Industrial Inorganic Chemistry

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Lecture - 32
Iodine and Iodine Compounds

Hello and welcome back to the class once again, where we have started our discussion on the Iodine and that Iodine Compounds.

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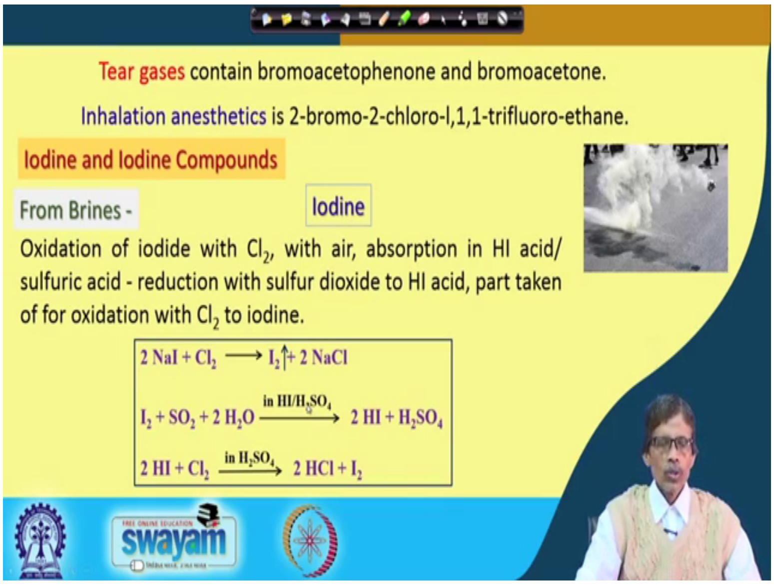

Tear gases contain bromoacetophenone and bromoacetone.

Inhalation anesthetics is 2-bromo-2-chloro-l,1,1-trifluoro-ethane.

Iodine and Iodine Compounds

From Brines -

Iodine

Oxidation of iodide with Cl_2, with air, absorption in HI acid/ sulfuric acid - reduction with sulfur dioxide to HI acid, part taken of for oxidation with Cl_2 to iodine.

$$2\,NaI + Cl_2 \longrightarrow I_2\uparrow + 2\,NaCl$$

$$I_2 + SO_2 + 2\,H_2O \xrightarrow{\text{in HI/H}_2\text{SO}_4} 2\,HI + H_2SO_4$$

$$2\,HI + Cl_2 \xrightarrow{\text{in H}_2\text{SO}_4} 2\,HCl + I_2$$

So, what are those compounds basically, we can have and how we produce iodine first let us see that, the production of iodine. So, if we have the typical supply of brine waters, so brine waters are everywhere. So, again from the brine we can make it and only thing that we should know the corresponding availability of the iodine or iodized compound. That means, it should have, the brine water should have a sufficient concentration of iodide salts. So, those iodide salts are there and those iodide salts how we can get it by simple chlorine oxidation.

So, iodide salts are there and as we all know that chlorine is much more stronger oxidizing agent then iodine if we go down from the along the group in the periodic table the halogen series, we know the fluorine, then chlorine, then bromine, then iodine. So, definitely the upper one that means, the chlorine will be higher oxidizing agent with a stronger oxidizing agent to produce or liberate bromine as well as to liberate iodine free iodine from the iodide salts.

So, what we do basically? That you have to make that means, you have to have the supply of the chlorine gas as we have seen earlier that how we can make chlorine gas. So, you have supply of chlorine in cylinders or the regular supply of chlorine. So, oxidation of iodine will do with chlorine with air and absorption in HI that means H hydroiodic acid and sulfuric acid.

Then the reduction with sulphur dioxide to hydroiodic acid and part then taken for oxidation with chlorine to iodine; so, it is not a very complicated oxidation of any iodized salt by chlorine will give you the free liberation of iodine. Then with air if we absorb this particular iodide salts in hydroiodic acid and sulfuric acid then sulphur dioxide can be used for your corresponding conversion to hydroiodic acid and part taken off for the oxidation of Cl 2 to iodine.

So, oxidation of Cl 2 will be available there to oxidized your iodide salt that particular one will tell us that how iodine production is dependent on many reactions. Three consecutive reactions we can have. The first thing we are considering is as your reaction of sodium iodide. Say in brine water you have plenty of available iodide salt as sodium iodide. So, that sodium iodide basically will oxidize by passing or purging chlorine gas.

So, passing chlorine in the gaseous phase also can liberate your iodine as the solid iodine because iodine is producing from a very small amount. And then when they combine together they crystallized it from the water medium and that aqueous medium containing more amount of sodium chloride it can be separated as the iodine crystals. So, the way we do any reaction in the reaction medium also the liberation of iodine in different types of titrimetric methods. So, we all know that the iodometric titrations and everywhere, that liberation of iodine slowly from the reaction medium because the solubility of iodine in water medium whatever amount of acidity it is it has is less. So, it will separate as the solid crystal, so it will float on the surface of the aqueous medium.

So, through this first reaction you have iodine in your hand. Then that particular iodine, with air and absorption in HI, so you can get it that means, the HI and sulfuric acid you have; so, put both together. So, with some amount of air and you have the corresponding moisture in it. So, that particular iodine, with sulphur dioxide, so sulphur dioxide will be available. So, sulphur dioxide is basically reducing it is the reducing agent to make I 2 again HI. It is a basically a typical purifications step that means, whatever amount of iodine is consumed we are producing that is in the solid lump if they are forming that may not be so pure, so again we react we treat it with sulphur dioxide to convert it to HI.

So, that is also a procedure for making hydroiodic acid, and that hydroiodic acid unlike your sodium iodide now you have the hydroiodic acid. So, hydroiodic acid again react with chlorine gas and in sulfuric acid medium. So, you produce now instead of NaCl it produces a Cl and iodine.

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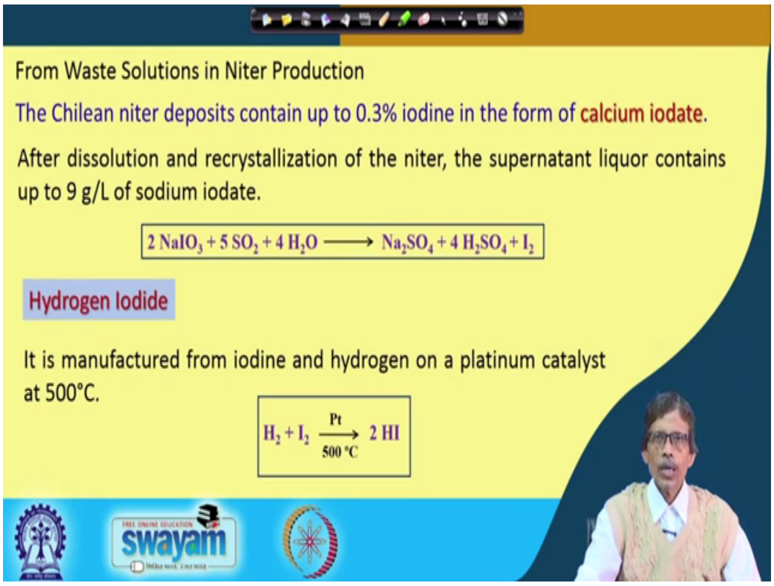

From Waste Solutions in Niter Production

The Chilean niter deposits contain up to 0.3% iodine in the form of calcium iodate.

After dissolution and recrystallization of the niter, the supernatant liquor contains up to 9 g/L of sodium iodate.

$$\boxed{2\,NaIO_3 + 5\,SO_2 + 4\,H_2O \longrightarrow Na_2SO_4 + 4\,H_2SO_4 + I_2}$$

Hydrogen Iodide

It is manufactured from iodine and hydrogen on a platinum catalyst at 500°C.

$$\boxed{H_2 + I_2 \xrightarrow[500\,^{\circ}C]{Pt} 2\,HI}$$

So, this iodine you have. So, iodine from the brine you directly produce it, but another technique is also available from the waste solutions during the Niter production the potassium nitrate preparation.

So, the Chilean Niter deposit basically which is a naturally occurring thing that means, the nature gives us huge amount of those potassium nitrate deposits and that deposits contain up to 0.3 percent of iodine in the form of calcium iodate. Sometimes we report it as the naturally occurring material what is available to us, in terms of certain percentage of iodine but that is not the free iodine. The way we consume our table salt which is known as the iodized salt, but that iodized salt we should always be knowing that it is not that free iodine is present over there. So, it is iodides are there and that iodise with a little bit amount of iodate is there. So, that iodate, iodate combination in when we consumed with the food material there will be slow release of that particular iodine which is available for your iodination or the production of your regular hormone the thyroxine hormone.

So, here also if you have calcium iodate; so, calcium iodate is there and how to liberate that particular calcium iodate? To give you the free iodine, because otherwise during this production it is basically a by product and we will throw away that amount of calcium iodate which are not utilized. So, what we do after dissolution and recrystallization of the Niter? So, Niter preparation is finished, we get it in the recrystallization form. So, you have a very strong mother liquor which is saturated also. The supernatant mother liquor contains up to 9 gram per litre of calcium iodate through that treatment which is converted to sodium iodate.

So whatever calcium iodate; the free calcium iodate in the natural sources of Chilean Niter is now converted through this particular process to its sodium salt or sodium variety which has a higher solubility compared to your calcium iodate. So, per litre of that mother liquor if you try to get that you it will be able to get the corresponding amount of iodate from that particular medium. Say again like that particular thing that means, now sulphur dioxide is utilized for the production of iodine from your iodate.

So, again sulphur dioxide is functioning as a reducing a agent. Earlier we have seen that how it is being reduced for is for reduction of iodine, to iodide now is iodate to iodine formation is again sulphur dioxide in water medium forming your free iodine along with sodium sulphate and sulfuric acid. So, this basically gives such that ok, in your hand you have sufficient amount of iodine and iodine is produced. Like that of our H b r production how you go for your hydrogen iodide or HI production.

So, already we have all these knowledge. So, it is basically a little bit difference in making of the industrial functionality that means how you use it or you have used some catalyst or any other thing. So, again like that of your direct combination that basically they are direct elemental combination, so elemental combinations of hydrogen and iodine at some elevated temperature which is 500 degree centigrade. So, that elevated temperature also is not sufficient you have to have some amount of catalyst and that catalyst is free metal based catalyst which is a noble metal platinum.

So, platinum based catalyst, so this surface is the platinum based catalyst. So, on that particular surface you have the direct combination and possible combination of H 2 plus I 2 giving you that twice of HI at 500 degree centigrade. So, platinum catalysed direct combination of H 2 and I 2 is able to give you huge amount of production of your hydroiodic acid or HI.

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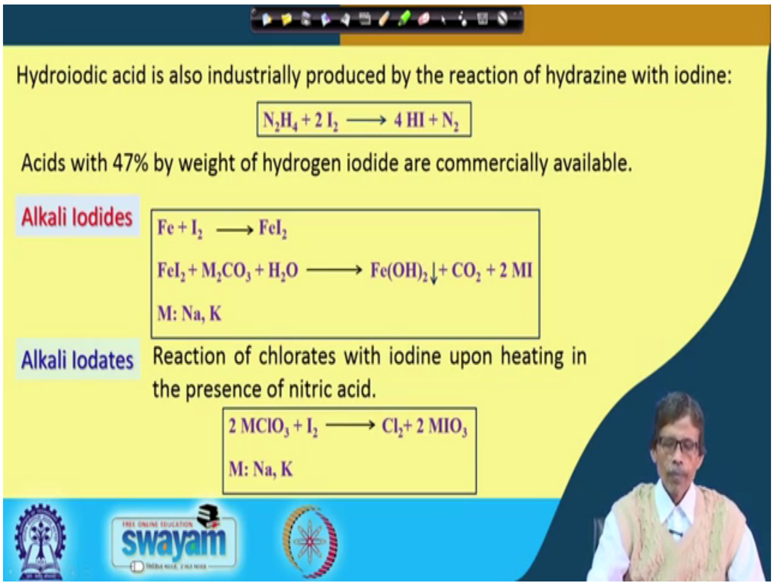

Hydroiodic acid is also industrially produced by the reaction of hydrazine with iodine:

$$\boxed{N_2H_4 + 2\,I_2 \longrightarrow 4\,HI + N_2}$$

Acids with 47% by weight of hydrogen iodide are commercially available.

Alkali Iodides

$Fe + I_2 \longrightarrow FeI_2$

$FeI_2 + M_2CO_3 + H_2O \longrightarrow Fe(OH)_2\downarrow + CO_2 + 2\,MI$

M: Na, K

Alkali Iodates Reaction of chlorates with iodine upon heating in the presence of nitric acid.

$2\,MClO_3 + I_2 \longrightarrow Cl_2 + 2\,MIO_3$

M: Na, K

So, this is industrially produced also apart from your direct combination the elemental combination because most of the time we will see, we will consider that inorganic chemistry is largely dominated by in such a way that what we can have that we always think of the direct combination.

So, if you have a compound available the inorganic compound available to us is of a b form or a b to form always we should think that whether it can be produced by direct combination of a and b. There are large number of (Refer Time: 10:17) where from we get it but the most easiest way of getting that is that you have the pure a in hand and you have also the pure b in hand how we can combine these together to give you the corresponding a b compound.

So, it can also be produced by the reaction of hydrogen and iodine. So, you see that hydrogen is well known reducing agent and hydrogen is sometimes we produce in a large amount what we have seen earlier, while we are talking or while we are considering the corresponding nitrogen compound. So, it is the most useful nitrogen compound which can be utilized because we already know how iodine is there in your hand. So, these two together can combine that means, N 2 H 4 can combine with iodine giving you HI plus nitrogen. So, the hydrogen is basically giving us nitrogen which is also not very harmful for the environment. So, basically, we are producing more amount of nitrogens which can be liberated to the environment or in the air and we will be living behind with the hydroiodic acid. So, hydroiodic acid is produced through a very simple reduction of hydrogen.

So, acids basically of a quality of 47 percent by weight of hydrogen iodide are commercially packed and commercially available because to increase beyond this concentration is sometimes not so helpful, is not economic also to increase the concentration beyond 47 percent. But this particular percentage of hydroiodic acid is useful for all other purposes starting from your laboratory used to industrial consumption.

Then like that of your chlorate and bromate which definitely considered the corresponding iodate also, because we are in every detail we are considering side by side all the compounds whether we are able to make chlorates, we are able to make bromates, as well as we are able to make the corresponding iodides and iodates. So, it is a typical procedure is industrially available procedure of making these that means, corresponding compound as the corresponding alkali iodides where you have sodium iodide and potassium iodide but is through some direct reaction which is also very much useful for making another new compound that means, when iron powder is allowed to react with iodine.

So powder and its form which we now a days call as if you have iron nanoparticles also. So, the small iron particles can directly react with iodine and iodine can function as an oxidizing agent, and which will produce your ferrous iodide FeI 2 and that ferrous iodide can be reacted basically with that of your corresponding sodium or potassium carbonate and water. So, what we expect? That already we have the corresponding iodide salt.

So, that iodide salt basically is in the form of iron iodide which is we are getting from again a direct combination what I just now told you that if you have a and if you have b we always think of getting a b type compound or a b 2 type compound. So, here we have for FeI 2 we have the a b 2 type compound and that a b 2 type compound is a directly available for making another a b type compound which is your corresponding sodium bromide or potassium bromide.

So, in some alkaline medium, so alkalinity in terms of your carbonate alkalinity that means, you simply add sodium carbonate or potassium carbonate aqueous solution of that and take the or transfer the entire amount of ferrous iodide. So, ferrous iodide will be separated from there as ferrous hydroxide and your thing will be liberated as the corresponding metal iodide salts sodium iodide or potassium iodide through the liberation of carbon dioxide. So, the reaction is pretty neat one. Only thing that you have to separate the ferrous hydroxide from the mother liquor.

Then, with that of your iodide how we get the iodate. So, iodate making like that of your bromate we should know the formula the formula is definitely is your IO 3 minus, so either it is sodium again potassium or ammonium salt. But in this particular case which is industrially important and industrially feasible also that reaction of chlorates with iodine. So, we will just allow the chlorates. The chlorates to react with iodine upon heating in the presence of nitric acid. So, it is basically a typical procedure for making your iodate salt.

So, if we have a regular supply of sodium or potassium chlorate that means, NaClO 3 or KClO 3 in your hand. Again direct reaction with iodine that means, iodine is a solid one in in powder form or in its suspension will be allowed to react with your chlorate salt and that chlorate salt through that particular case that means, it will be utilized is as oxidizing agent and that oxidation will convert your iodine to iodate through the liberation of free chlorine. We are utilizing free iodine and we are producing free chlorine.

So, that is also little bit of advantages in terms of your industrial production. That if we are able to produce huge amount of chlorine, we can take that we can trap that particular chlorine and we can reuse for some other purpose or we can use that particular chlorine for making other chlorine compounds. So, the industry which is being devoted to in all other areas. So, halogens halides and all other halogen compounds are from the same group because we are utilizing fluorine for chlorine, chlorine for bromine or bromine for iodine and all others.

So, if something is very useful because the different companies have different routes of making all these things because they always compete to each other to produce in a very low cost and very cheaply the corresponding one that compound. So, always they try to go for something depending upon your availability of the sources that means, the source material they try to adopt newer and newer procedures for the production of all these. So, chlorate will be utilized for making this iodate through the utilization of elemental iodine.

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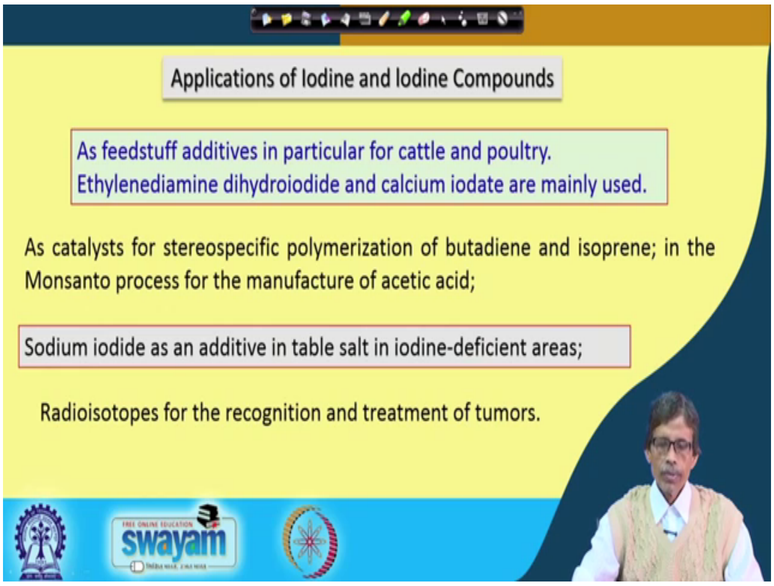

Applications of Iodine and Iodine Compounds

As feedstuff additives in particular for cattle and poultry. Ethylenediamine dihydroiodide and calcium iodate are mainly used.

As catalysts for stereospecific polymerization of butadiene and isoprene; in the Monsanto process for the manufacture of acetic acid;

Sodium iodide as an additive in table salt in iodine-deficient areas;

Radioisotopes for the recognition and treatment of tumors.

Now, like that of our other bromine and iodine other fluorine chlorine and bromine compounds, we should also see we should also take care of the thing because until and unless you do not know the application of these compounds.

So, this particular course has been designed in that way, that the brief outline we are not going in detail of all the industrial thing little bit of this corresponding reactor thing and all these thing but we are focusing our attention mostly on the corresponding inorganic chemistry what should be applicable for your industrial production. So, definitely we should know the corresponding use and application of the compounds until and unless we know these, we cannot say that these iodine compounds will be useful industrially and which is also useful for production in industrial scale.

So, this iodine and iodine based compounds can be very useful as the feedstuffs additive in particular for cattle and poultry. So, the food material that means, the feed feedstuff we call it as a food material for the cattle, cattles and the poultry items all the corresponding hence and others the chickens and all. So, they are basically typically additives. So, when we add additives means basically used for improving its corresponding life and it improves also or stop its degradation with time or oxidation in air or moisture.

Similarly, ethylenediamine dihydroiodide and calcium iodide these are the compounds we should know these compound because already we have seen that the calcium iodate is a naturally occurring compound. So, that particular calcium iodate if we are able to, get it in a purified form because you are adding in a food material it is a feedstuff. So, it should be highly pure one, otherwise you have to go through iodine production and then formation of your sodium iodate and that sodium iodate should be converted to your calcium iodate.

Similarly, ethylene diamine di hydro iodide is nothing but is the hydro ionic salt of ethylene diamine. Ethylene diamine is amine which is a di basic amine which is NH 2 CH 2 CH 2 NH 2. So, that ethylene diamine which is a liquid one it can form salt with any acid. It can form salt with hydrochloric acid, it can form with hydrobromic acid, similarly it can form with hydroiodic acid. So, with hydroiodic acid with HI it gives you the salt that means, it is dot 2 HI of e n ethylene diamine. So, that salt is a solid one and that solid can be utilized for your feed additives for your cattle and poultry.

It can be useful as a catalyst for say this hydroiodic acid if it is there the stereospecific polymerization is a very useful reaction for the polymerization process and the polymerization industry is also use a utilizing this of the polymerization of butadiene and isoprene. Isoprene we all know that isoprene is a corresponding monomeric unit, the monomer for the naturally occurring rubber, rubber material.

So, sometime iodine hydroiodic acid and all these things we have earlier also we have seen that iodine can function as a very good catalyst. So, small amount of all these are very much useful for your development of new catalyst in different industrial sectors. One such is also for the production of acetic acid. Monsanto is the company which is producing and which is producing from the basic ingredients the large amount of acetic acid and they are also that iodine based compounds are utilized as the catalyst.

So, if we if you have the very basic idea that large number of these iodine based compounds are utilized as the catalyst, so always you think of utilization of iodine or any iodine based compound for a catalytic reaction such that the rate of the reaction the conversion of this particular product also can be enhanced through the introduction of new and newer type of your catalyst system.

Then, the sodium iodide as we have already told that along with your table salt which is your sodium chloride, so along with your table salt sodium chloride we add sodium iodide as an additive we are considering as an additive because a very small amount of that. Iodine is required to make the salt as the iodized salt and which is being supplied for iodine deficit areas. So, again since we are talking in terms of your application in the food material you must have a very high purity of those material. That means, the sodium iodide or some amount of iodate what you can have which is of food quality. So, food quality material should be used for addition of these table salts.

Then radio isotopes, that iodine radio isotopes for the recognition and treatment of tumours also. So, we have not discussed anything related to the development of that isotope that other isotopes the iodine 54. The iodine 54 is very useful for diagnosing or sometimes the treatment of the tumour because it is emitting radio active radiations and which can basically attack your tumour. So, it has also the medicinal application or the corresponding application in the medical industry. So, radio isotopes if we are able to get those radio isotopes of iodine which are useful for some treatments or medically.

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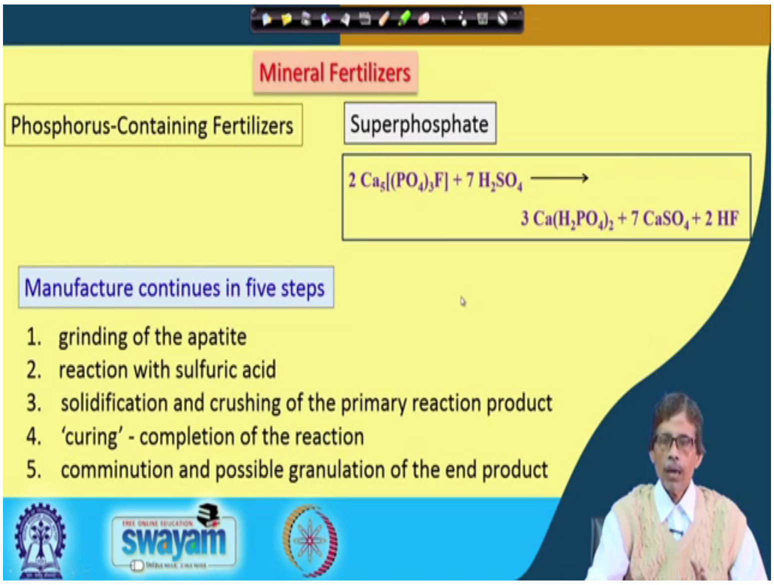

Mineral Fertilizers

Phosphorus-Containing Fertilizers

Superphosphate

$$2\,Ca_5[(PO_4)_3F] + 7\,H_2SO_4 \longrightarrow 3\,Ca(H_2PO_4)_2 + 7\,CaSO_4 + 2\,HF$$

Manufacture continues in five steps

1. grinding of the apatite
2. reaction with sulfuric acid
3. solidification and crushing of the primary reaction product
4. 'curing' - completion of the reaction
5. comminution and possible granulation of the end product

Then, we just move now after all these things that means, whatever we are considering so far related to halogen analyte compounds, now we will move to the sector where we will have the fertilizers. So, fertilizer has a huge industrial sector. And how we get the mineral fertilizers? That means, that we must have the sources the mineral sources. So, natural sources are there and we try to go for some of these reactions, some of these conversions and some of the industrially important in organic reactions.

Typical inorganic reactions or typical inorganic conversions can be utilized for the production of other derivatives of the fertilizers which are not available naturally. Basically, the chemical modification or the chemical treatment of these will tell us that how we get these compounds. So, we know that we have phosphorus, we have nitrogen and we have potassium as your corresponding elemental sources of these fertilizers because we call sometimes that n p k fertilizer or n p k material which is utilized as the fertilizer. So, which has nitrogen source which has potassium source and which has phosphorus source also.

So, the mineral is now phosphorus and the phosphorous containing fertilisers what you can have phosphorus containing fertilizers can be obtained as super phosphates. We call sometimes the super phosphate sublimes how you make. Though these super phosphates basically can be prepared from a reaction what we know that the elemental form of these that means, the material what you use the floor apatite we use. So, the floor apatite we can have, so it is Ca 5 PO 4 whole 3 F.

So, that floor apatite can have calcium. So, elemental composition of these for making super phosphate if you use floor apatite that that F, F is substituted by OH we know that is the hydroxyapatite. So, that floor apatite when it is being treated with sulfuric acid it is giving you calcium phosphates that means, Ca H 2 PO 4 hole to calcium sulphate and HF. So, this basically a mixture of this calcium phosphate and calcium sulphate and this particular one is typically giving you the super phosphate preparation and the super phosphate making the phosphate based fertilizer. So, what you have that calcium sulphate if we remove our hydrofluoric acid if we remove only we are having with the corresponding calcium dihydrogen phosphate.

So, calcium dihydrogen phosphate can be utilized for making these and the manufacturing process basically takes 5 different steps. So, your starting material is your appetite and that appetite will grind it, so industrial sector is there. So, there is a grinding part is there. So, you have to grind the apatite and any found powder form is obtained and that particular powder form can be now allowed to react with sulfuric acid because these are very sometimes very big lumps very big blocks of these apatite molecules.

So, these appetites will not be able to react molecule by molecule with that of the added sulfuric acid. So, you must have to increase the corresponding area of reactivity that means, you should make it a powder. So, grinding will give you the powder and that powder basically is reacted with this sulphuric acid and then solidification and crushing of the primary reaction product. So, what you get that initially something is settling down, so all the sulfuric acid is being absorbed by your powdered material giving your initial solidification so that solid product we next level we just crush it from that reaction product.

Then, we go for curing of that particular till we allow the completion of the reaction we finish the reaction after initial solidification breaking the solidification the thing. Then comminution of the possible granulation of the end product, so the granulation part should again be avoided such that we can have everything in the powder form and we just try to get the separation that means, hydrofluoric acid in the gaseous form will be removed. Only thing the separation of your calcium sulphate from that of your this dihydrogen calcium phosphate material.

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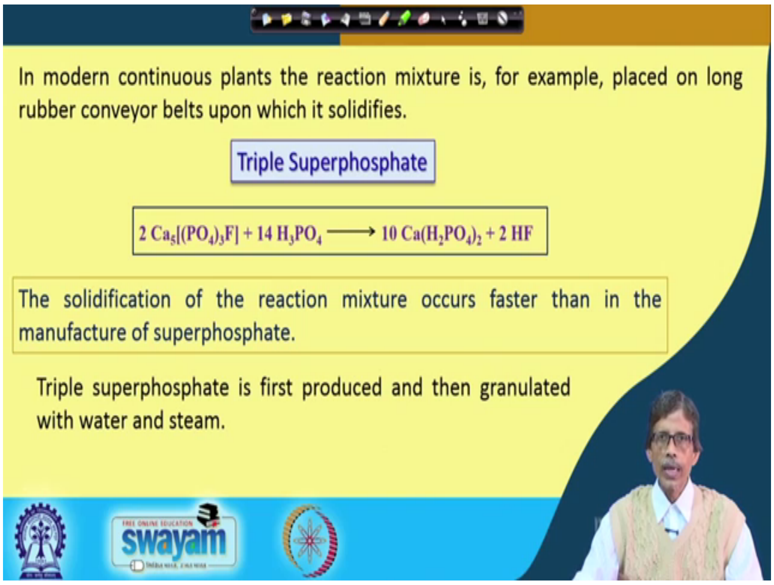

In modern continuous plants the reaction mixture is, for example, placed on long rubber conveyor belts upon which it solidifies.

Triple Superphosphate

$$2\ Ca_5[(PO_4)_3F] + 14\ H_3PO_4 \longrightarrow 10\ Ca(H_2PO_4)_2 + 2\ HF$$

The solidification of the reaction mixture occurs faster than in the manufacture of superphosphate.

Triple superphosphate is first produced and then granulated with water and steam.

Basically, in modern plants where we have the corresponding continuous plants the reaction mixture is placed on long rubber conveyor. So, you have the rubber conveyors available and on that rubber conveyor belts the solidification is allowed to take place. So, the entire material is being solidified on the conveyor belts. So, that particular solid product what we get is for the making of the super phosphate, then one particular material as again the phosphate fertilizer is known as your triple super phosphate.

So, the triple super phosphate also has some industrial demand, but now we use instead of using the corresponding sulfuric acid. Because the sulfuric acid was utilized to take care of some part of calcium as calcium sulphate because we know that the calcium sulphate is your component for the gypsum. So, that can be removed as a simple calcium sulphate material, but if we try to retain the entire phosphate what is available in the floor apatite as the typical phosphate material of your phosphate.

So, the amount of that superphosphate, so it is basically a superphosphate and consider it as a triple superphosphate because the whole amount of the material is now retained as your calcium dihydrogen phosphate with the elimination of your hydrofluoric acid. And in this particular case the solidification of the reaction mixtures occurs faster than in the manufacture of the super phosphate.

So, we have two types of phosphate based material one is your super phosphate, another is your triple super phosphate only procedures are different is there that you one case you use sulfuric acid in another case we use phosphoric acid. And this particular triple super phosphate is first produced and then granulated with water and steam. So, when it react with the phosphoric acid which is nothing but your syrupy phosphoric acid. And that syrupy phosphoric acid can give you that immediate solidification when you have the powder material of your appetite and that appetite powder material can be consumed that particular syrupy phosphoric acid and everything has been solidified.

And now the entire material can be granulated and with steam and water it can be granulated because the solubility of this material with that is very little or very less.

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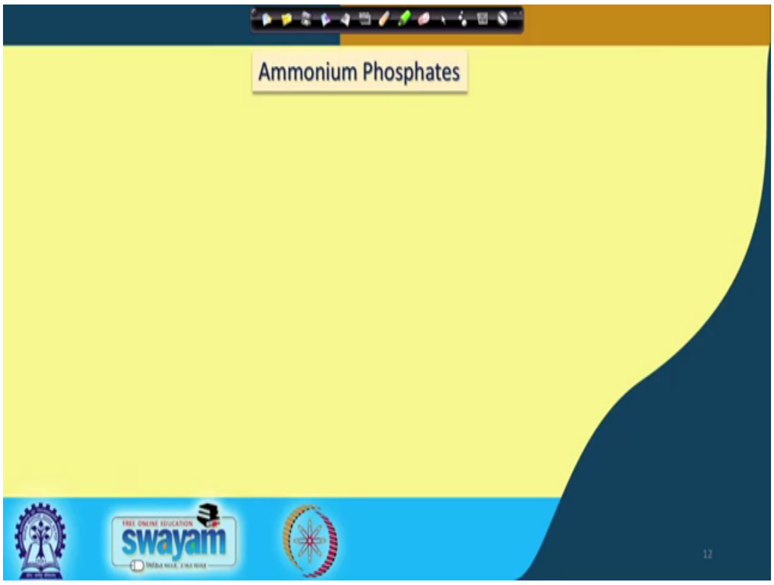

Ammonium Phosphates

So, this basically gives us some idea how the phosphate based materials are we are making, where which phosphate the super phosphate and the triple phosphates are nothing but is the calcium salts.

Next day, we will see how the corresponding other variety having a higher solubility and if we bring now the cation as the ammonium ion, so we will be able to supply to the soil both nitrogen as the ammonium ion. That means the ammonium as the fertilizer component of your nitrogen supply. So, both nitrogen supply as well as phosphorus supply can be achieved through the introduction of this ammonium phosphate as your mineral fertilizer to the soil.

Thank you very much.