Industrial Inorganic Chemistry
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Lecture – 42
Chromium and its Compounds

Hello everybody. Welcome back, where we are finishing our calcium part. Now, we will move to the next element the alkaline earth element, we call is the barium. Because, barium is also very much useful industrially large number of compounds and well-known, what we produce from those barium salts and the barium ores and the minerals.

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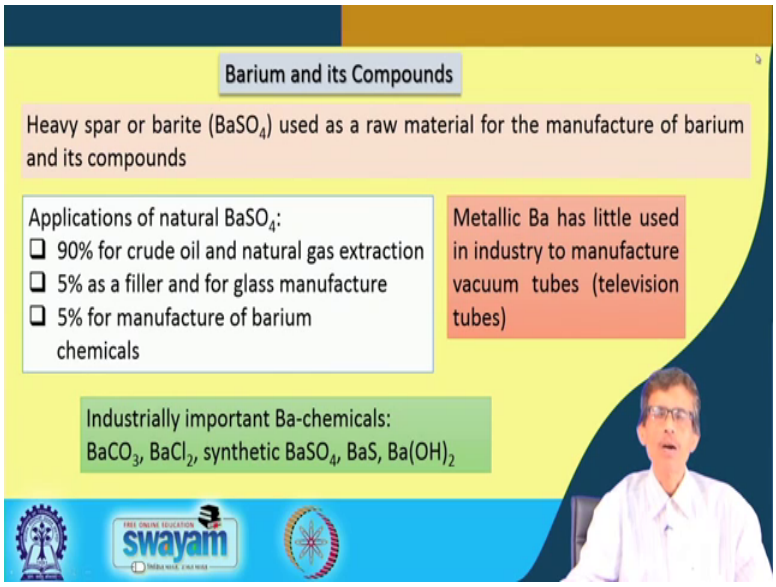

So, we have we will only go for some useful compounds only that is why it gives us a very good idea that what are the elements starting from the whole entire periodic table. The metallic part and the nonmetallic part, what we can think of industrially and which can be useful industrially and historically also how the journey has been started earlier, for the getting some useful compound from these particular elements.

So, we get the barite, so barite is your barium sulfate. So, barite is your barium sulfate, which is known also as the heavy spar thing earlier we know that one is we can also considered as the acid spar and other thing. So, it is basically used as a raw material for the manufacture of barium and its compounds. So, any barium compound if you think of any barium salt basically, sometimes we can make some huge organic molecule, also as

its barium salt. When we do not go for its corresponding sodium salt or the potassium salt, we go for it as its barium salt.

So, first we see that how we apply all these barium sulfate. So, this barium sulfate is basically, the entire amount almost the entire amount of that production, the 90 percent is utilized for crude oil and natural gas extraction. So, this is a most useful inorganic compound, which is utilized in the oil sector, because the mod we handle the drilling process we handle, there people use this particular barium sulfate for both oil extraction as well as gas extraction.

And out of these only 5 percent is being used as the filler for glass manufacturing, glass we all know that it is the corresponding silicate material. So, you have sodium silicate material, then we add boron, sometimes to improve its quality to get the borosilicate glasses. Now, we can get little bit of barium salts also. So, these are all additives. So, these additives basically can give rise to the improved structure of the gas glass material, so that is why some amount of barium can be utilized for making up glass. Then rest the remaining 5 percent is manufacture for making useful barium based compounds or barium chemicals.

And what are those barium chemicals which are industrially important, because industrially important compounds we basically produce in a large scale. Huge amount of some of these materials will produce one is barium carbonate, next is your barium chloride, then synthetic barium sulfate which we are not getting from heavy spar process for the heavy spar material, then barium sulfide and barium hydroxides. All of them have very useful applications. And the metallic barium if we want to have it, earlier people make it industrially also it is available for making television tubes, because it is used as a material for making of your vacuum tubes.

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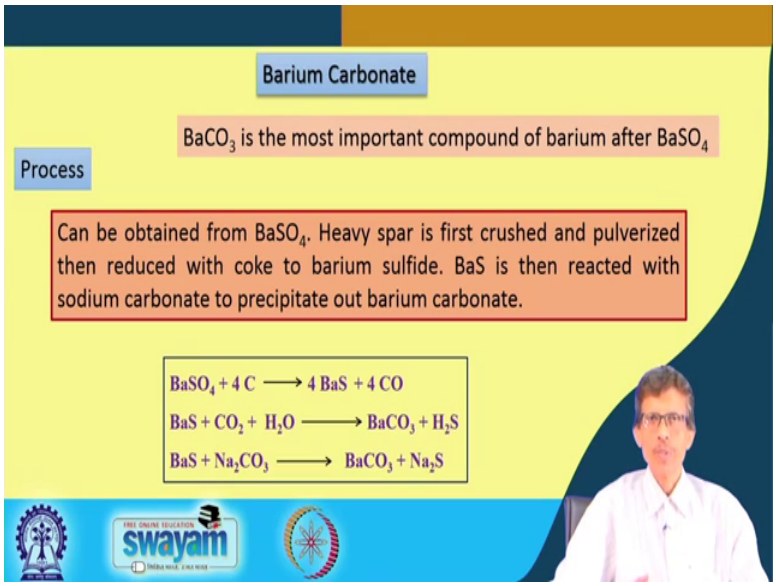

The first compound, what we can think of and what we can understand over here is your barium carbonate. And that barium carbonate, you what we get from here is the most important compound of barium after barium sulfate. So, after barium sulfate the next compound, what we can think is your barium carbonate. And how we make that particular compound is from barium sulfate, because it is readily available as heavy spar is fast it is crushed, we make the powder. Before, powder it is after crushing, we pulverized it. And it is almost powder form and then carbon is utilized as coke that is utilized for the reduction process.

So, barium sulfate gives you the reduction with carbon to give you barium sulfide, because the reverse process, sometimes we can think of is also a very useful question to be asked to anybody is that if you have a sulfur in your organic molecule or any other molecule, how we can estimate that the amount of sulfur present in your material.

So, best way of doing that thing is the reverse process that means, sulfur we all know that there are system, where this can be very easily oxidized to sulfate. And that sulfate, whether it is a organic sulfate like your some long surfactant molecules earlier we have seen or some inorganic sulfate material that can be removed as sulfate anion. And that sulfate anion can be trapped as barium sulfate, because it is a very useful molecule and insoluble molecule and you take, it as the amount of barium sulfate which can be available from your sulfur bearing compounds.

So, the same thing that means, there now we use as a reduction. So, reduction by carbon reduction, we get that particular barium sulfate, then barium sulfate is reacted with sodium carbonate, because our goal is to make barium carbonate and we precipitate out it as your barium carbonate. So, you we can handle three basically industrially important chemical reactions in large scale, because huge scale reaction or large scale reaction can be utilized over here for the first one, for the second one as well as for the third one.

So, first step immediately gives you barium sulfide through carbon reduction and that barium sulfide is converted to barium carbonate by two different processes. One is by utilization of gas molecule carbon dioxide. So, you pass gas basically in presence of water, basically you are supplying carbonic acid.

So, mixture of these two can give you the corresponding conversion of sulfide to carbonate or in other case you add sodium carbonate, where the process of making that thing will be costlier, because sodium carbonate you have to identify that also as a separate material and it has also some price. But, carbon monoxide is a very cheap material and water is also readily available so.

The first reaction that means, the reaction of BaS with CO 2 and H 2 O, what you get is a very cheap one and where you can trap basically the carbon dioxide, whether it is the industrial effluent gas or it is available from some exhaust or it is available from the environment. Only thing that it should be highly concentrated one, because in the environment we do not have that much carbon dioxide, which can be easily converted to your barium carbonate through the use of barium sulfide so.

We should know that particular process, because the carbonate formation from carbon dioxide is well known. And in strongly alkaline medium, like sodium hydroxide we use it, and their sodium hydroxide can trap or calcium hydroxide can trap your carbon dioxide to convert it to sodium carbonate or calcium carbonate. But, making this carbonate directly from sulfide sample is a unique one, because by doing so you will be producing in the first case hydrogen sulfide gas or in the second case sodium sulfide.

So, in the second case may not be so expensive, if you use also sodium carbonate, because sodium carbonate we all know, it is a very cheap material, so that cheap material can be used for making a barium carbonate which is a costlier one. Because, your barium sulfide is a cheap one cheap material, because it has been obtained from barium sulfate.

It can be converted to barium carbonate, which is a costly material as well as your sodium sulfide, which has also some price.

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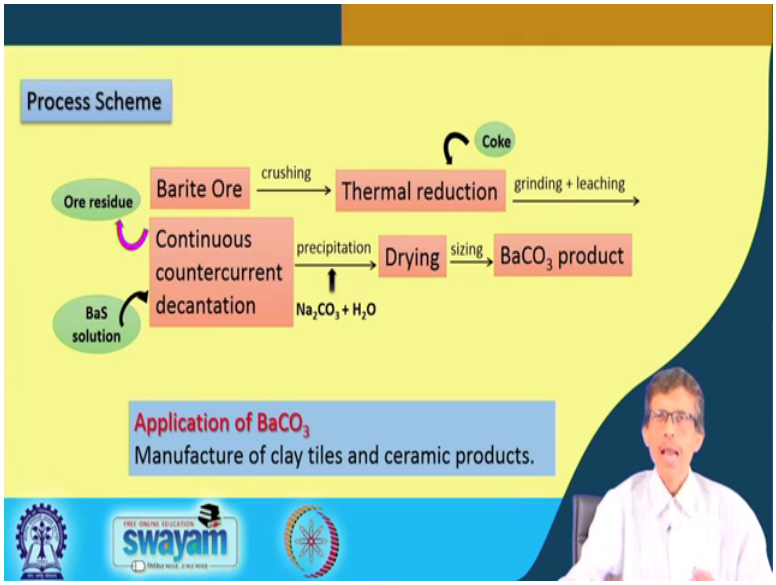

Then the process what we can think of, so you start from the ore you have the barite ore, so you have to take that particular ore and you crush it. So, this is basically the whatever I told just now is your block diagram presentation. So, block diagram presentation will tell you. And move you from your ore to your thermal reduction step by the addition of coke. You add coke, you go for the thermal reduction and by that time you go for the grinding and pulverizing also.

And while you go for both grinding and leaching, you get the barium sulfate sulfide solution that means, the reduction is completed. And is a continuous countercurrent decantation that means, you know against the flow, you decant something, and that decantation from the barium sulfide solution, you remove the other part. So, removal of one part is your erode residue. The unreacted ore basically.

So, you have this that means, the barium sulfide in solution, so basically whatever think was there from the sulfate material, you converted it to sulfide and that sulfide is in aqueous medium. So, you can remove that particular one through decantation, because the liquid material you can transfer to some other reaction vessel and your ore will remain over there. And the residual ore can be reutilized for this particular process.

Then we have to go for the precipitation from the solution of barium sulfide, you add sodium carbonate by water and water. So, this is the second process what we are utilizing, then we go for the drying process of the material. And then sizing that means, the different sizes of the shapes, and the whether you get the lumps, whether you get the some ball type of thing or the blocks. So, you get the barium carbonate as your product starting from your ore.

This barium carbonate is very useful in manufacturing the clay base tiles and ceramic products, ceramic pottery to any other thing. So, some amount of barium is there barium is basically improving the material quality the thermal resistance and its longevity, so that is why some amount some recommended amount is added during the manufacture of this clay tiles and ceramic products.

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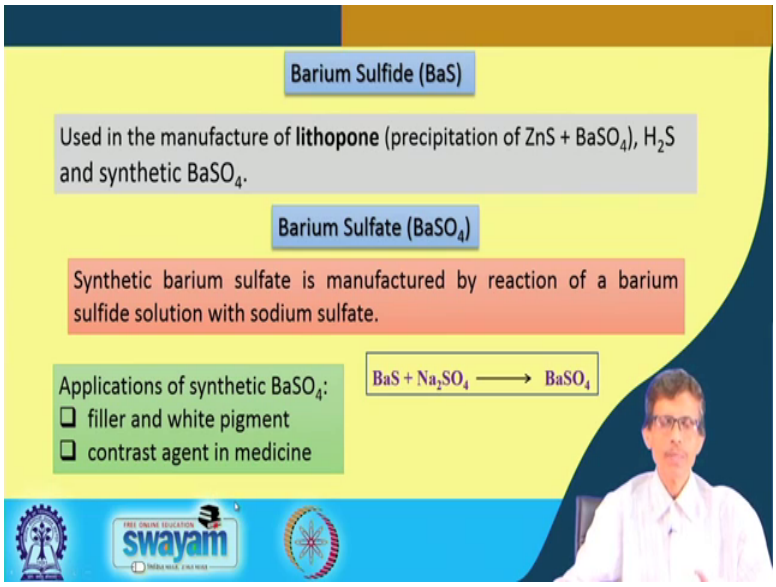

Then the sulfide one just now we have discussed how we get this sulfide, and how we make this particular sulfide for this particular production. So, it is used in the manufacture of lithopone that we all know that it is mixed with zinc sulfide is for the bending purpose also. So, basically a co precipitated one, co precipitated mixture of that particular thing, what we get from sulfides that means, barium sulfate plus zinc sulfide H 2 S for making of H 2 S and for the synthetic barium sulfate through oxidation.

So, synthetic barium sulfate, because the ore is you are giving you the natural sulfate, so that is why we call it as barium sulfate. So, ore is also a barium sulfate material your

barite ore is your barium sulfate material, so synthetic barium sulfate when you manufacture it, when you prepare it in the industry, its purity will be higher.

So, you take the barium sulfide solution, and again like that of your addition of sodium carbonate, now you add sodium sulfate. So, is there basically a metathetic reaction and that metathetic reaction is not a double metathetic reaction, but it is the addition of these thing that means, barium is converting to barium sulfate and sodium is producing your sodium sulfide.

So, our ultimate goal is to making of these barium sulfate, but at the same time you will be also producing sodium sulfide. And this formed barium sulfate, what we prepare is used as a filler as a white pigment that just now I told you that lithopone is well known, white pigment we use it as for painting purpose also.

Then we use this as the contrast agent in medicine, because we know that sometimes we go for the X-ray for our body for our inside body, so we go for the barium mill X-ray. So, some barium sulfate salt is given to the patient, patient is taking some dilute version of that particular salt is basically not solution, it is a salt type of thing, because it is insoluble one, so that is all is there.

And it gets a very thin layer on your intestine, whether it is a large intestine or small intestine, but is a basically that particular deposition of that particular barium sulfate material is detected through X-ray. So, we can find out where you have that means, if you have some cavity, if you have some ulcer, all these thing can be detected by your barium sulfate X-ray, we call it as the barium mill we add. And that barium mill give you the barium mill given exist thing.

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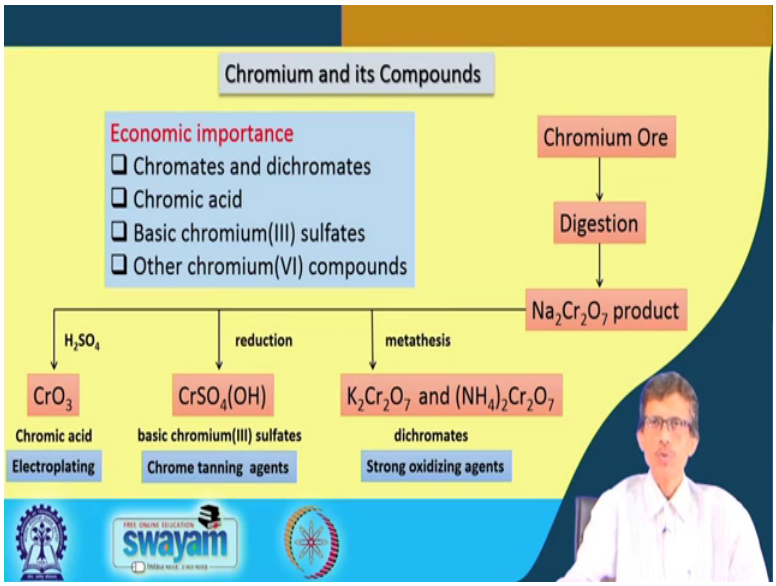

So, after barium we just now go to the most important compound industrially based on chromium, because chromium we all know is industrially also very important, because while we make while you go to the iron industry for the steel industry, chromium is the most important contribution, it gives for making you stainless steel.

So, how we get chromium? So, is this particular subject will be very interesting to everybody. If you try to understand element wise that if you get these all in a form that when you get this particular material as element wise in the periodic table, that you have chromium. So, we think of that particular chromium, how that particular chromium is available to us in terms of its ore.

So, what is the most common material, what will be available for getting chromium, and that particular one through digestion or processing to convert it to some value added compound, which will be industrially very important as well as industrially very useful.

So, the economic importance of all these chromates and dichromates are there, which will be very useful. And we can get this from the different chromium sources, we will see what is that chromium source. Then we can make chroming acid which is Cr O 3, which is hexavalent chromium.

Then basic chromium three sulfates we can have and another chromium six compounds. So, both chromium 3 and 6, these are the well-known most readily available chromium

oxidation states as we all know. Including your starting compound for laboratory use also the chromium trichloride, we know that the chromium is in trivalent state or the dichromate or chromate, which is in chromium in the hexavalent state.

So, both these chromium, whether you have a trivalent chromium or hexavalent chromium can be obtained through your chromium ore. So, you have the chromium ore, and that chromium ore one you have, you go for the digestion. And the digestion of that particular chromium ore can ultimately give you the product, so that is your most important compound of chromium, which is your sodium dichromate.

So, next we will see how we can make this sodium dichromate from your ore. So, once you get this sodium dichromate, so this industrially important compounds, we can very quickly make. So, chromium ore through this digestion is getting to its highest level of oxidized form that means, you are not only the chromate form it can be converted to the dichromate form.

So, once you go to this dichromate forms, a dichromate form from the dichromate form how you quickly go back to your chromic acid form, so you add concentrated sulfuric acid only. So, addition of concentrated sulfuric acid to the pure and dry product of sodium chromate dichromate Na 2 Cr 2 O 7. So, dichromate will be converted to your chromic acid Cr O 3. So, dimeric form is gone, because the dichromate has a chromium oxygen chromium bond, so that is gone, so only you have the chromativinity you with you first.

And then through the removal of water molecule further you get the corresponding Cr O 3, so this can be utilized. So, chromic acid is very useful in electroplating not only the steelmaking component chromium, but also these chromic acids, the hexavalent chromium acid, directly we use for plating of some material electrochemically so for electroplating.

Then from sodium dichromate, we go for the basic chromium sulfate, basic thing always we know that our menology, we always you industrially also very important terminology. What you use that when you have some extra hydroxide ion or hydroxide group in the molecular formula, so that hydroxide bearing chromium is a trivalent one.

So, if you have CrO HSO 4 that is your basic chromium sulfate, so that chromium sulfate can be utilized for chrome tanning agents. So, in the tanning industry for removal of the getting the skin very well to remove the hair the skin hairs from the different animal skin, we use this particular material that means, the basic chromium three sulfate.

It is a huge amount of this basic chromium three sulfate is consumed in the leather tannery industry. So, the tanning process is dependent on that and we should also be very much careful. Because, when the effluent water is coming from the tannery, basically is highly concentrated with the chromium salt, because if we do not able to consume the entire amount of chromium for this particular process.

So, in the tanning industry, we should be careful enough to utilize the entire amount of that particular chromium. And we should not leave behind any unreacted chromium or any other form of chromium in your effluent water or what we are rejecting to the drain water or ultimately to the river or the sea, which is basically contaminating our corresponding marine life or the aqua life.

Then this particular compound that the sodium dichromate is also useful through metathetic reaction that means, you change the corresponding cationic part to potassium as well as ammonia, to give you potassium dichromate and ammonium dichromate. These dichromates together with that of your sodium salt, so all three sodium, potassium, and the ammonium salts of dichromate are very useful and strong oxidizing agent starting from our laboratory. Titrimetric method we learned from our very old days from our school level that potassium dichromate titration that oxidizing is in for your redox titrations.

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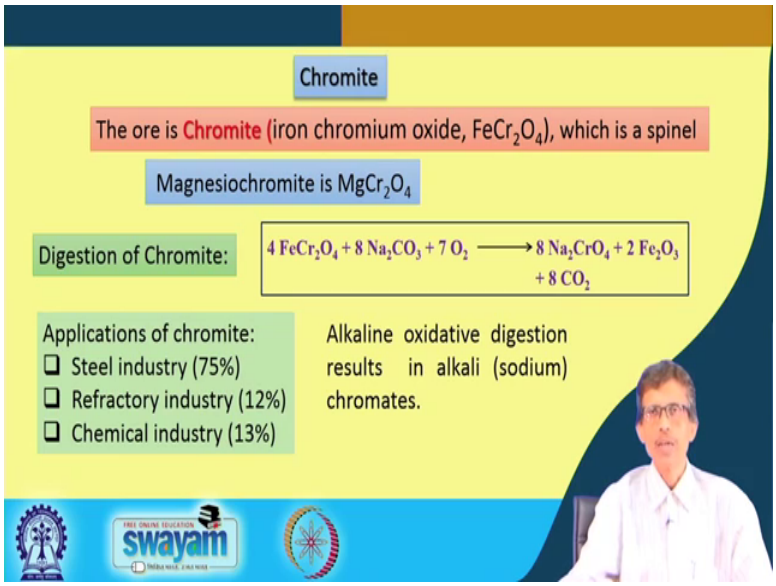

So, we will take chromite as your ore, so this chromite is in your hand. So, chromite is nothing but your iron chromium oxide ore. So, is formula is FeCr 2 O 4. So, is a double metal containing ore and which is therefore a spinel type of thing, because we know that this mineral can have a double metal oxide forms. So, oxide lattice you have. And you have different sides, one is the tetrahedral sides and another is the octahedral sides.

So, due to the occupation of those sides, the tetrahedral sides and the octahedral sides by the bivalent and the trivalent form of those compound, because here chromium is in the trivalent state and iron is the bivalent state that is why, you are balancing the entire 8 negative charges, which we are coming getting from four oxygen centers.

So, two types of spinel we can have; one is the normal spinel and another is the inverse spinel. But, right now we will be only interested to know the spinel structure and that spinel structure you have to destroy, to get chromium out of that compound along with some other metal ion. In case of your chromite ore you have iron, in case of your magnesia chromite, you have magnesium.

We go for your digestion in presence of sodium carbonate and sufficient amount of air and air gives you that oxygen. So, your chromite is being digested to give you sodium chromate. And the amount of iron present in it will be converted to your ferric oxide and carbon dioxide will be liberated to give you the sodium chromate.

And this sodium chromate is the sodium salt, so alkaline oxidative digestion we call, because we have added some alkaline salt as your sodium carbonate salt. And we go for the digestion in presence of excess air or excess oxygen, which is coming from your air also. And in solution we get the corresponding sodium chromate, so Na 2 CrO 4 we are making out of this.

And that can be utilized for utilization of this chromite, because these chromite can be useful in steel industries a large amount, so almost 75 percent of this is utilized for making stainless steel, because it is very useful material for making stainless steel through incorporation of chromium. Then the refractory material, the tiles, the bricks, and all these thing can be made through the incorporation of your chromite ore. And lately the remaining amount that mean 13 percent can be utilized for chemical industry for making, some very useful compound like that of your sodium dichromate.

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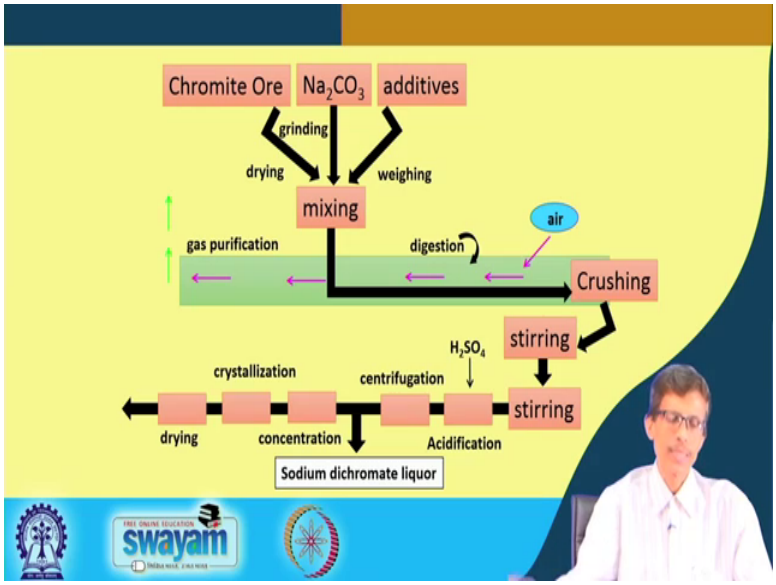

So, you have these thing, how you go for the digestion. So, you take the chromium bearing ore that chromite ore, you add sodium carbonate and other additives if you try to get it. So, grinding, drying, and weighing process is give you the mixture. So, three different processes grinding, drying and weighing that means, how much you are adding and yours particular composition that means, the void ratio is also important, so mixing gives you.

And you go for the digestion. And the digestion is giving you something, where you get that after crushing. So, everything is mixed, then you go for the crushing process and the crushing, then you mixed with air. And air give that particular digestion and then you have the gas what is coming out. So, after crushing basically, we go for the stirring and stirring and stirring.

So, then we go for addition of sulfuric acid, so sulfuric acid process of the sulfuric acid path for acidification. And then the process of acidification followed by centrifugation, and centrifugation gives you the corresponding development of the sodium dichromate formation. So, addition of your chromite ore, sodium carbonate, air that is digestion. And everything will giving you the corresponding sodium dichromate liquor.

And at the same time, what you are producing the gas? The gas basically from the digestion step, gas is going out and gas purification chamber should be there and that can take out the gas for storing and for that utilization. Then we can go for the concentrated form of that liquor and giving you the sodium dichromate the crystals through crystallization.

So, either you have some very concentrated liquor form in the liquid form or you go for concentrated one. And once you exceed the super saturation level, you think that you can go for crystallization. And the crystallized form still you have the trapped water molecule is we are not a dry one is a wet one, so you can go for the drying process. So, after the drying process, you get in your hand the sodium dichromate crystals.

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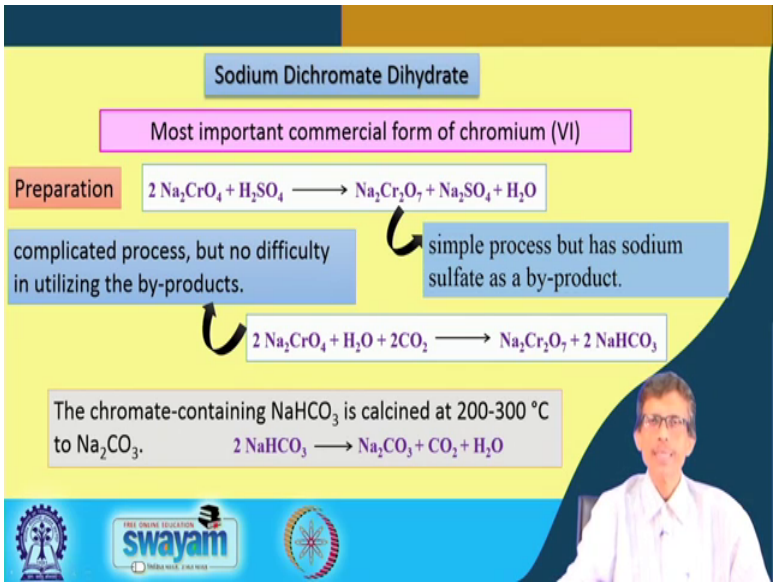

So, we get basically the sodium dichromate in the dihydrate form, because what we get what we use in the laboratory also it is the anhydrous form, no water of crystallization. So, but in the crystallized form, what we get in the water medium is your corresponding process, what you get is as your sodium dichromate, so that sodium dichromate is in dihydrate form. It is a simple process, but it has sodium sulfate as their by product. So, when you react with sulfuric acid, obviously there is sulphate will come out as your sodium sulfate from the material.

So, you have to take care of that particular amount of sodium sulfate, what is being formed over there, so that sodium sulfate should be taken out. Now, the sodium chromate can also be digested in some other way that I already told you that you can go for carbon dioxide also.

So, these are the very simple processes, what you require basically to add, whether you are able to add sodium salt of your chromate to your sulfuric acid or you directly treat with carbon dioxide as a gas molecule converting that. In both the two cases two dichromate, because you require these thing, because in both the two cases you require the acidic medium, because the chromates we know we can follow the dimer formation the condensation of two chromate, you needs to give you the dichromate which is catalyzed by protons the H plus.

So, this H plus can come from sulfuric acid or that H plus can come also the mixture of carbon dioxide and water which is nothing but your carbonic acid. When we get a mixture of carbon dioxide and water we know that this is your carbonic acid, so that carbonic acid through the removal of bicarbonate anion also gives you the proton, so that proton is still available for converting your chromate to dichromate. So, is a basically a reaction, which is driven by proton.

So, the second process can be considered as a complicated process, but no difficulty in utilizing the bi product, because sodium bicarbonate can be very easily utilized. The chromate containing bicarbonate, what is available you can separate it out and that separation of that bicarbonate can gives you a huge amount of sodium bicarbonate formation. Because, develop the amount, what we get as sodium dichromate is formed as a sodium bicarbonate and that bicarbonate when heated at 200 to 300 degree centigrade giving you sodium carbonate.

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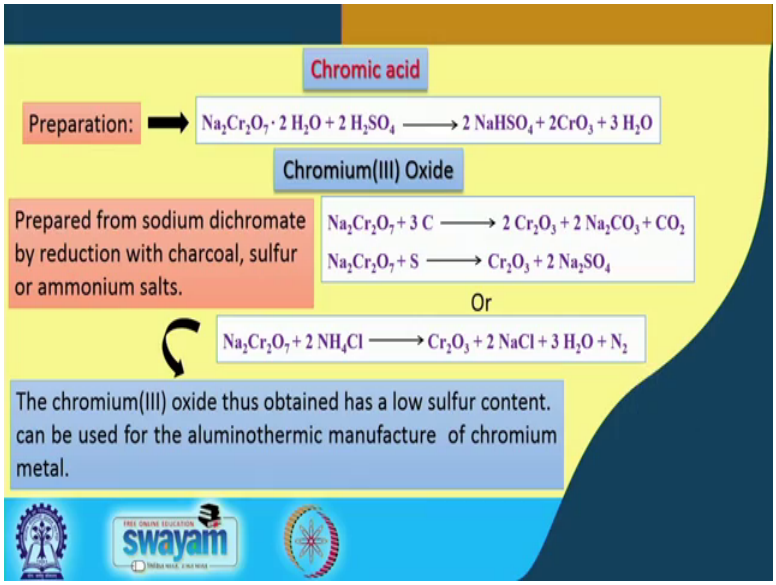

Then we see how we see the get the chromic acid and that chromic acid preparation is a simple one. From the other case that you get that means, the removal of these things that mean chromium as in only oxide. So, is the metallic oxide M O 3, so that metallic oxide can be obtained again by the use of sulfuric acid.

So, this can be utilized as a chromium hexavalent oxide, and the chromium three oxide can be prepared from sodium dichromate with the reduction of charcoal. And that

charcoal or sulfur or ammonium salts basically, so you have the dichromate directly, then once again the dichromate when gives you chromic acid, it can also give you the chromium in the trivalent state, which are Cr 2 O 3, either by the use of carbon reduction or by the use of sulfur reduction or ammonium chloride.

So, ammonium chloride you have their corresponding ammonium chloride, so ammonium chloride that ammonia basically ammonia we all know is also a very good reducing agent, so that ammonia of ammonium chloride can also be utilized for making of your chromium 3 oxide that means, Cr 2 O 3. So, when dichromate is being burnt in presence of your ammonium chloride, we get these reaction. And the same reaction we know from our school days again that if you burn ammonium dichromate, the same reaction can take place.

So, these basically gives us some idea that how we utilize the different chemical reactions the in organic chemical reactions for the productions of all these things, so up to this point that means, the formation of these chromium compounds, the chromium 3 oxide a low sulfur content for this particular process, because we have not utilize sulfur can be used for the aluminothermic manufacture of chromium metal. So, this can be utilized further for the production of chromium metal also. So, this can be very useful starting material these oxides.

So, oxides if we are not able to get as the ore material that means the chromium that chromous oxide the chromium in the trivalent state Cr 2 O 3, we can convert it to some other form and get it in a readily available form to the production of chromium metal, which is which has a very high demand in the industrial sector for the steel industry or any other industry ok.

Thank you very much.