Industrial Inorganic Chemistry
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Lecture - 33
Mineral Fertilizers

Good morning everybody. So we will still continue with the Mineral Fertilizers where we talking about the 3 particular elemental thing, that means the nitrogen phosphorus and potassium based fertilizers which we are calling as the mineral fertilizers.

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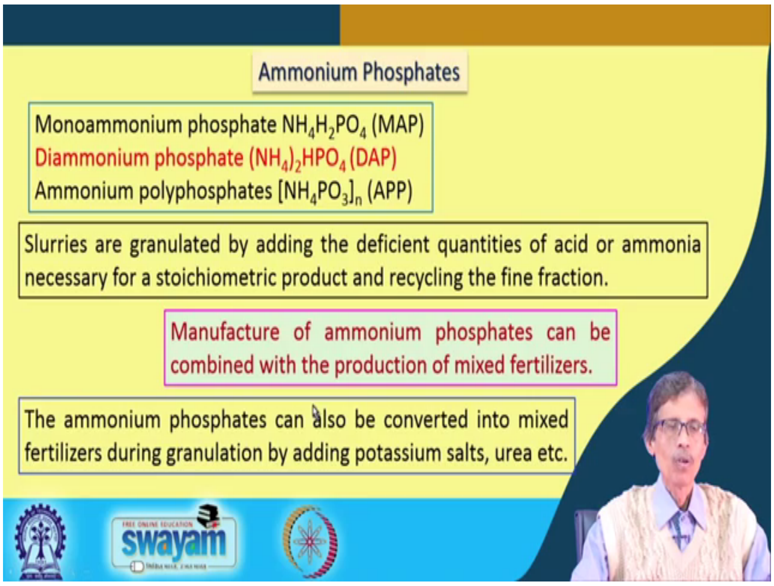

Ammonium Phosphates

Monoammonium phosphate $NH_4H_2PO_4$ (MAP)
Diammonium phosphate $(NH_4)_2HPO_4$ (DAP)
Ammonium polyphosphates $[NH_4PO_3]_n$ (APP)

Slurries are granulated by adding the deficient quantities of acid or ammonia necessary for a stoichiometric product and recycling the fine fraction.

Manufacture of ammonium phosphates can be combined with the production of mixed fertilizers.

The ammonium phosphates can also be converted into mixed fertilizers during granulation by adding potassium salts, urea etc.

So, now, we are talking here as the different types of a combined form; that means if we have a compound like ammonium phosphates how do you think about it is potential as a fertilizer. So, thing is that from the raw starting materials you have to make the ammonium phosphates, then the slow assimilation in the soil it is regular hydrolytic pattern and all these things will contribute to something where we can consider that the mineral supplement for the soil is from the tools, again elemental thing. That means, the ammonium ion the cationic part will give you the nitrogen supplement and the phosphates the phosphorus part will give you the phosphorus supplement.

So, with this single fertilizer what we can have? We can have the 2 species, that means the nitrogen based micronutrients or the corresponding supplement for the soil is available as well as the phosphorus base. So, what are the different types of compounds you can think of and you can make. So, there are 3 types of compounds or 3 categories of compounds one is the mono, another is the dye and another is the poly phosphate type.

So, the first one is your mono ammonium phosphate we know that for all these things the basic material is simply your syrupy phosphoric acid, what we have prepared earlier we have seen that how we can industrially prepare that phosphoric acid from the source of elemental phosphorus.

So, the mineral source there was typically the phosphorus or the phosphate rock materials, the chlorapatite the fluorapatite any phosphate rock can be useful for making this phosphoric acid and now we are consuming that phosphoric acid for it is regular ammonium salts. Because we will try to incorporate the ammonium ion in the inorganic salt species as it is one of the cationic part for it is supplement as nitrogen and the phosphorus part is coming from the phosphoric acids phosphate, because phosphate is everywhere. So, we also know that how the phosphate is there and which is required for your plant growth.

So, if we only substitute out of the 3 protons which is there in the phosphoric acid which is a H_3PO_4. So, if only one of them, that means one of the hydrogen atom or the proton around your phosphoric acid is replaced by the ammonium ion, it is the mono ammonium phosphate which we can get. So, it is $NH_4H_2PO_4$.

So, it is some kind of a basically acidic salt what we all know that if you have a acid like dibasic acid of sulphuric acid type or a tri basic acid of phosphoric acid type one after another or in a stepwise manner we can replace all the 2 protons of sulphuric acid and all the 3 protons of the phosphoric acid. So, if it allows that partial replacement of the proton around your phosphoric acid part we get the mono ammonium phosphate material or which is known as MAP M A P.

Similarly, the replacement of 2 of them give you the di ammonium phosphate or DAP which is very well known which is popularly known as the DAP fertilizer because, it is the common source of both nitrogen as well as the phosphorus as the micronutrient of the plant. Then we can go for ammonium polyphosphates where, you have 1 is to 1 ammonium ion as the phosphate ion is ammonium PO_3 and is a polymeric chain type of thing, where you have the whole n formula which is APP.

So, why we are going for this suddenly this ammonium polyphosphate because, phosphorous we know have always the tendency to go for dimer formation, the trimer formation the way we know for our nucleotides and nucleotides, in our living world we get the di phosphate or the triphosphates all the time very quickly for the preparation of ADP and the preparation of AMP and all these things.

So, the phosphate ester linkages are always there and if we can have some type of that phosphate ester polymerization, we get the polyphosphates, the one of the major advantage of making or getting this particular species out of the former one; that means, compared to MAP and DAP. Why we are getting APP suddenly is that the solubility differences because we do not want to degrade the corresponding fertilizer in the soil so quickly because, we can have the different agricultural seasons in our country also. You can have the agriculture season in winter, we can have agriculture season in summer and we can have in the rainy season also.

So, the moisture content or the water content in the soil level is completely different, if we add some compounds some inorganic compound like your MAP or DAP because they will also have the different solubility characteristics in water medium or in aqueous medium. So, they immediately can go for it is solubilisation and they immediately start degrading or start evaporating or start leaching out from the soil medium.

Compared to that if we have with the APP, which has a less soluble one so we expect that, if we want to get through hydrolysis the ammonium part as well as the phosphate part from the soil medium slowly. So, it can be functioning as a slow release mineral fertilizer.

So, how we get this because the challenge of making these fertilizers is not the dust particle or the powder form what we get in the laboratory, you must have the typical shape and structures of this. So, granulated form is always advantageous form because we have the granules we just throw those granules in the field in the agricultural field we basically throw those.

So, what we make that initially we have the slurries are granulated first by adding the deficient quantities of acid or ammonium necessary for stoichiometry product and recycling the fine fraction. So, initially the lumps basically what you have, so if we have the corresponding lumps we make the slurry and we check the corresponding balance of acidic part that means, the proton content of that particular material or the ammonium content because, if we can vary these 2 we can get either the mono salt or the di salt in different proportions.

So, stoichiometric product and recycling the fine fraction. So, if we get that so through separation depending upon the particle size, that means if you have the very quartz particles we separate them and then we can take the fine fraction and then fine fraction again recycle for it is ammonium content or the proton content.

So, manufacture of this particular phosphate so all the different categories of ammonium phosphates can be combined with the production of mixed fertilizers because, already I told you that what we are making is giving us the chance to get a source of a material, in organic compound contributing nitrogen or phosphorus together to the soil. So, it can function as NP fertilizer. So, is con as a mixed fertilizer because it is not that if you are able to make a potassium salt also then can I can have all 3 together as NPK type of salts.

So, it can also be converted into mixed fertilizers during granulation process that means the corresponding bigger particle formation by adding potassium salts urea etcetera. So, as I told you that if you can convert it to some of them that means you have still if you consider the formula a mono ammonium phosphate which is NH 4 H 2 PO 4 there are still 2 replaceable hydrogen's present. So, if we are able to convert any one or both of these 2 hydrogen's or the protons around this particular salt by potassium replacement by potassium, so it will be a mix salt of potassium ammonium phosphate.

So, that potassium ammonium phosphate can be the corresponding mixed fertilizer and then sometimes it can be mixed with urea. So, urea is a separate compound that we will see also how we can make urea and that will see in our following part of this particular class.

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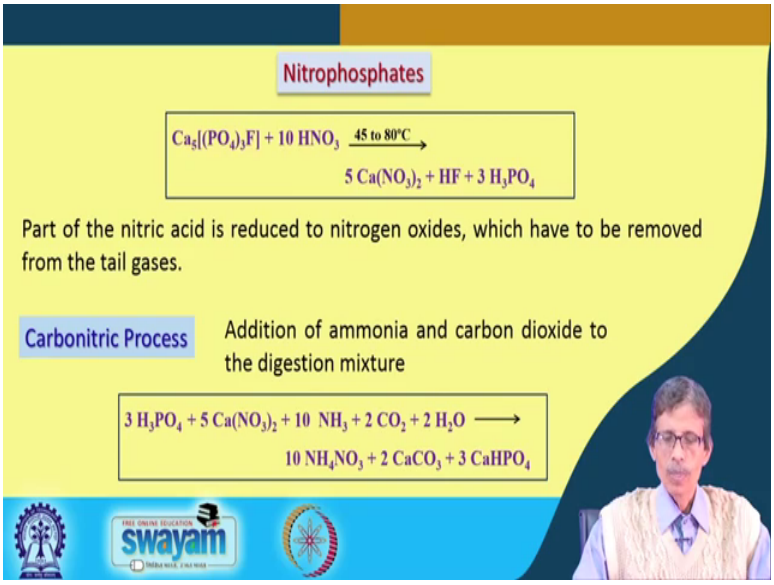

Nitrophosphates

$$Ca_5[(PO_4)_3F] + 10\ HNO_3 \xrightarrow{45\ \text{to}\ 80^\circ C} 5\ Ca(NO_3)_2 + HF + 3\ H_3PO_4$$

Part of the nitric acid is reduced to nitrogen oxides, which have to be removed from the tail gases.

Carbonitric Process

Addition of ammonia and carbon dioxide to the digestion mixture

$$3\ H_3PO_4 + 5\ Ca(NO_3)_2 + 10\ NH_3 + 2\ CO_2 + 2\ H_2O \longrightarrow 10\ NH_4NO_3 + 2\ CaCO_3 + 3\ CaHPO_4$$

Then we bring another one instead of ammonia we can bring some nitro function or the nitro group and those compounds are known as commercially known as nitro phosphates. So, if we consider that if we are not expert in chemistry but we try to understand the industrial aspects of this basic in organic chemistry, what we are talking about only we are discussing the basic one.

But any non chemist can understand these what are the micronutrients what is available for the soil what should be given to the soil, in the soil characteristics or the soil health chart or the health report can her health card can give you that it is deficit in nitrogen or it is deficit in phosphorus or it is deficit in potassium, then we can add selectively the nitrogen supplement the potassium supplement or the phosphorus supplement.

But sometimes we can have the advantage that if we can get these because the nitro can also give you the corresponding nitrogen supplement, but it is in the oxidized form of the nitrogen as it is corresponding anionic radical, that means the nitrate anion or the nitrate radical.

So, as fertilizer these 2 parts that is the ammonium part which is coming from these ammonium phosphate type of fertilizers and the nitrate part their behaviours are completely different in terms of it is fixation of nitrogen in the soil, then that nitrogen which is being assimilated by the plants. So, ribozyme we know that which can fix the corresponding nitrogen from the air and that can be converted to the corresponding nitrate salts. So, those nitrate fixation is sometimes very easy and soil can be supplemented with the nitrate salts.

So, apart from your ammonium salts we should always think of the corresponding nitrate salt as well, because its assimilation process is completely different if we consider that. I am giving you 2 of the typical nitrogen based inorganic compounds one is ammonium chloride another is say potassium nitrate which forget about the potassium component but it has the nitrate component.

So, how these 2 can function as a useful fertilizer the mineral inorganic fertilizer for the soil that we should know we should have some basic idea about it. But since we are going for a typical industrial processes the corresponding outline of those processes and how we get all the different types of important inorganic compounds what can be used as the fertilizer. So, one of them is again we take the same starting material all the time we are talking this particular starting material as your fluorapatite which is calcium phosphate fluoride.

So, that can be treated with nitric acid because we are trying to get the corresponding nitrate as a salt of any of these particular cationic form which is your calcium in your Fluorapatite. So, fluorapatite will be typically converted to that of your calcium nitrate and free hydrofluoric acid as well as free phosphoric acid. So, in the bulk liquid part you have a mixture of hydrofluoric acid as well as phosphoric acid, but the reaction condition is a very mild one, only 45 to 80 degree centigrade is sufficient to get your formation of calcium nitrate. So, you get the calcium nitrate and you have to separate that calcium nitrate you have to crystallize that calcium nitrate from the media as a particular fertilizer.

So, when we go for this, so part of the nitric acid is reduced to nitrogen oxides one of the disadvantages of this particular process, if we consider that the reduction of nitric acid. So, all the nitrates what is coming out is not directly reacting with your calcium ion producing your calcium nitrate. So, you have the reduced form of the different nitrogen gases which have to be removed from the tail gases; for the reaction, you have the corresponding remaining part the unreacted part or the by products in the medium if the by-products or the unreacted part from the reaction is the gaseous product.

So, that gaseous product what you can have, you can have the corresponding gas which is accumulated within the chamber reaction chamber or the reactor. So, which has to be removed from the thing since it is gas, so from the top of the corresponding reaction chamber or the reactor we can take out and this we can consider as a tail gas, because is a tail product from a particular type of reaction.

So, for this particular process one of the process is known as industrially Carbonitric process and that carbonitric process is always we are still with the formation of the nitrates and why we bring it as the carbo, so it is a carbo nitric process what is that. So, it is nothing but we are bringing now carbon dioxide. So, that is the carbo part and nitric acid or the nitrate part is the corresponding nitric part.

So, is a carbonitric part is but the thing is that you have to add ammonia to carbon dioxide or carbon dioxide can be passed in to ammonia in a digestion chamber. So, you have a digestion chamber and that digestion chamber what you can have what we have seen here at the top that the formation of calcium nitrate is there and that calcium nitrate the formed calcium nitrate whatever there in it. So, if we just try to remove this as the tail gas so not only nitrogen oxide, but you can have the removal of hydrofluoric acid gas also or the hydrogen fluoride gas.

So, that hydrogen fluoride can be removed, so we are having with phosphoric acid and calcium nitrate in the liquid medium because this is basically a thick liquid that phosphoric acid we call is a syrupy phosphoric acid when we take or when we buy for our laboratory use the syrupy phosphoric acid for our consumption is a very thick liquid.

So, that will not go away from the reaction medium so it will still be there. So, then we add ammonia as well as carbon dioxide. So, addition of ammonia and carbon dioxide and alone along with the water because all these reactions we are doing in water medium. So, the availability of that particular water medium is always there so how you get the product.

So, the basic understanding in terms of inorganic reactions typical inorganic reactions nothing else you have the acid base reactions, the redox reactions or the metathesis part of the reactions in a all these different or very simple, inorganic reactions what we are talking here also they are all covered in the school level.

So, all the school level reactions if we try to apply for the industrial production because, when you write a particular reaction is very easy to write it, but industrially all these things is very difficult to perform. Because there are large number of obstacles large number of difficulties you have to perform a particular simple inorganic reaction in the laboratory scale to the industrial scale or the corresponding pilot project of the pilot scale.

So, what do you have now addition of ammonia and carbon dioxide and we can have already calcium nitrate. So, calcium nitrate in a metathetic way can give you ammonium nitrate formation, calcium carbonate formation and calcium hydrogen phosphate formation. Why because your ammonium nitrate part is a more soluble part which will still remain in the solution if you have sufficient amount of that used water molecules the 2 water molecules, if you have more number of water molecules the aqueous medium will take care of the entire amount of ammonium nitrate what is being formed over there.

Then calcium carbonate which has also some solubility depending upon is temperature, because most of the time the reaction is if the reaction is exothermic. Even the mixing process the inorganic mixing processes are also sometimes exothermic. So, the solubility of calcium carbonate is also a check point for us, then the calcium hydrogen phosphate.

So, if we can have the difference in solubility we can go for fractional crystallization process. So, industrially important process in this particular regard is your fractional crystallization and that fractional crystallization is basically can be applicable in this carbonitric process for the separation of ammonium nitrate, calcium carbonate and calcium hydrogen phosphate.

So, what do you see apart from your calcium carbonate this is one of the by product from the reaction medium, but we get another type of fertilizer what we all know that is can also be functioning as a ammonium nitrate. As a fertilizer or many other industrial processes where ammonium nitrate can be used and as well as you have the calcium salt of your phosphoric acid.

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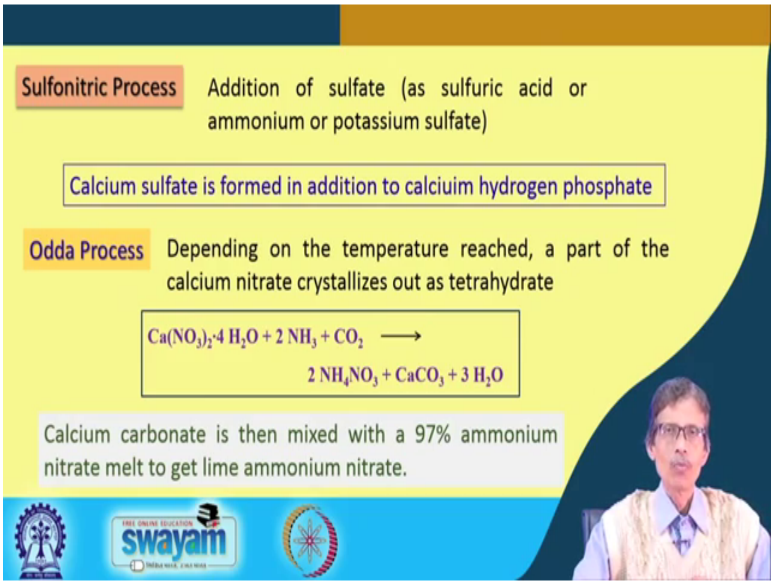

Sulfonitric Process Addition of sulfate (as sulfuric acid or ammonium or potassium sulfate)

Calcium sulfate is formed in addition to calciuim hydrogen phosphate

Odda Process Depending on the temperature reached, a part of the calcium nitrate crystallizes out as tetrahydrate

$$Ca(NO_3)_2\cdot 4\,H_2O + 2\,NH_3 + CO_2 \longrightarrow 2\,NH_4NO_3 + CaCO_3 + 3\,H_2O$$

Calcium carbonate is then mixed with a 97% ammonium nitrate melt to get lime ammonium nitrate.

Then like carbonitric process we have the Sulfonitric process, carbonitric process we have used we are using carbon dioxide and in sulfonitric process we have to add the corresponding contribution from sulphate ion. So, which is being added as sulphuric acid or the different salts of sulphuric acid, that means the ammonium or the potassium sulphate salts. So, we add now sulphates so addition of sulphates how can help this particular process.

So now, since we add sulphate so calcium sulphate is formed, again there is a difference between the solubility of calcium carbonate with that of your calcium sulphate. In addition to the formation of calcium hydrogen phosphate in the previous case also in case of your carbonitric process what we are forming as your KCAH PO 4. So, your calcium hydrogen phosphate is similarly forming over here along with your calcium sulphate. Then another industrially important process is Odda process, because why we are talking about all these processes.

Because all these processes have the benefits and those benefits are basically dependent on the availability of the raw material, the cheaper availability of the electricity manpower obviously and the country what is basically having that particular process, the patented process if it is the country is Germany if it is US of it s China of it is India because these are all 4 major fertilizer producing countries, there is a huge amount of fertilizers for throughout the globe.

So, they can have the different types of processes and sometimes basically the older companies the countries which are dealing with very old companies, if they do not go for the modification the corresponding modernization processes for industrial sector for production of mineral fertilizer. They can still go with these older processes, but the production cost will rise and the company and the country may not be in the corresponding competitive field of this fertilizer industry or the fertilizer business or the economics or the economic health of the country depending on the fertilizer.

So, the particular process the Odda process is depends on the temperature what is being reached a part of the calcium nitrate crystallizes out as the tetra hydrate. So, if we have a heated solution or due to the production of heat through the reaction, if simply the dissolution process the solubilisation process is exothermic in nature.

So, temperature of the reaction medium will rise and what we can have, we can have the solubility increases up for the calcium nitrate, but when we cool down the thing we have to have a particular type of temperature. If we are not able to reach the room temperature, so when a particular type of temperature is reached so, the excess amount of calcium nitrate which is giving you the supersaturated solution. So beyond that so over the super saturation level of your calcium nitrate the remaining amount, the excess amount will be crystallized out from the medium taking out 4 water of molecules as the water of hydrate or water of crystallization. So, the good crystals of calcium nitrate will be obtained as it is tetra hydrate form.

Then the remaining part what we then follow that once you make or once you crystalize it the tetra hydrate of communion nitrate sorry calcium nitrate. So, the tetra hydrate of calcium nitrate then is reacting with ammonia and carbon dioxide giving you ammonium nitrate and calcium carbonate, then the calcium carbonate what is formed or the extra amount of calcium carbonate is mixed with 97 percent of ammonium nitrate melt to get the corresponding ammonium nitrate.

So, the calcium carbonate what is being formed over here along with your ammonium nitrate which can further be treated with your ammonium nitrate melt, basically if these 2 of these melt together and get a lime ammonium nitrate. So, you have the ammonium nitrate then you have the calcium content over it. So, the product what we are getting as a mixed fertilizer part is your lime calcium nitrate. So, some amount of calcium will be there, but the most of the part will be your ammonium nitrate which can be prepared out of this process this Odda process without going for the separation of your calcium salt.

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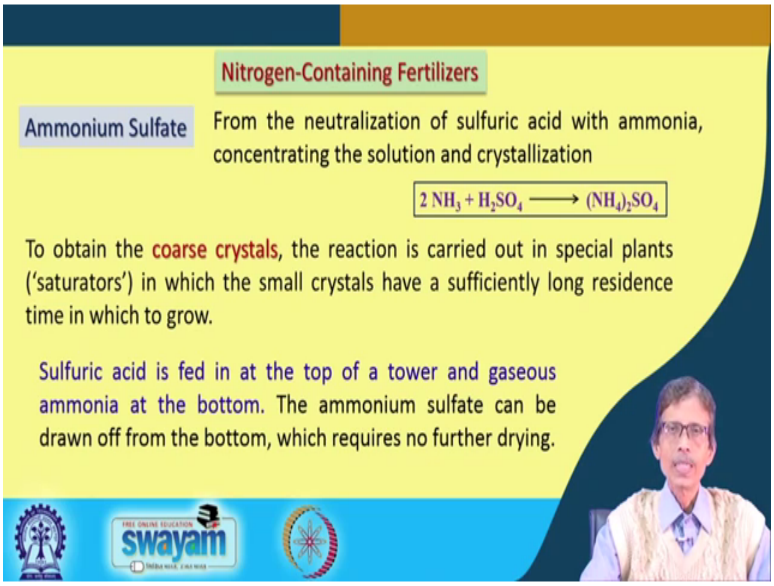

Nitrogen-Containing Fertilizers

Ammonium Sulfate

From the neutralization of sulfuric acid with ammonia, concentrating the solution and crystallization

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

To obtain the coarse crystals, the reaction is carried out in special plants ('saturators') in which the small crystals have a sufficiently long residence time in which to grow.

Sulfuric acid is fed in at the top of a tower and gaseous ammonia at the bottom. The ammonium sulfate can be drawn off from the bottom, which requires no further drying.

Then we can go for the other part that means, the nitrogen containing fertilizer. So, this nitrogen containing fertilizers what we can have we can make very easily the ammonium sulphate, what we know that you have the ammonium component and the sulphate component and we can mix it together giving you ammonium sulphate. So, the neutralization of basically sulphuric acid the way we are neutralizing phosphoric acid can give you the corresponding direct salt of ammonium sulphate from school days we know we write this reaction.

But how to get it basically in a large scale in metric ton basically several tons not only several kilogram or 1000 kilograms in tons of this material how will you make it, because in the test tube scale in a laboratory scale in the round bottom scale or in the bigger scale it is very easy to get because when the component the reactants are in less concentrated form you go the reaction very easily and the reaction is going towards the completion towards 100 percent or 90 percent.

But when you have huge amount of all these things so the local concentration is different if you do not have thorough of mixing and all these things. So, it is very difficult sometimes to make this simple salt like ammonium sulphate preparation in industrially.

So, if we want to get then bigger crystals or coarse crystals. So, the coarse crystals what can be formed is obtained in a particular type of plant the industrial plant which is also known as your saturators, where we get or dissolved the small crystals with sufficiently long residence time in which to grow. So, if we just only the way we make a saturated solution and allow it to live it in a laboratory on a Petri dish or a open dish for evaporation.

So, evaporation gives you saturation and it is giving you also the super saturation and once it is crossing the super saturation level the excess amount of the solid material will be crystallized out of the salt solution. So, you have to have their corresponding time to allow; that means, long residence time to which it is growing.

So, the feeding of sulphuric acid in the reactor is from the top of the tower and gaseous ammonia at the bottom because, the thing is very simple that ammonia that sulphuric acid is a liquid which will you can add drop by drop or you can spray the sulphuric acid from the top of the reactor and from the bottom of the gas because the gas molecules will go up will rise. So, the liquid can come down from the top and gas can go up from the below and there will be the reaction.

So, the ammonium sulphate can be drawn from the bottom. So, whatever ammonium sulphate is formed will be settled down in the bottom. So, you can have some separation we can have some boundary at the bottom of the reaction chamber and we can separate out that ammonium sulphate from the bottom and which requires no further drying basically. Because, it is already dried because we are doing some reaction where sulphuric acid we all know that in the typical dehydrating agent. So, direct reaction of sulphuric acid with ammonia gas will give you a pretty dry product of ammonium sulphate.

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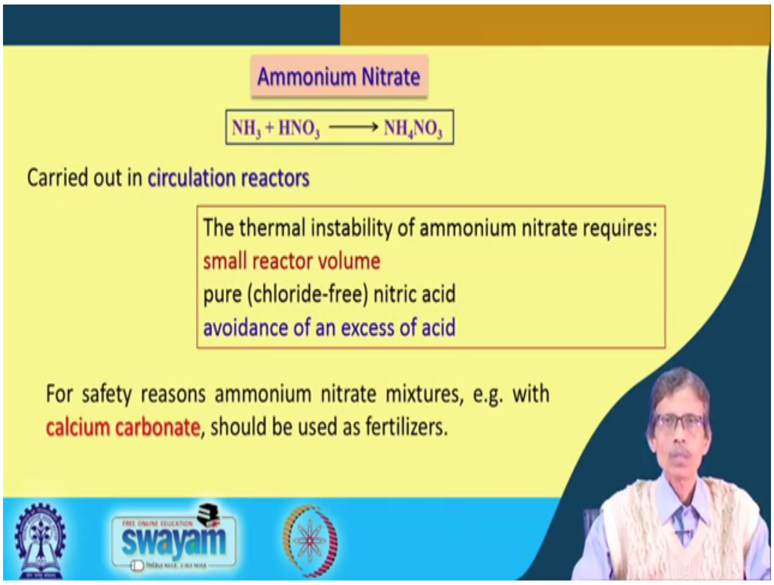

Ammonium Nitrate

$NH_3 + HNO_3 \longrightarrow NH_4NO_3$

Carried out in circulation reactors

The thermal instability of ammonium nitrate requires:
small reactor volume
pure (chloride-free) nitric acid
avoidance of an excess of acid

For safety reasons ammonium nitrate mixtures, e.g. with calcium carbonate, should be used as fertilizers.

Then the other variety that means, ammonium nitrate preparations; ammonium nitrate preparation will tell us the direct reaction of ammonium salt with nitric acid will give you the ammonium nitrate and it is carried out typically not from the feeding from the top or feeding from the bottom it is typically known as circulation reactor.

So, there are circulation reactors available, and those circulation reactors are basically used for this particular ammonium nitrate, but remember it has basically the ammonium nitrate in a very big amount is can function as a explosive. So, it has less thermal stability so its thermal stability or rather we can consider is the thermal instability is really a concern for industrial production.

So, what we can do we just reduce the size of the reactor, so small reactor otherwise you can have the explosion within the reactor also because, is depending upon the mass of the material what we can have that mass will tell you that how much heat can be generated. And if the generated heat is huge one basically there will be an explosion the boiling of the liquid, that means boiling of the water and all these things.

So, the better way of getting this particular reaction industrially is you can have a very small reactor; then we can go for a chloride free nitric acid because, we do not want to have chloride because otherwise you will produce also ammonium chloride and that ammonium chloride will contaminate your product. Then we should avoid the addition of excess acid. So, the reaction should be very much stoichiometric in nature because, we are handing a gaseous component for this particular reaction.

And for the safety reason that if we are able to make in small volume from a smaller type of or smaller size of these reactors, for the safety reason if we want to store in our warehouse or in our godown the huge amount of ammonium nitrate it is not always a very safe technique or safe procedure to keep the pure ammonium nitrate there.

Sometime that why it is mixed with calcium carbonate say or any other inert material which will not help the explosion of your ammonium nitrate and the mixture because already we have seen the calcium as calcium carbonate can also be there as a typical dilute into your mineral fertilizer.

So, the mixed form basically because your cost is less now, if your ammonium nitrate cost is higher because it has the industrial demand also, you have the demand for all other explosion industry also for our deadly use also different making of different types of RDX also we use ammonium nitrate. So, the cost will come down through the addition of calcium carbonate and it will increase the safety of that particular material even we are handling this in the solid form.

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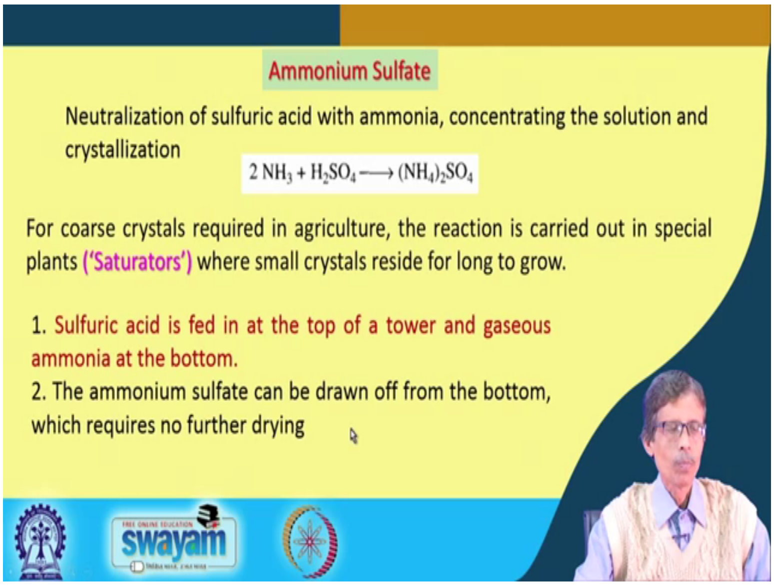

Ammonium Sulfate

Neutralization of sulfuric acid with ammonia, concentrating the solution and crystallization

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

For coarse crystals required in agriculture, the reaction is carried out in special plants ('Saturators') where small crystals reside for long to grow.

1. Sulfuric acid is fed in at the top of a tower and gaseous ammonia at the bottom.
2. The ammonium sulfate can be drawn off from the bottom, which requires no further drying

Then ammonium sulphate the other one, their neutralization of sulphuric acid with ammonia concentrating the solution and then crystallizing. So, these are the all very simple and very straight cut reactions what we are following that we directly we react it, then we can go for this particular one and the saturators what we have seen that small crystals already we have seen this in this case and the gaseous ammonia we have added and drawn from the bottom which required further is not required further drying.

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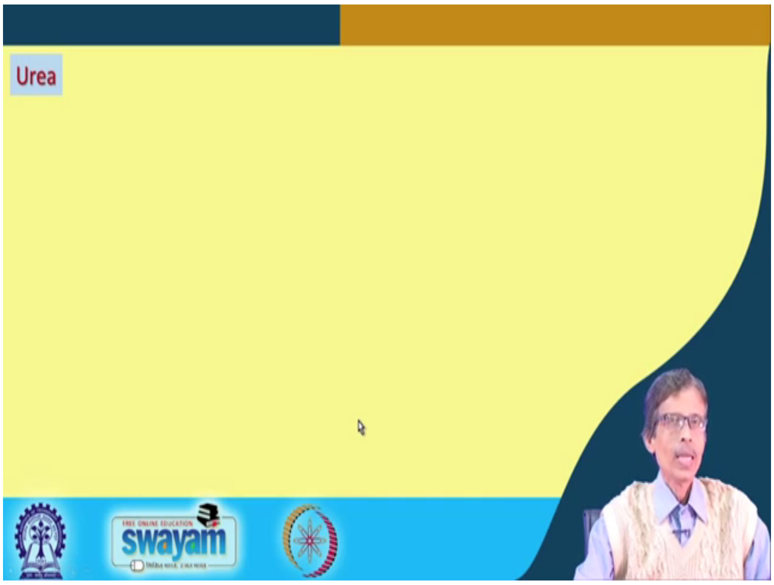
Urea

Then we just go for other compound which will be your urea. So, before talking of all these things that means, sulphate, nitrate and all these things in our next class what we will be talking is your another particular important compound that how we can derive the urea which is historically also very important.

So, the urea compound is nothing, but your NH 2 CO NH 2 and when we are talking about large things of these that already we are the basic component type we have already discussed, that we are reacting ammonia with carbon dioxide. And that if it gives you only the ammonium carbonate and the formula of the urea if it tells you that this formula is very much similar to that individual components.

That means, you have the corresponding NH 2 then you have the CO then another NH 2. So, your central carbon which is attached to the CO function the carbonyl function is also attaching to the 2 of the groups which is NH 2 functions. So, how you get this thing and the chance is that through it is decomposition and through it is hydrolysis as we all know that ureases are there which are responsible for urea hydrolysis can produce ammonia.

So, production of ammonia in a nicer way and it is also dependent on the corresponding rate of hydrolysis. So, the rate of hydrolysis will control its production and that production will be dependent on the amount of urea what we are adding to the soil. So, we will just see how we can produce urea and how we can utilize it urea, this urea and this particular urea can have other several types of uses ok.

Thank you very much.