Electrochemical Energy Storage
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Module - 11
Li resources and recycling of Li ion batteries
Lecture - 55
Recycling of Lithium and Other Battery Constituents from Used Battery (Contd.)

Welcome to my course Electrochemical Energy Storage and this is module number 11, where I am discussing lithium resources and recycling of lithium ion batteries. And this is the final lecture of this module lecture number 55, where I will be talking about recycling of lithium and other battery constituents from used battery.

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So, the basis of recycling process that first will be introduced and there are four companies and their particular process RECUPYL process, UMICORE process, TOXCO and Inmetco processes that exactly I will describe.

So, as you can see from electric vehicles end of life vehicles the spent batteries you get and this spend batteries from that you extract iron, aluminum, electrode materials copper organic toxicants, these things are extracted and then directly they can be used for lithium ion battery or with the help of some other chemicals etcetera.

They can be you can make a process, so that finally, again you can make the same new lithium ion batteries and again put it back to the electric vehicles. Apart from that the other component they are also recyclable, so the idea is to get a 0 waste from this whole recycling process.

And then you can see at the background there are tonnage of lithium ion spent battery already are there particularly in China, where a huge producer of the batteries as well as electric vehicles. So, already we have started getting lot of waste batteries I mean the used batteries.

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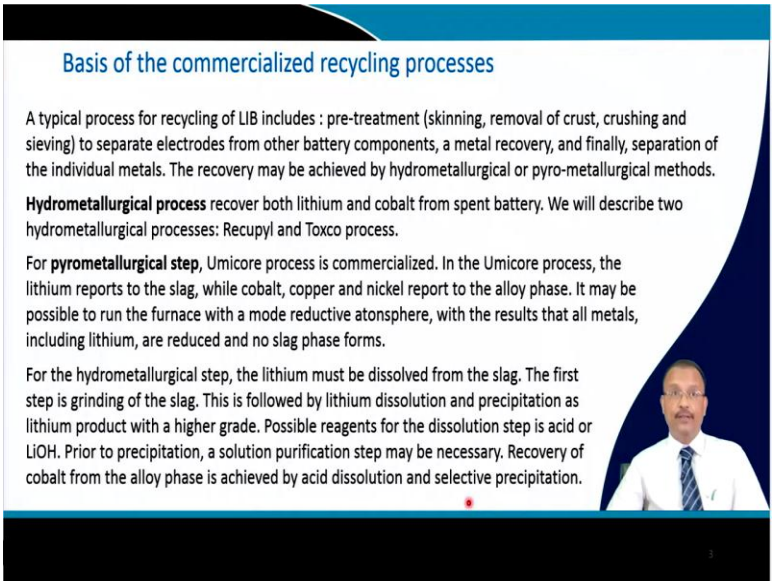

Typical process of recycling of lithium ion batteries that basically includes the pre treatment where is included the skinning and removal of crust then crush and sieve to separate the electrode from other battery component, then a metal recovery and finally the separation of individual metals.

So, the recovery may be achieved as I said already in my last lecture Hydrometallurgy and pyro metallurgical methods. So, in hydrometallurgical process it both recovers the lithium and cobalt from the spent battery and this we will describe two hydro metallurgical process developed in Recupyl and Toxco. So, according to the name of the company and the process name is also known.

In pyrometallurgical step that is actually adopted by Umicore this is commercialized lithium reports to the slag and cobalt nickel form the alloy phase. So, it may be possible to run the furnace with more reductive atmosphere. So, there are 2 spelling mistake I can see that result all metals including lithium are reduced and there is no slag phase, otherwise the lithium will go with the slag phase and it goes basically to the concrete industry so that is possible.

And in hydrometallurgical step the lithium must be dissolved from the slag, the first step is grinding the slag and this is followed by lithium dissolution and precipitation as lithium product with higher grade and possible reagents for these dissolution steps could be either acid or a base like lithium hydroxide.

And prior to the precipitation a solution purification steps may be required for this purpose and recovery of cobalt from the alloy phase. That is basically achieved by from acid dissolution and selective precipitation. So, these are the basic use for this two process.

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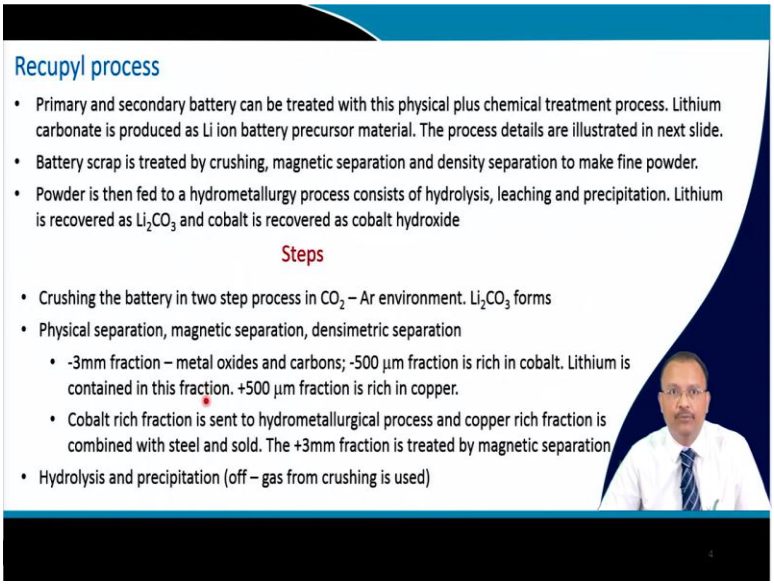

So now, we can talk about this Recupyl process ah. So, primary and secondary batteries both can be treated with this physical plus chemical treatment process. So, this is quite well known lithium carbonate is the final product and that is used as lithium battery precursor material and I will describe the process step in the next slides.

And battery scrap is treated by crushing then magnetic separation and density separation to make fine powders, then powder is fit to a hydrometallurgy process that consists of several reaction like hydrolysis then leaching and then followed by precipitation. And lithium is recovered as lithium carbonate and cobalt is recovered as cobalt hydroxide. So, this is in brief the Recupyl process.

Now if you look the steps the first one is crushing this crushing is done in two step process one is carbon dioxide argon environment and finally lithium carbonate forms, physical separation magnetic separation and dens metric separation. So after this separation steps are also involved.

So, it contains a minus 3 millimeter fraction which basically is metal oxide and carbons and then minus 500 after the sieving micrometer fraction which is basically rich in cobalt. And lithium contained in this fraction in this particular size fraction and plus 500 micrometer is rich in copper. So, when you separate it by sieving technique then the rich material content is already separated.

Now, cobalt rich fraction that is sent to hydrometallurgical process and copper rich fraction that is combined with steel and sold and this plus 3 millimeter fraction is treated by magnetic separation. So, iron is involved in it. And hydrolysis and precipitation from the crushing step this gas is coming out, so that is basically used. So, these are the steps and what is their function that is described here.

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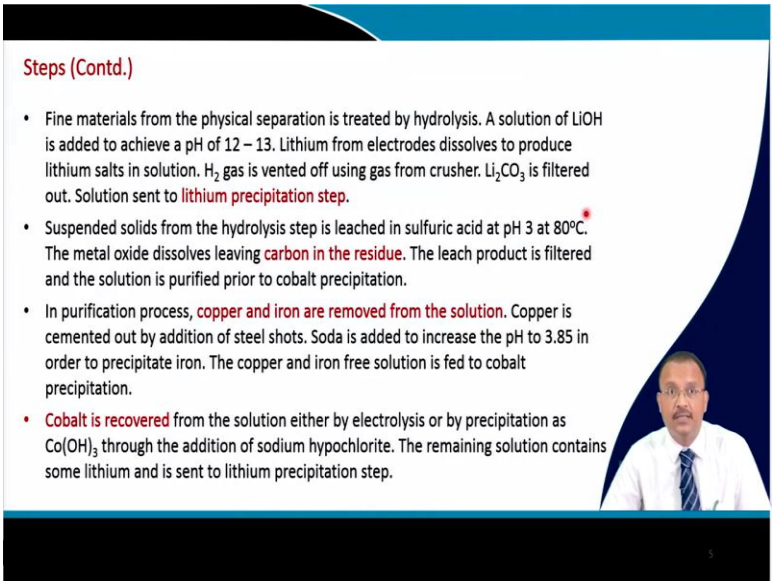

Now, fine materials that you get from the physical separation that is treated by hydrolysis and in this hydrolysis process a solution of lithium hydroxide is added to achieve a pH about 12 to 13. And lithium from the electrodes they dissolve to produce lithium salts in the solution.

And the resultant hydrogen gas is vented off using the gas from the crusher and lithium carbonate is filtered out the solution is sent for lithium precipitation step. Then the suspended solid from the hydrolysis step that is leached in sulfuric acid, typically at a pH around three and slightly warm condition around 80 degree Celsius.

So, the metal oxide that dissolves leaving carbon in the residue the leach product is filtered out and the solution is purified prior to this cobalt precipitation. The purification process copper and iron is removed from the solution and copper is cemented out by addition of steel shots that is mentioned and soda is added to increase the pH to 3.85 in order to precipitate the iron and the copper and iron free solution is fed to the cobalt precipitation.

So finally, cobalt is recovered from the solution either by a electrolysis process or a precipitation process. So, cobalt hydroxide through the addition of sodium hypochlorite, so you can get this material and the remaining solution contains some part of lithium that is sent to the lithium precipitation step.

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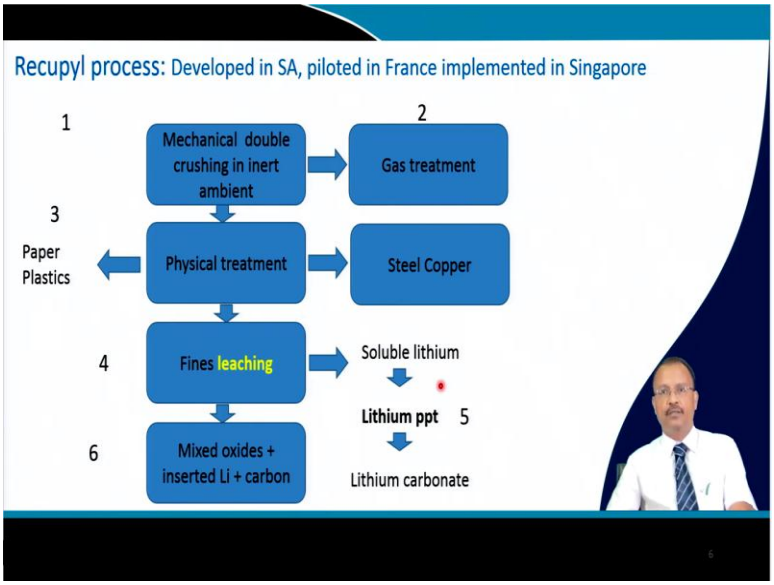

So, that is the Recupyl process and it was originally developed in South Africa and the pilot plant was in France and finally it is implemented in Singapore. So, this process steps the first one is mechanical double crushing in an inert ambient, then there is a gas treatment as I have mentioned.

Then there is a physical treatment where this plastic and papers are coming out and other part is steel and copper you follow the last slide the in the step what exactly has been done and that is pictographically schematically shown here. Then you have the fine, fines the powders the leaching process is involved. And then from the leaching process you get mixed oxides and lithium and carbon and from here the soluble part the lithium can be precipitated and finally lithium carbonate you get as the raw material. So, this is the process that was developed by Recupyl.

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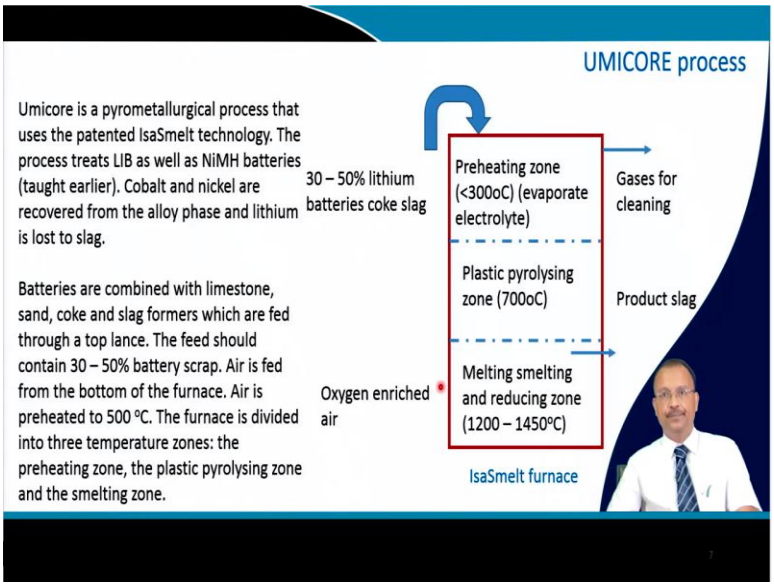

Umicore process that is a pyro metallurgical process it use a patented isasmelt technology and this process treat lithium ion battery as well as nickel metal hydride batteries which I think I have mentioned earlier. Cobalt and nickel are recovered from the alloy phase and lithium is lost to the slag.

So, that is one disadvantage that they cannot extract lithium out of it and as you can see the furnace has three zones the first one is preheating zone, temperature is less than 300 degree Celsius this is just to evaporate the electrolyte. The gas that is coming out they are used for a cleaning purpose to extract something else.

Then there is a plastic pyrolysing zone about 700 degree Celsius here the product is slag and then melting smelting and reducing zone. So, this temperature is raised to 1200 to 1400 degree Celsius. So, the batteries here are combined with limestone sand and coke and the slag formers which are fed through the top lens of the furnace.

And this feed should at least contain 30 to 50 percent of battery stock and remaining this material and air is basically fed from the bottom of the furnace. So, oxygen enriched air is supplied from the bottom of the furnace and as I said the furnace is divided into 3 temperature zones, one is Preheating another, one is Plastic pyrolysing zone and third one is the Smelting zone.

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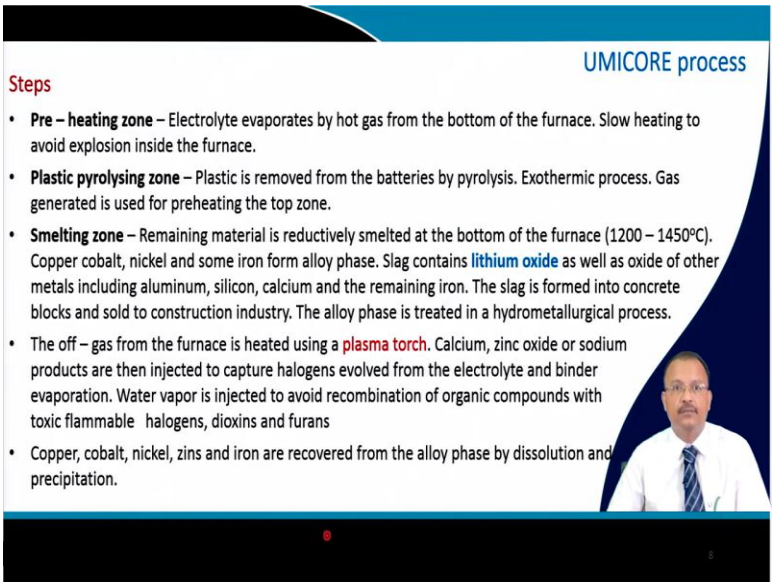

Now, in the preheating zone electrolyte evaporates by hot gas from the bottom of the furnace and usually slow heating is done to avoid the explosion inside the furnace. Then you have a plastic pyrolysing zone and plastic is removed from the battery by pyrolysis its exothermic process.

And the gas whatever is generated that is used to preheat the top zone then finally the smelting zone comes. So, remaining material is reductively smelted at the bottom of the furnace the temperature is pretty high here about 1200 to 1450 degree Celsius. And copper cobalt nickel and some iron they form a alloy phase and the slag it forms contains lithium oxide as well as oxide of other metals that include aluminum, silicon, calcium and remaining iron.

So, this slag is formed into concrete block and sold to the construction industry. So, you are losing lithium and basically the alloy phase is treated in a hydrometallurgical process. The off gas from the furnace is heating is heated using a plasma torch and calcium, zinc oxide and sodium products then they are injected to capture the halogen that is evolved from the electrolyte and binder evaporation.

Water vapor is injected to avoid the recombination of organic compounds with the relatively toxic flammable halogen and there are other dioxins and furans. Copper, cobalt, nickel, zincs and irons are recovered from alloy phase by dissolution and precipitation sorry for the spelling mistake here.

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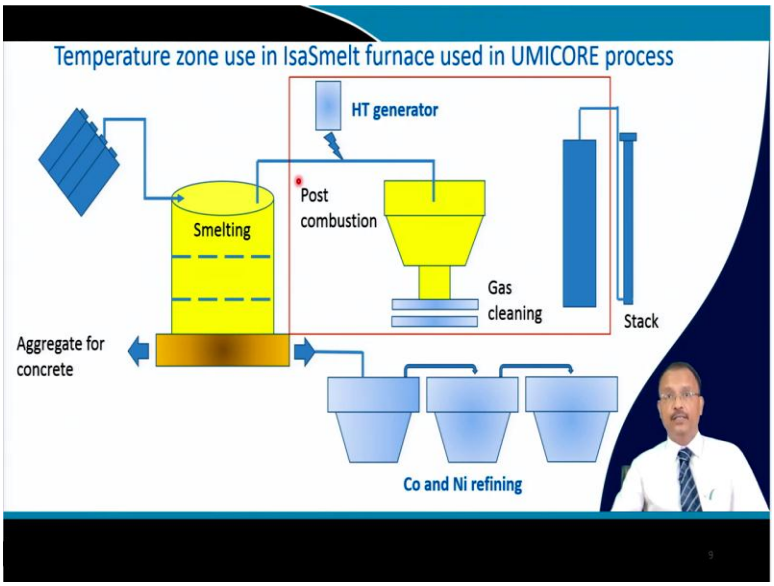

So, the temperature zone that is used in IsaSmelt furnace that is used in Umicore process. So, you have the batteries here the furnace is the main part and then the post conduction combustion this gas is coming out, so you have a HT generator. So, generate the plasma and then there is a gas cleaning takes place and from the lower part of the furnace you get basically the transition metal cation through several refining process, which I just described and the lithium is coming out for I mean forming the aggregate and that is used in construction industry.

And here from this part you can see that the gas cleaning is important you cannot throw it out this gas in into open ambient. So, this process the plasma treatment it is done in

this for particular region to process this post combustion gases. So, that is in brief the process that is followed by Umicore.

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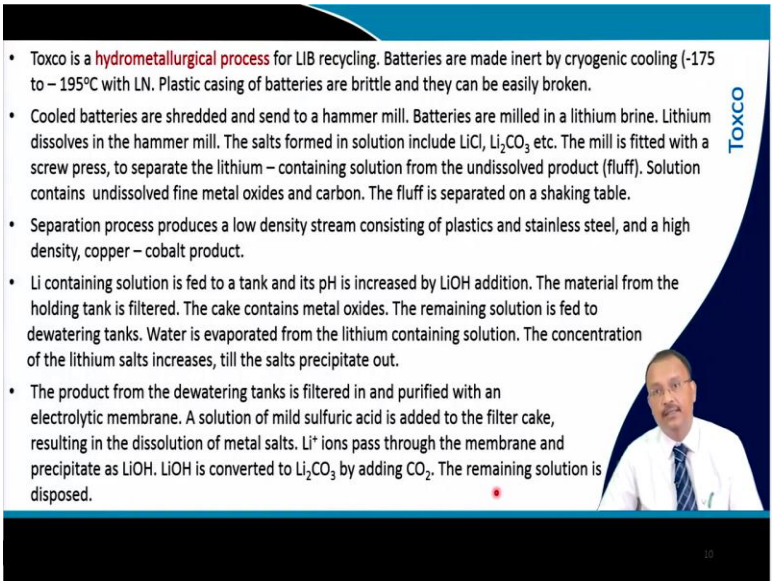

Now, Toxco this is having a hydrometallurgical process for lithium ion battery recycling. So, batteries are made inert by cryogenic cooling, so minus 175 to 195 degree Celsius with liquid nitrogen. So, that is inert battery you can make by such a low temperature and plastic casing of the batteries are brittle and they can easily be broken.

In case of the prismatic battery now this cooled battery they are shredded and sent to a hammer mill. So, batteries are milled in a lithium containing brine and lithium dissolves in this hammer mill and the salt formed in the solution that basically includes lithium chloride, lithium carbonate this kind of salts are generated.

Now, this mill is fitted with a screw press to separate the lithium containing solution from the undissolved product we call this is a fluff. And solution contain undissolved fine metal oxides and carbon and this fluff is separated on a shaking table. Now, the separation process produces a low density stream that consists of plastics and stainless steel and a high density copper and cobalt product.

Now, the lithium containing solution here this is fed to a tank and the pH is increased by adding lithium hydroxide and the material from the holding tank that is basically filtered and the cake that is formed that contains metal oxides. And the remaining solution again

fit to the dewatering tanks and water is evaporated from the lithium containing solution, the concentration of the lithium salts thus increase and the salt is precipitate out.

Now the product from this dewatering tank is filtered and then it is purified with an electrolytic membrane in this case a solution of mild sulfuric acid that is added to the filter cake. And that result in the dissolution of the metal salt, lithium ion pass through this membrane and precipitate as lithium hydroxide basically LiOH is then converted to lithium carbonate. If you add carbon dioxide and the remaining solution is finally disposed.

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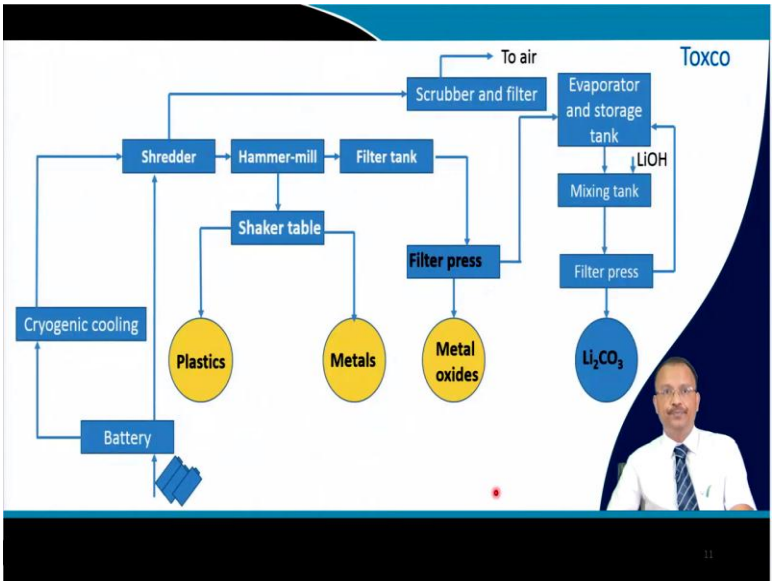

So, this is the whole process. So, start from here so first you do the cryogenic cooling then you send it to the shredder and the gas here is fed to the scrubber and filter and finally, disposed to the air. And from the hammer mill you one part goes to the filter tank and then through a filter press you get metal oxides and the hammer mill part the other part from the hammer mill that goes to a shaker table and you can separate plastics and metallic part.

And from the filter press the solution the precipitated is the metal oxide the solution is evaporate in a storage tank, then it goes to a mixing tank then again filter press and here in this stage lithium hydroxide is added here. And then finally lithium carbonate is produced. So, you can separate all the metals in oxide form and then metallic form and

lithium carbonate as a source of lithium. So, this is a quite manageable and effective process for lithium extraction.

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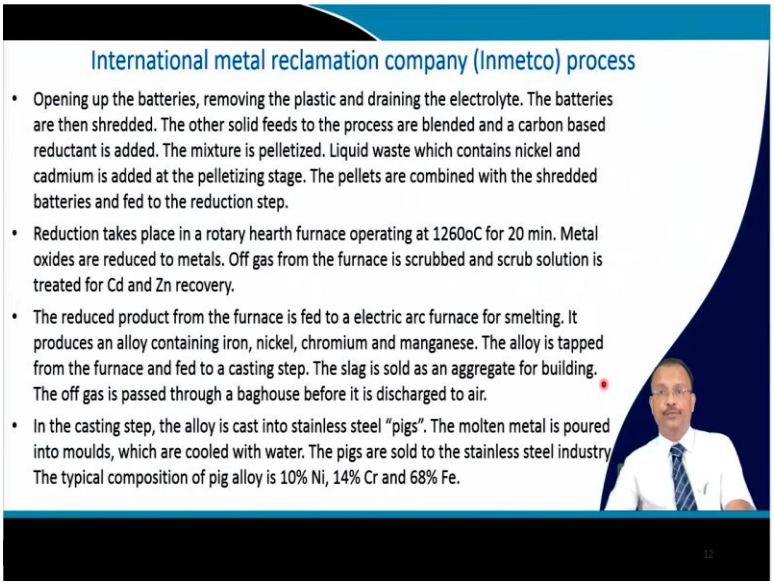

Then finally, the US based company Inmetco International metal reclamation company, so the steps are as follows first the opening of the batteries removing the plastic and draining the electrolyte that is we will have to be done manually. Leave apart the whole battery pack extraction, so that will have to do the do actually manually because there is no automated process because of the shape of the battery already I described it in my earlier lecture.

So, these batteries are again shredded and other solid fits to the process are blended with carbon based reductant. The mixture is forming in the form of a pellet and the liquid waste this contain nickel and cadmium is added in the pelletizing process in the in this particular stage.

So, the this pellets are combined with the shredded batteries and fed to the reduction step. So, the reduction takes place in a rotary hearth furnace that basically operates at 1260 to degree Celsius for about 20 minutes. So, metal oxides are reduced because you are using carbon here the reductant carbon based reductant. So, metal oxides are reduced to metal and off gas from the furnace that is go that goes to the scrub solution and treated for cadmium and zinc recovery.

And the reduced product from the furnace is fed to a electric arc furnace for smelting and it produces basically alloys of iron nickel chromium as well as manganese. The alloy is tapped from the furnace and fed to the casting step and the slag is sold as an aggregate for building and the off gas is passed through a baghouse before it is discharged to air.

In the casting step the alloy cast into stainless steel pigs the molten metal that is poured into the moulds which is cooled in the water, these pigs are sold to the stainless steel industry and the typical composition of this pig alloy is 10 percent nickel 14 percent chromium and 68 percent of iron. So, this process almost all the recoverable profitable metal you can extract out of this process.

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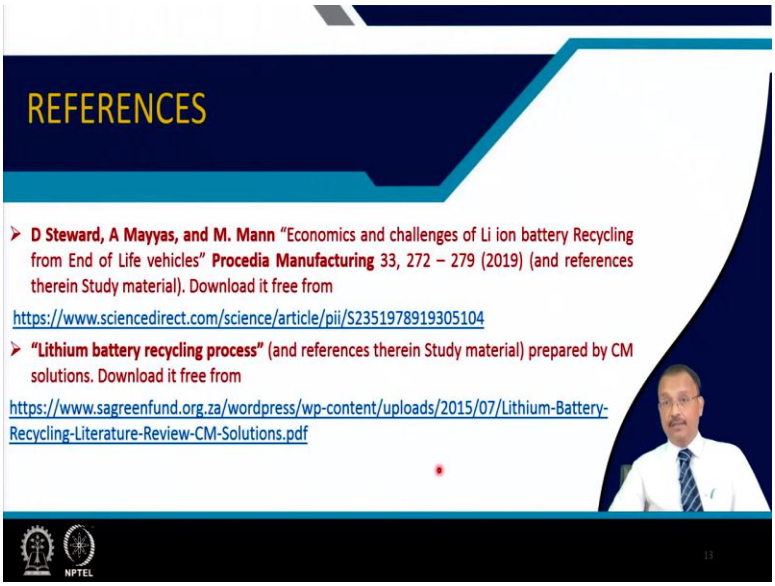

But lithium extraction is difficult because like your Umicore process this process also is not using any hydrometallurgy step. So, lithium extraction is possible if you integrate a hydrometallurgy step during slag extraction, but for this typical company they probably they do not do it. So, they go to the concrete industry, so this economics and challenges of lithium ion battery recycling from the end of the life vehicles.

So, this is the study material and it is freely available it is a good source of the topics that I have covered and lithium battery recycling process and take care of all the references there in this particular literature and this is prepared by CM solution and you can download it free from this link. So, these two I have explained the process I went a bit

fast without describing line by line due to time constraint, in this type to particular lecture but the process is reasonably well defined in this 2 literatures.

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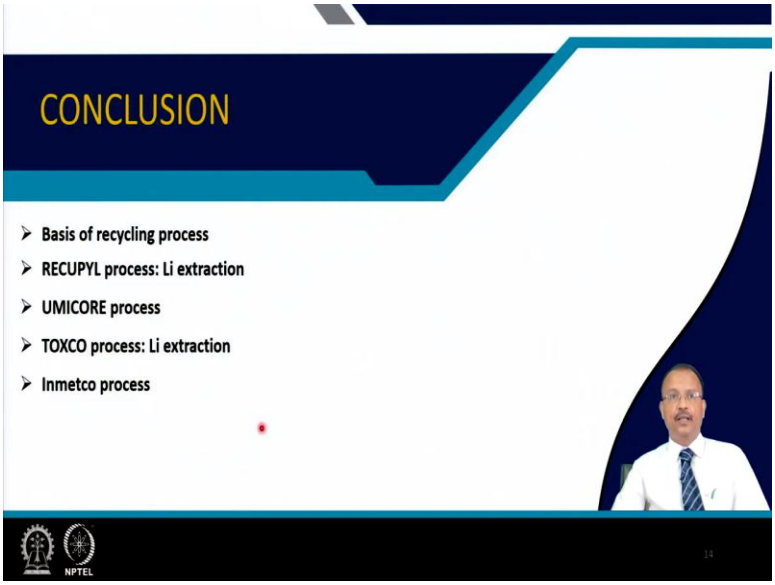

So, in this particular lecture we talked about the basis for the recycling process and we started with Recupyl process for lithium extraction, then Umicore process where the lithium is not extracted. The Toxco process again it is based part of it is hydrometallurgy base and that is used for the lithium extraction. And finally, the Inmetco process there also lithium is not extracted, but the other material gets extracted.

Thank you for your attention.