.

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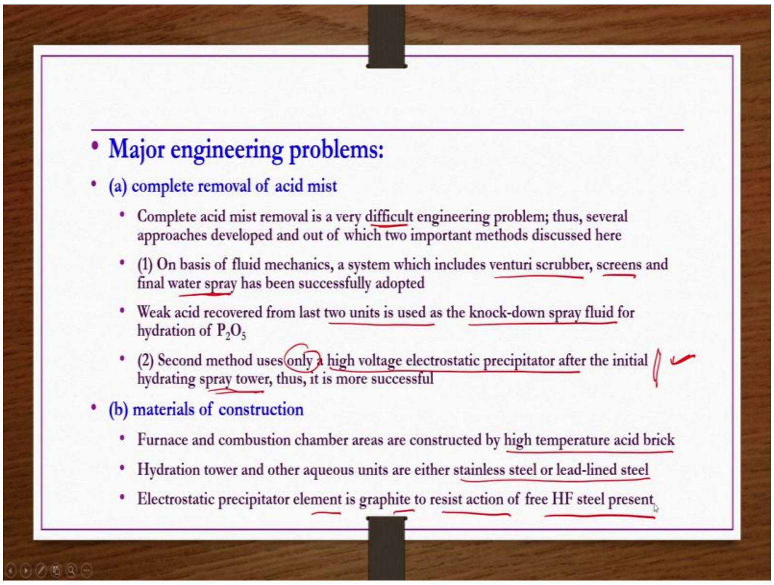

- **Major engineering problems:**
- (a) complete removal of acid mist
  - Complete acid mist removal is a very difficult engineering problem; thus, several approaches developed and out of which two important methods discussed here
  - (1) On basis of fluid mechanics, a system which includes venturi scrubber, screens and final water spray has been successfully adopted
  - Weak acid recovered from last two units is used as the knock-down spray fluid for hydration of P_2O_5
  - (2) Second method uses only a high voltage electrostatic precipitator after the initial hydrating spray tower, thus, it is more successful
- (b) materials of construction
  - Furnace and combustion chamber areas are constructed by high temperature acid brick
  - Hydration tower and other aqueous units are either stainless steel or lead-lined steel
  - Electrostatic precipitator element is graphite to resist action of free HF steel present

Now, coming to the major engineering problems two engineering problems are there in this phosphoric acid production by the direct conversion at the plant site in the electric furnace method. One is the complete removal of the acid mist another one is the material of construction because of the corrosiveness of the products that are being found material of construction is very essential.

So, complete removal of acid mist is very difficult engineering problem the several approaches developed and out of which two important methods discussed here one is the electrostatic precipitator method that we have seen anyway in this slide. Another one is the on the basis of the fluid mechanics a system which includes venturi scrubber screens and final water spray has been successfully adopted whereas, the weak acid recovered from the last two units is used as knockdown spray fluid for hydration of P 2 O 5.

The second method is use of high voltage electrostatic precipitator you don’t need to do so, many operations only one right and then that also after the initial hydrating spray tower itself. So; obviously, because of this one you know in which the capital cost is reduced and then operational cost is also reduced ok.

So, that is the reason it has become more successful and then same we have seen in the flowchart also after removing CO from the electrostatic precipitator whatever the acid mist collected that is the crude 85 percent phosphoric acid and then that has been subsequently purified as we have seen in the flowchart.

Now, coming to the materials of construction furnace and combustion chamber areas are constructed by high temperature acid bricks. Hydration tower and other aqueous units are either stainless steel or lead lined steels. Electrostatic precipitator element is graphite to resist action of the free HF steel plant.

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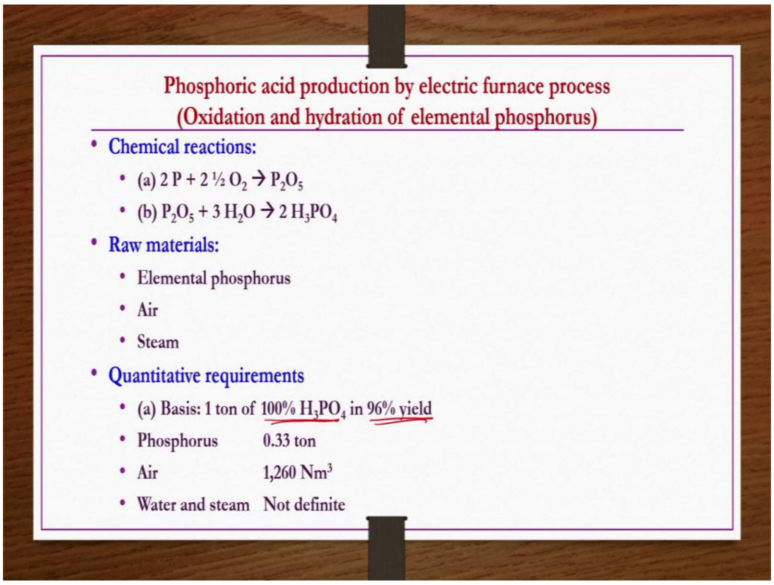

Phosphoric acid production by electric furnace process
(Oxidation and hydration of elemental phosphorus)

- Chemical reactions:
  - (a) $2 P + 2 \frac{1}{2} O_2 \rightarrow P_2O_5$
  - (b) $P_2O_5 + 3 H_2O \rightarrow 2 H_3PO_4$
- Raw materials:
  - Elemental phosphorus
  - Air
  - Steam
- Quantitative requirements
  - (a) Basis: 1 ton of 100% H_3PO_4 in 96% yield

Phosphorus	0.33 ton
Air	1,260 Nm^3
Water and steam	Not definite

Now, we see phosphoric acid production by electric furnace process, oxidation and hydration of elemental phosphorous. Here the chemical reactions whatever the elemental phosphorous is there that you do oxidation then you get P 2 O 5. This P 2 O 5 reacts with water to give phosphoric acid raw materials; obviously, elemental phosphorous and then air and then steam.

Quantitative requirements basis one ton of 100 percent H 3 PO 4 in 96 percent yield if you wanted to produce then phosphorous that is elemental phosphorous 0.33 tons, air 1260 normal cubic meters and then water and steam not definite depends on the process requirements.

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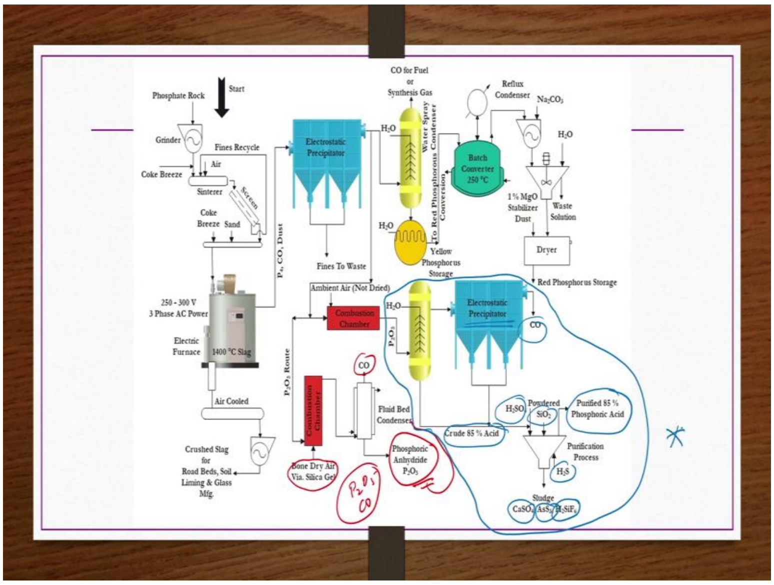

Now, this process actually is done in small quantities as per the requirement of consumer and because of that one that reason these are far away from the you know plants usually away from the phosphoric acid plants. So, then what happens here? Whatever the elemental phosphorous that is there that is taken to a combustion chamber where bone dry air via silica is provided because this air has to be dry enough then when it passes through here.

So, then the reaction takes place then when this reaction takes place the temperature rises to the very high temperature something like 2000 degrees centigrades etcetera. So, the vapors whatever are formed are having combination of P 2 O 5 and then CO etcetera. Here. So, this mixture is sent to a fluid bed condenser where you remove the CO and then phosphoric anhydride P 2 O 5 you get as a product right.

This P 2 O 5 again you follow the same process again from here we follow the same process whatever we have seen in oxidation process to get phosphoric acid. So, once you get the P 2 O 5 by this method this P 2 O 5 has to be water sprayed to remove whatever the crude 85 percent acid if it is not completely removed.

So, then that has to be gases or uncondensed gases has to be taken to the electrostatic precipitator from where you can remove the CO if required if it all traces are there otherwise most of the acid mist is removed as a crude 85 percent phosphoric acid here. This crude acid is treated with H 2 SO 4 silica H 2 S depending on the impurities whatever are there and then those impurities are removed as sludges in the form of calcium sulphate arsenic sulphide and then you get purified phosphoric acid ok.

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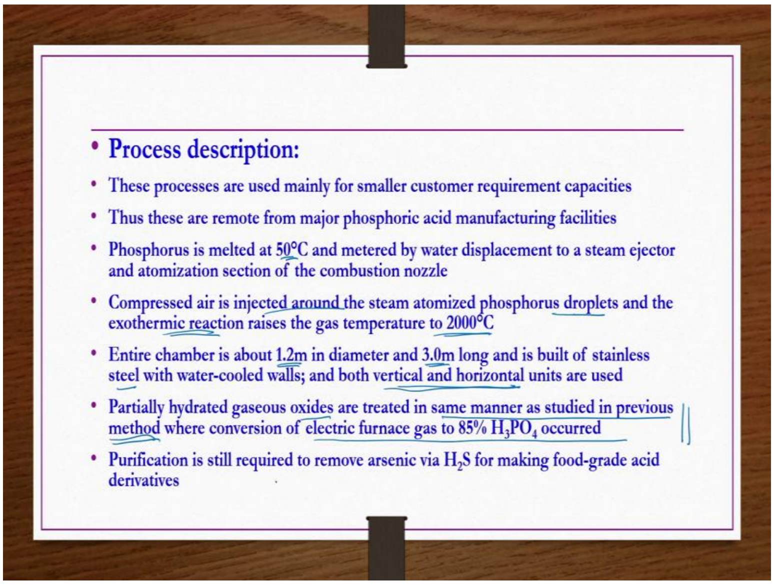

- **Process description:**
- These processes are used mainly for smaller customer requirement capacities
- Thus these are remote from major phosphoric acid manufacturing facilities
- Phosphorus is melted at 50°C and metered by water displacement to a steam ejector and atomization section of the combustion nozzle
- Compressed air is injected around the steam atomized phosphorus droplets and the exothermic reaction raises the gas temperature to 2000°C
- Entire chamber is about 1.2m in diameter and 3.0m long and is built of stainless steel with water-cooled walls; and both vertical and horizontal units are used
- Partially hydrated gaseous oxides are treated in same manner as studied in previous method where conversion of electric furnace gas to 85% H_3PO_4 occurred
- Purification is still required to remove arsenic via H_2S for making food-grade acid derivatives

So, this is the third method right. The same method description we are saying these processes are used mainly for smaller customer requirement quantities thus these are removed from major phosphoric acid manufacturing facilities. Phosphorus is melted at 50 degree centigrade and metered by water displacement to a steam ejector and atomization section of the combustion nozzle.

Compressed air is injected around the steam automized phosphorous droplets and the exothermic reaction raises the gas temperature to 2000-degree centigrade entire chamber is about 1.2 meters in diameter and 3 meters in length. These are built of stainless steel with water cooled walls and then both vertical and horizontal configurations are available or indeed used.

Partially hydrated gases oxides are treated in same manner as studied in previous method oxidation method to produce sulfuric acid whatever we have seen where conversion of electric furnace gas to 85 percent H 3 PO 4 occurred the same thing has to be followed as explained. Purification is still required to remove arsenic via H 2 S for making food grade acid derivatives.

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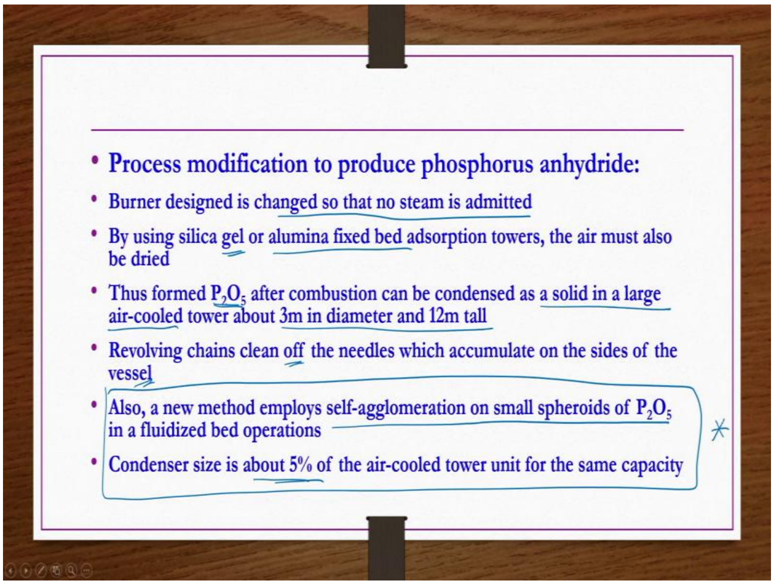

- Process modification to produce phosphorus anhydride:
- Burner designed is changed so that no steam is admitted
- By using silica gel or alumina fixed bed adsorption towers, the air must also be dried
- Thus formed P_2O_5 after combustion can be condensed as a solid in a large air-cooled tower about 3m in diameter and 12m tall
- Revolving chains clean off the needles which accumulate on the sides of the vessel
- Also, a new method employs self-agglomeration on small spheroids of P_2O_5 in a fluidized bed operations
- Condenser size is about 5% of the air-cooled tower unit for the same capacity

Process modification to produce phosphorous anhydride. Burner designed is changed so, that no steam is admitted and then by using silica gel or alumina fixed bed adsorption towers the air must also be dried. Thus formed P 2 O 5 after combustion can be condensed as a solid in large air cooled tower about 3 meter in diameter and 12-meter-tall. Revolving chains clean off the needles which accumulate on the sides of the vessel.

Also, a new method employs self-agglomeration on small sparoids of P 2 O 5 in a fluidized bed operations, condenser size is about 5 percent of the air cooled tower unit for the same capacity. So, this method you know having certain advantages. So, these are the modifications available in the current scenario, but anyway we have not discussed them here.

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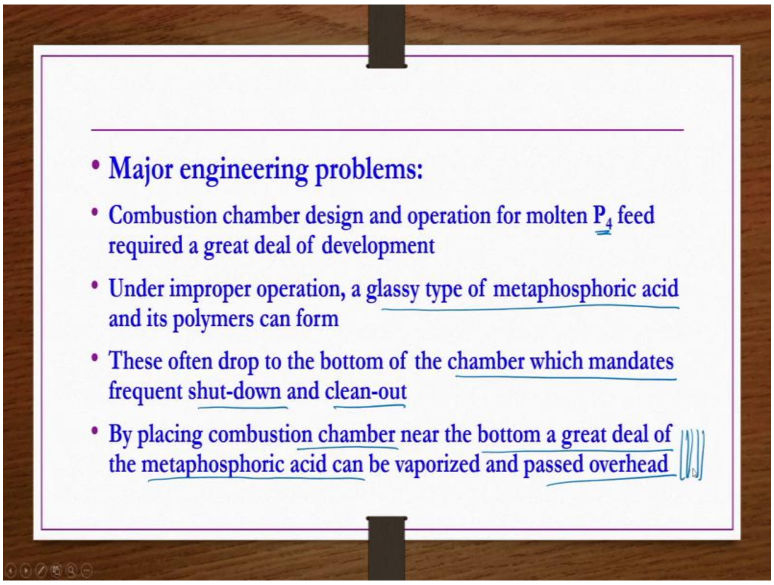

- Major engineering problems:
  - Combustion chamber design and operation for molten P_4 feed required a great deal of development
  - Under improper operation, a glassy type of metaphosphoric acid and its polymers can form
  - These often drop to the bottom of the chamber which mandates frequent shut-down and clean-out
  - By placing combustion chamber near the bottom a great deal of the metaphosphoric acid can be vaporized and passed overhead

Major engineering problem combustion chamber design and operation for molten P 4 feed required a great deal of development under improper operation a glassy type of meta phosphoric acid and its polymers can form which is not desirable product. These often drop to the bottom of the chamber which mandates frequent shutdown and clean out. So, one has to control the feed ok.

So, that because combustion chamber design and operation has to be done properly with the proper molten P 4 feed. By placing combustion chamber near the bottom of a great deal of meta phosphoric acid can be vaporized and passed overhead. So, this is one of the alternative if you cannot avoid the formation of meta phosphoric acid this can be one of the alternatives to remove it.

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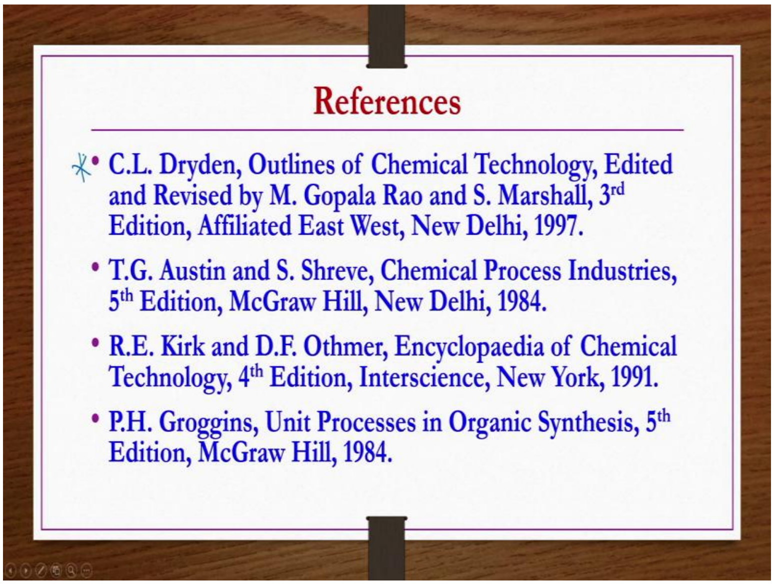

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References for this lecture are provided here, but entire lecture is prepared from this reference book.

Thank you.