Industrial Inorganic Chemistry
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Lecture – 35
Potassium Fertilizer

Hello, good morning everybody. So, welcome to this class where we are talking about the mineral fertilizers and we were with urea.

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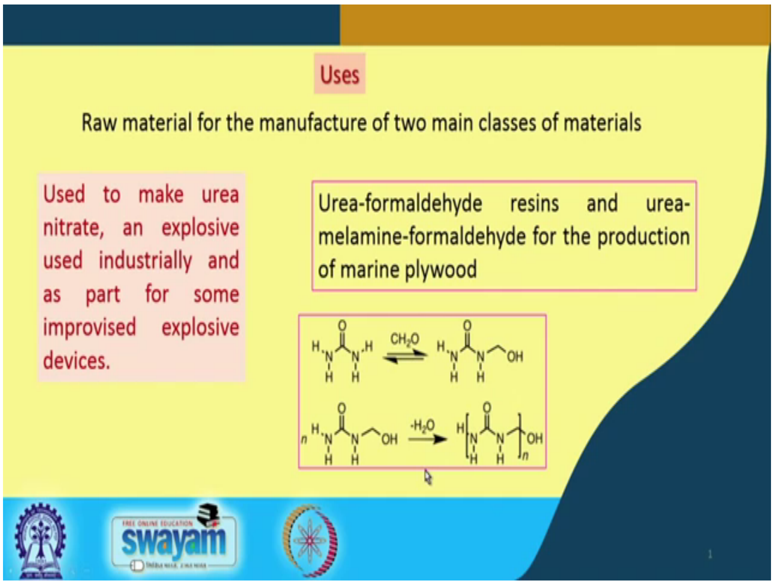

Uses

Raw material for the manufacture of two main classes of materials

Used to make urea nitrate, an explosive used industrially and as part for some improvised explosive devices.

Urea-formaldehyde resins and urea-melamine-formaldehyde for the production of marine plywood

So, we are talking in the last class about the how we use the different kinds of is activity for urea and we have reached here where we have seen that the certain kind of resin which are also made of urea. And, so, if urea if you have as a raw material you can get the corresponding urea formaldehyde resin as well as urea formaldehyde with another component the third component is the melamine and you get that resin and we have also told you that how that reaction-wise how the formaldehyde molecules are important in coupling this urea formaldehyde resin formation; that means, the polymerization.

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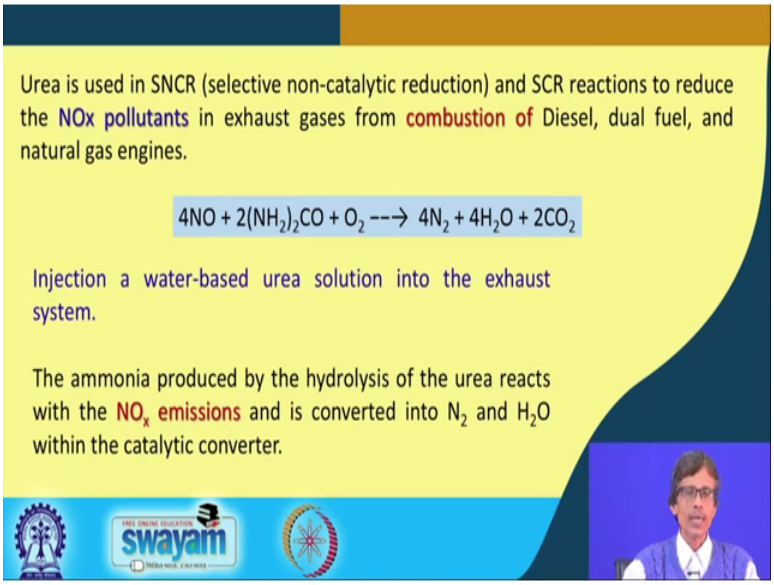

Urea is used in SNCR (selective non-catalytic reduction) and SCR reactions to reduce the NOx pollutants in exhaust gases from combustion of Diesel, dual fuel, and natural gas engines.

$$4NO + 2(NH_2)_2CO + O_2 \dashrightarrow 4N_2 + 4H_2O + 2CO_2$$

Injection a water-based urea solution into the exhaust system.

The ammonia produced by the hydrolysis of the urea reacts with the NO_x emissions and is converted into N_2 and H_2O within the catalytic converter.

So, there are large other number of users also urea has. So, one such example is typically a different one where we can use urea as a selective non catalytic reduction material. So, the process is known as SNCR selective non-catalytic reduction process or selective catalytic reaction. So, we should have something where we see that urea can function or can trigger those catalytic reactions to reduce the NO x pollutants; that means, NO x pollutants we all know that these are the different types of nitrogen oxides because we know starting from your NO symbol, NO – the nitric oxide and where you have the nitrogen oxidation state is plus 2 because the when you have a nitrogen oxidation state of plus 1 it is N 2 O the nitrous oxide. So, nitrous oxide nitric oxide to up to you can reached up to N 2 O 5 where the nitrogen oxidation state is plus 5.

So, these properties we know a well and we studied a lot about their reactivity pattern. So, in this automobile exhaust which is basically polluting our environment particularly the large cities and the towns and the metropolitans are heavily polluted with this NO x pollution. So, NO x pollution is nothing, but depending upon the magnitude of x and the number of nitrogen; that means, the corresponding oxidation states of the nitrogen it is corresponding potential for oxidation reduction whatever you think off is completely different. So, when you have the oxygen you get that; that means, that those NO x can be used as the typical oxidizing agents.

So, if you have some very cheaply available and suitable reduction agent or reducing agent such as urea what happens? So, if you collect those exhaust gases because the initial trial, the laboratory trial or some bigger scale trial for this reaction we see that whatever amount of this NO x were present from the corresponding exhaust gases; that means, the combustion of diesel, the dual fuel or the natural gas engines because nowadays we know that we are running large number of auto rickshaws and all others by LPGs or CNGs.

So, the natural gas burning process where you have the corresponding hydrocarbons and we have some the nitrogen also because it is burning in presence of the air as cynical amount of nitrogen. So, during that burning process also we produce the NO x. So, this NO x can now be used for the reduction reaction with the urea. So, it can either be a catalytic process; that means, in presence of some catalyst or it can be simple selective catalytic reduction and non catalytic reduction also.

So, we take the example of simple NO the nitric oxide where x is equal to 1. So, the nitric oxide where the nitrogen oxidation state is plus 2 react with urea which is CH NH 2 double NH 2 whole 2 CO with presence of oxygen. So, the burning process what is taking place in presence of O 2 giving you such a simple things; that means, it is producing nitrogen, it is producing water and it is producing carbon dioxide. So, is a very interesting one that we are destroying the NO x which has a severe polluting effect in the environment to convert that NO 2 di-nitrogen molecule which is already a constituent in our air in our atmosphere. So, urea can that way is a very useful material for tracking a tray tracking the corresponding polluting effect of NO or NOx.

So, what the companies are trying to make that they are trying to make something where you can have the corresponding chamber where you can have a 32 to 35 percent solution of urea and through that urea solution if we allow to pass this particular automobile exhaust gas which is known as the diesel exhaust solution. You see the name basically the companies have already arrived into the market they are producing that particular solution, they are simply selling the urea solution. But, they are marked as the corresponding diesel exhaust solution because it can trap the NO x from the diesel exhaust and it can destroy those NO x.

So, if the reaction is only water based nothing is required because urea has a certain amount of solubility in water; so, injecting a water based urea solution into the exhaust system or you can pass the exhaust gasses through the urea solution it is again the same thing what you are trying to get. So, when you get this we can basically destroy the NO x from there. So, the thing is that what ammonia is produced during hydrolysis we have seen last time that we can talk in terms of the corresponding urea's activity that urea's is there in the soil material also.

So, ureas which is available so, that ureas is responsible for the hydrolysis of urea producing simply the material were from we got urea; that means, the carbon dioxide and ammonia. So, ammonia which is being produced from the hydrolysis of the urea can react with NO x how this reaction is going on whether it is a reaction of urea only with NO or ammonia with NO and is converted to N 2 and H 2. So, this reaction is only that NH 3 which is coming out through the hydrolysis of urea.

So, we must have certain condition that in C 2 we should be able to hydrolyze urea to ammonia and that ammonia is basically reacting with your NO or NO x producing N 2 and H 2 and at the same time during the production of your ammonia carbon dioxide is getting liberated. So, within the catalytic converter everything is happening. So, this particular one is the urea based catalytic converter which can destroy the NO x molecules.

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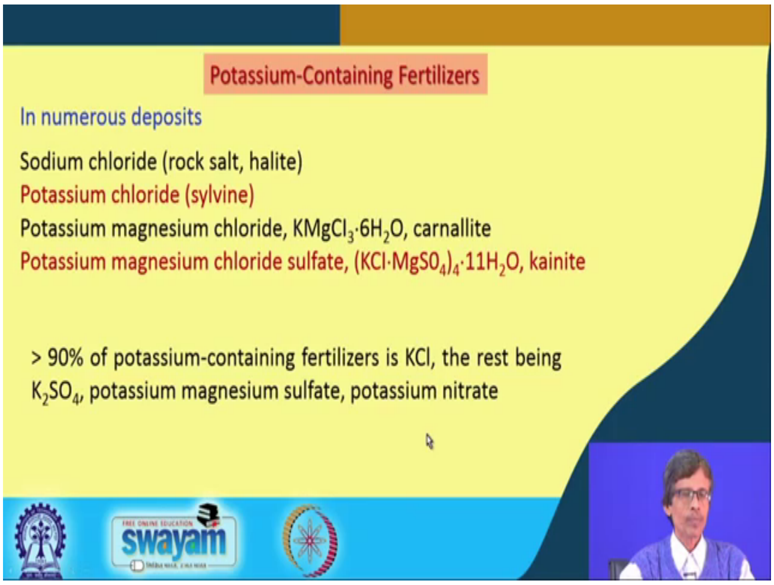

Potassium-Containing Fertilizers

In numerous deposits

Sodium chloride (rock salt, halite)
Potassium chloride (sylvine)
Potassium magnesium chloride, $KMgCl_3 \cdot 6H_2O$, carnallite
Potassium magnesium chloride sulfate, $(KCl \cdot MgSO_4)_4 \cdot 11H_2O$, kainite

> 90% of potassium-containing fertilizers is KCl, the rest being K_2SO_4, potassium magnesium sulfate, potassium nitrate

Now, we moves to the metal ion based fertilizers; that means, the potassium containing fertilizer. So, we have seen nitrogen we have seen phosphorus and now we will see the metal ion containing fertilizer. So, phosphorus is basically a micronutrient for the plant life it is available where is you get it. So, the availability is always very much important otherwise you cannot start off, you cannot think of an industrial thing. So, if you last looking for the production of potassium based fertilizer you must have a good source or cheaply available potassium sources over there. So, we must know where from we cheaply get the potassium like that of your sodium.

So, we can have numerous deposits like your sodium chloride. So, sodium chloride we have seen that from the sodium chloride stock; that means, the brine water or the sodium chloride deposit the rock salt deposits we get sodium for its isolation and the isolation of sodium as the different compounds. So, this rock salt, the halite we call it is the rock salt is also once again another source very good source of potassium because it also gives certain amount of potassium chloride from it because potassium chloride is there within the rock salt.

Then only the silver potassium chloride which is sylvine; so, sylvine is another ore type of material or a deposit natural deposit where from you get potassium chloride. So, these are from sodium chloride certain amount of potassium chloride and the potassium chloride itself in sylvine we can think of certain thing where you can have also the magnesium and depending upon your percentage availability and how quickly you can get that thing your magnesium bearing another production chloride salt which is nothing, but a double salt type of thing of magnesium chloride and potassium chloride which is potassium magnesium chloride which is carnallite. So, carnallite is $KMgCl_3$.

So, in some amount of is the typically a double salt formula 1 is to 1 double salt formula, but interestingly when it crystallizes out it has a definite composition otherwise you cannot go for its crystallization. So, the challenge is that how you get the typical ore source the mineral source the powder form and how you ultimately crystallize it because during crystallizes and you are also improving the quality of the material, the purity of the material. So, with hexahydrate form the carnallite is crystallizing in it is pure form and when the composition of that carnallite is 1 is to 1 potassium chloride magnesium chloride you must be sure that we have that particular composition and it is separating as a pure salt. So, this industrial processes based on this type of salts is largely looking on the typical crystallization process or the fractional crystallization process.

We can also have instead of magnesium chloride we can have magnesium sulfate also what we known as magsulf. So, magnesium sulfate can also be useful and now potassium magnesium chloride sulfate again you have a formula of one is to one of KCl and Mg s SO 4, but four of these double salts are entangled or having a network with eleven water molecules which are known as water of crystallization in kainite.

So, these are the typical sources little bit we should know and we should know about the sources where from we get because some countries are very rich in these materials and some are not. So, looking at from the industrial point of view where you can start this industrial process of making potassium compound or making the potassium based fertilizers we should always look at the corresponding availability or the cheap availability of that particular material in pure form.

So, what we get is that when you make the fertilizer we just simply put potassium chloride. So, the salt like your sodium chloride is the simplest possible salt once we just simply give the input within the fertilizer whether you have a nitrogen based fertilizer or a potassium based fertilizer, but we put potassium chloride and the remaining being potassium sulfate because you can have a corresponding check in the solubility. So, you have a basically a potassium chloride and potassium sulfate double salt into 9 is to certain percentage not even 9 is to 1. Then, you can have the potassium magnesium sulfate the last one the kainite type of thing and the potassium nitrate is also added.

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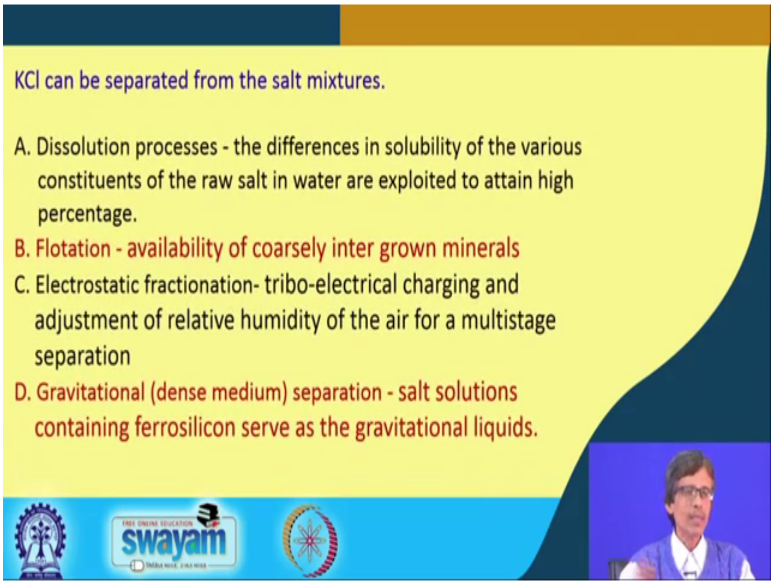

KCl can be separated from the salt mixtures.

A. Dissolution processes - the differences in solubility of the various constituents of the raw salt in water are exploited to attain high percentage.

B. Flotation - availability of coarsely inter grown minerals

C. Electrostatic fractionation- tribo-electrical charging and adjustment of relative humidity of the air for a multistage separation

D. Gravitational (dense medium) separation - salt solutions containing ferrosilicon serve as the gravitational liquids.

So, when we have these things and how we separate out potassium chloride only because our basic intention is to produce quickly the potassium chloride like your crystallization of sodium chloride. So, the first step from a mixture of other material; that means can the separation technique so, is the dissolution process where you can see that the differences in solubility of the various salts even if you think of that you have potassium chloride and you have sodium chloride these two have different solubility.

So, we must have a very good idea about the solubility of the corresponding salts when we talk in terms of your dissolution process as well as separation by crystallization. So, the various constituents what you have of the raw salt in water and exploited to attain a high percentage because if you can go for dissolution and crystallization dissolution and crystallizes; that means, fractional crystallization you can increase the corresponding concentration of say potassium chloride at this point.

Then, we can go for the flotation where you can have the different grain size different particle size depending upon the availability of the coarsely inter grown minerals. During crystallization as well as when the mineral is forming on the earth crust basically the size of those particles are different. So, we can have a different separation technique through protation.

Then, we have the electrostatic fractionation. Tribo-electrical charging which is some kind of charging and the charging is different for the different salt species; if you have potassium chloride, if you have a sodium chloride, you have potassium nitrate or potassium sulfate the tie tribo-electrical charging the tribo-electrical charging basically can give you difference in the charge and the corresponding relative humidity of the air is required for a multi stage separation technique based on the corresponding electrical field applied.

So, electrical charge separation which can be achieved on the conveyor belt when the material is transported from one side to the other and that particular electrostatic fractionation is always very important so that we just take the help of electrostatics. So, electrostatic will help depending upon the different charges, what the particles are accumulated, we can go for a very useful separation which is a basically a physical separation.

Then, lastly we can go for a gravitational separation because depending upon your particle size, depending upon your density of the particles, density of the source; that means, the density of the particles for the corresponding minerals or the ores because depending upon it is different types; that means, whether you have a pure potassium chloride sample or it is mixed with magnesium chloride or it is mixed with magnesium sulfate, you can have the differently dense material in your hand.

So, we go for salt solutions containing ferrosilicon sub as the gravitational liquid. So, one particular gravitational liquid because dense liquid you should use and particularly that dense liquid can separate the heavier particles will settle down and the lighter particles will float like that of our separation based on water or any other solvent.

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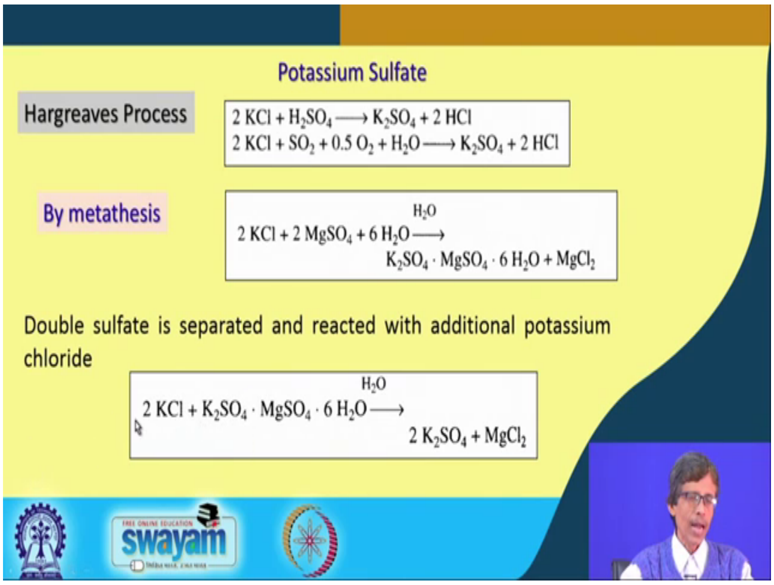

Potassium Sulfate

Hargreaves Process

$$2\,KCl + H_2SO_4 \longrightarrow K_2SO_4 + 2\,HCl$$
$$2\,KCl + SO_2 + 0.5\,O_2 + H_2O \longrightarrow K_2SO_4 + 2\,HCl$$

By metathesis

$$2\,KCl + 2\,MgSO_4 + 6\,H_2O \xrightarrow{H_2O} K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O + MgCl_2$$

Double sulfate is separated and reacted with additional potassium chloride

$$2\,KCl + K_2SO_4 \cdot MgSO_4 \cdot 6\,H_2O \xrightarrow{H_2O} 2\,K_2SO_4 + MgCl_2$$

How we make now potassium sulfate if we are able to make potassium chloride nicely in an industrial scale to a huge amount. So, the reaction the typical reaction text book reactions are very simple that if you have huge amount of potassium chloride you try to react with sulfuric acid already we know that this mineral sulfuric acid we have already we know how we prepare it. So, the industrial supply of that mineral is very much in hand. So, you directly react with sulfuric acid giving you potassium sulphate.

But, sometime the whole potassium chloride can be reacted in C 2 with sulphur dioxide also when we do not want to use sulfuric acid because the sulphuric acid is a costly material. So, if we want to go down its corresponding price for the process we can use directly the sulphur dioxide which is the raw material for sulfuric acid production and the equivalent amount of oxygen from the air or some other sources and water which is ultimately giving you during this reaction process the sulfate formation.

So, in presence of KCl what you can think of this particular second reaction you look at that particular second reaction, you try to write it that reaction and what you can think of that in presence of KCl what we are doing we are also forming sulfate anions from sulphur dioxide which is not so easy all the time; that if you have sulfur dioxide it will not very much react with what are as well as O 2 to give you sulfate very quickly. But, potassium chloride now can have some catalytic effect for that particular conversion because the form material what is being separated from the medium is your K 2 SO 4.

So, this particular process or the procedure is known as Hargreaves process. So, Hargreaves process is that particular process either you use sulfuric acid or sulfur dioxide for the production of K 2 SO 4.

Then, a particular technique all the time we should follow this particular one and we should be you should be asked also when during your exam time that a particular type of metathesis reaction you always keep in your mind that what is that particular metathesis reaction and how this metathesis reaction can be useful to get some useful compounds. So, how metathetically the reaction is useful for the conversion of potassium chloride to potassium sulfate. Just now we show that one particular process is useful in presence of sulphur dioxide, but if we are able to go for a corresponding metathesis reaction and that metathesis reaction is nothing, but the exchange of the cation and the anion part.

So, what you should use whether you use sodium sulfate, aluminum sulfate, iron sulfate or that particular magnesium sulfate which can be available at a low cost or low price. So, if you have a very low price material magnesium sulfate in your hand you can try for that reaction in presence of water and that reaction will give you a double salt of magnesium sulfate because magnesium sulfate what is being used is directly giving you the corresponding double salt when you produce also the potassium sulfate which is also known as the Epsom salt. So, that type of all sorts of double salts there are available.

So, your starting component; that means, whatever magnesium sulfate is we are using, your basic intention or basic idea is very simple that you are not only producing potassium sulfate because our idea is not you produced potassium sulfate because the price of potassium sulfate would be less compared to your this particular complex double salt. The way we know also that when we make the more salt which is ferrous ammonium sulfate.

So, it is basically a stable one and which is not easily oxidized in air to ferric sulfate. So, definitely the usefulness of that material is higher compared to your starting ferrous sulfate. So, your cost will be more, the market demand is high. So, industry will try to produce that double salt fast. Similarly, this particular double salt the Epsom salt so, is very useful and is costlier compared to your both potassium chloride and magnesium sulfate. So, it is the typical crystallization process or double salt formation which is we can consider as a value added process and that value added process directly give you a good quality a very pure quality of the corresponding salt which can be marketed directly from there.

So, this double sulfate what is formed in the medium what is formed in a saturated solution can be separated and can further be reacted with additional potassium chloride because whatever part one part is going as the magnesium chloride, so, this double salt can be separated and reacted during the reaction with the addition and potassium chloride you can get that again you have the magnesium source again you have the potassium chloride salt. So, only thing that if you think of now for the next step you can think of that you can have certain amount of sulfate salts.

So, this particular one so, in between that as intermediate you have this double salt and that double salt is further reacted with the starting potassium chloride. So, the starting potassium chloride is reacting and when you think that the entire amount of sulfate anion what was available from your magnesium salt is converted to your potassium salt and always remember that the solubility of potassium sulfate is more. But, due to this typical mass action reaction more and more amount of potassium sulfate will be forming and less amount of magnesium chloride it may remain in solution in a supersaturated form, but it will not crystallize out with that of your potassium sulfate.

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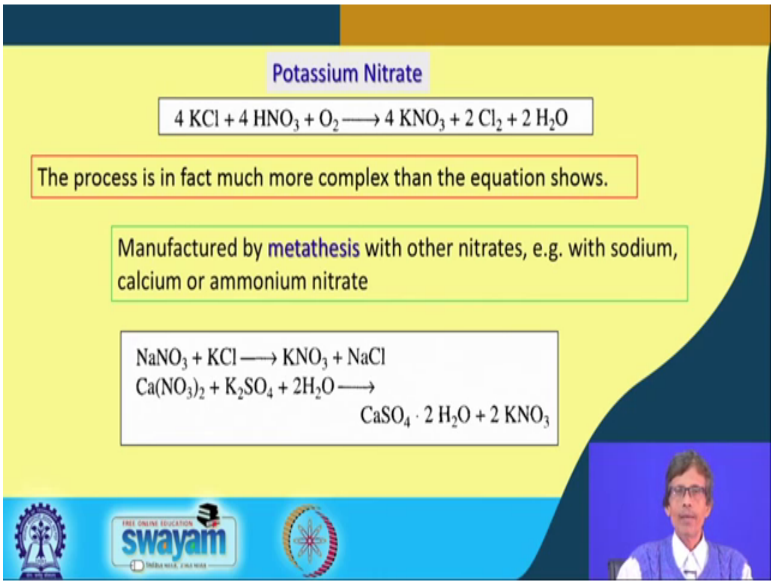

Potassium Nitrate

$$4\,KCl + 4\,HNO_3 + O_2 \longrightarrow 4\,KNO_3 + 2\,Cl_2 + 2\,H_2O$$

The process is in fact much more complex than the equation shows.

Manufactured by metathesis with other nitrates, e.g. with sodium, calcium or ammonium nitrate

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

$$Ca(NO_3)_2 + K_2SO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2\,H_2O + 2\,KNO_3$$

So, this crystallization technique are all the time very useful and it can apply for also your formation of potassium nitrate because the nitrate salts are much more soluble than your corresponding sulfate salts. And, now directly we can use this particular one and you can remember where we can have the corresponding chlor-alkali process that where we see have seen that electrolysis of sodium chloride can produce you give you the sodium hydroxide can give you the chlorine can give you the hydrogen also.

Similarly, during the production of potassium nitrate which can be industrially very beneficial also and you can use the mineral acid nitric acid; not any other nitrate salt by metathesis or double metathesis type of thing, but directly the acid is used for it is corresponding anion supply in presence of oxygen because oxygen is utilized for your oxidation. So, as we all know, that both nitric acid and oxygen both of them are oxidizing agent.

So, you can have this particular effect, but the consumption of nitric acid as the oxidizing agent is not taking place here because we want to have the intact nitrate as the anion from nitric acid to be converted to be taken away by potassium ions to form potassium nitrate. Only the oxygen what is used for it is reaction that oxygen is utilized for your oxidation of chloride ion to produce chlorine.

So, not only you are making potassium nitrate in this particular reaction, but also you are producing chlorine. So, you have to separate that is a gas which is coming out from the reaction medium, from the top you can collect it and that particular collection we can store it and we can in you can put everything in the cylinder for storing chlorine also.

And, the process is in fact, much more complex than the equations shown because this rate equation. So, everywhere as I told repeatedly every time I mention that whenever a particular reaction is shown because we are talking in terms of the and then we are talking about the corresponding part where you can have the corresponding complications. So, whenever we write a particular type of reaction, it is not very easy to do that particular thing in industrial scale.

So, the reaction is much more complex because you are using huge amount of the material and that material is not able to react directly when you increase the bulk of the material say for this example of this KCl this KCl here when this KCl is a reacting that KCl amount basically because you have a huge amount of that KCl whether you take that as the granules whether you take that as the powder or in some other form basically in solution also.

The contact with nitric acid as well as the contact with another gas component which is your O 2 is not uniform not all the time very easy to go for molecule by molecule or ion by ion reaction because everything what is happening at the molecular level. So, molecular level reactions always we should think in terms of the reactions with one molecule to the other and when the reactions is in very dilute form. So, whenever we have some reaction in test tube in a very low concentration not even the molar concentration or the normal concentration less then deci normal it can be centi normal or it can be mill normal or milliliter scale.

So, we should always think of the reaction is very simple and reaction is very straight cut, but when you use some kg scale only; sometimes some kg scale gives us all the difficulties that is why the industrial process engineering is there because the processes would be different, the reaction chambers should be different, the reactor should be different otherwise you cannot achieve that particular reaction by looking at only the feasibility of that particular reaction. So, reaction can be pretty complex.

So, when we go for manufacturing these with metathesis with other nitrates like sodium, calcium and ammonium nitrate it is also possible instead of using nitric acid. So, you now know that: what are the different things you can use to convert your potassium chloride to potassium nitrate. It is the choice which will be in your hand whether you go for the reaction what is given in the equation; that means, the direct reaction of the material with nitric acid in presence of O 2 or you can use some other nitrates which can be even costlier than the product which you are looking for like your potassium nitrate.

So, use of sodium nitrate, use of calcium nitrate or use of ammonium nitrate whether they are giving you any kind of benefit with regard to the cost we should always be very much careful for that otherwise we can go for some traditional processes. Because, to make this salt we always look at the very cheaply available nitrate source if your nitric acid is cheaper than sodium nitrate which we should go for this particular reaction.

So, the metathesis reaction is very simple and is a very direct one. So, you have KCl reacting with sodium nitrate you have the corresponding one; that means, you can get it for your simple thing; that means, the sulfate salt also. Why you are taking the second equation is that if your potassium chloride is costlier than potassium sulfate, so, we directly take potassium sulfate because we are using some nitrate which is your calcium nitrate and as you all know calcium sulfate has a component of the gypsum material is readily available and also it is solubility is less as is monohydrate and dihydrate is the calcium sulfate what is available.

So, gypsum what we use as the calcium disulfides and the plaster of Paris; plaster of Paris is the monohydrate one while one of the water of hydration we take out and that can readily take back that particular material and give you the corresponding plaster of Paris for very many purposes like your simple coating of the our walls into a interior walls of the building. So, POP coating we call this a POP: Plaster of Paris coating which is we can get it from your calcium sulfate dehydrate. So, along with your potassium nitrate what we are making here is that we are getting some amount of gypsum type of material in our hand.

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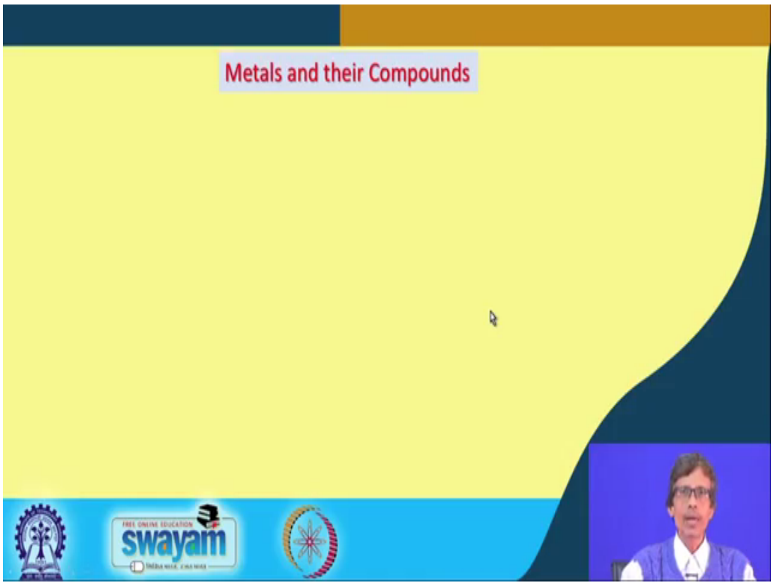

Metals and their Compounds

So, we are finishing here the mineral fertilizer part. So, we will be coming here next like in our next class that the other area where we can talk about the metals as well as they are compounds. So, far whatever we have talked about particularly this mineral fertilizers we have also talked about the potassium as your potassium sulfate, potassium nitrate and potassium chloride preparation. So, if you consider that can also be a corresponding metal as well as the metal compounds that will see our in our next class, ok.

Thank you very much.