Electrochemical Energy Storage
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Module - 11
Li resources and recycling of Li ion batteries
Lecture - 53
State of the Art Extraction Techniques and known Production Reserves

Welcome to my course Electrochemical Energy Storage and this is model number 11 we are talking about Lithium resources and recycling of Lithium ion batteries. This is lecture number 53 where I will be describing the State of the Art Extraction Techniques and known Production Reserves what we have for lithium ion percussive materials.

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So, I will cover extraction techniques and lithium resources that we get after extracting from the ore called spodumen, then also lithium resources from the extraction of lithium from brine and these are all surface brine, surface salt lake and also we have underground brine extraction. We will talk about it.

Then we will compare the mining and the brine extraction what are the plus and minus, positive and negative things and other possible lithium resources. Apart from this minerals and salt like brines, what are the other possible lithium resources which could

be today it could be lithium reserves, but tomorrow it could be profitable reserve for lithium resources.

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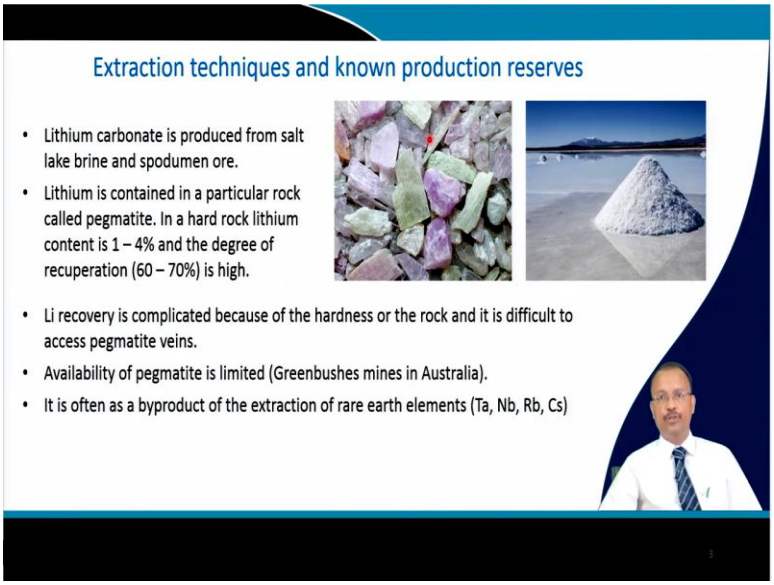

Lithium carbonate is basically produced from salt lake brines and spodumen ore and the spodumen ores basically looks like this. And if you see the brine it is just like salt extraction. So, these are the salt lake brines and you can extract lithium by suitable chemical processing from this brines. So, this is a particular rock that is there in the spodumen ore and that is called pegmatite.

So, lithium content of this pegmatite in the spodumen ore that is about 1 to 4 percent and the degree of recuperation is considered to be about 60 to 70 percent that is quite high. So, lithium recovery is basically complicated because these are very hard rocks and also it is difficult to access the so called veins of pegmatite in the spodumen ore and the availability of course, it is limited you have seen it what are the global resources for this ores that is that already you have seen.

So, pegmatite is availability is also limited. So, one of the famous famous place is this Greenbushes mine in Australia and sometimes lithium is actually the byproduct of the extraction of other rare earth materials or the rare earth materials that is the material like tantalum, niobium, rubidium, caesium. So, along with that it also gets extracted.

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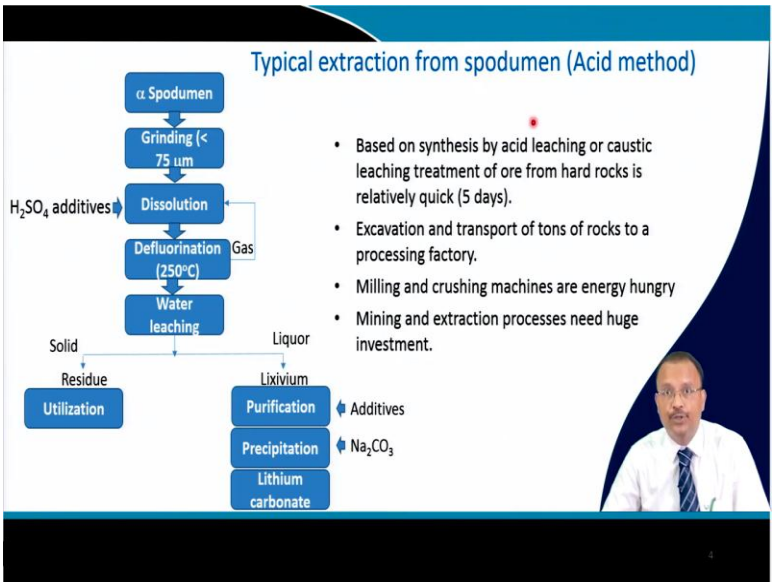

So, there are acid method and base method of a typical extraction of the spodumen and roughly I have summarized that how they are extracted. So, alpha spodumen is used and then it is a very hard rock. So, you will have to grind it to a typical size about 75 micron by using the brushing units.

And, then using acid typically H 2 SO 4 and other additives, it is dissolved and then de fluorinated at little bit high temperature about 250 degree Celsius. So, that process is required and then you do water leaching and you get solid residue and solid residue you have this utilization steps to get other material from this residue. The liquid part which is called liquor, again you add a certain additive and purify it and then using sodium carbonate you basically precipitate that.

And, then there are the washing of the sodium ions from the ultimate material which is lithium carbonate that is basically used for as a precursor material for lithium ion cell manufacturing. So, depending in the process this extraction could be of acid type, acidic type or you can use caustic base material and this technique also can be used along with the acid base extraction; you can have base-base extraction as well.

And, the whole process that is from this hard rock till this end product it is relatively quick it takes about 5 days and you will have to consider from the mines you will have to transport this heavy rocks which are very hard to the processing factory where you do

this processes from the mine. So, that transport cost sometimes it is high because you cannot place it very near to the mine, that is one problem.

And, second problem is this milling and crushing these are not soft rocks. So, milling and crushing machines are energy hungry. So, that will also add to the cost. So, this mining and extraction process including this whole acid or base-base process crushing of the material. So, these are expensive. So, this cost lot of investment. So, that one should prepare to meet the cost of the extraction from the hard rock.

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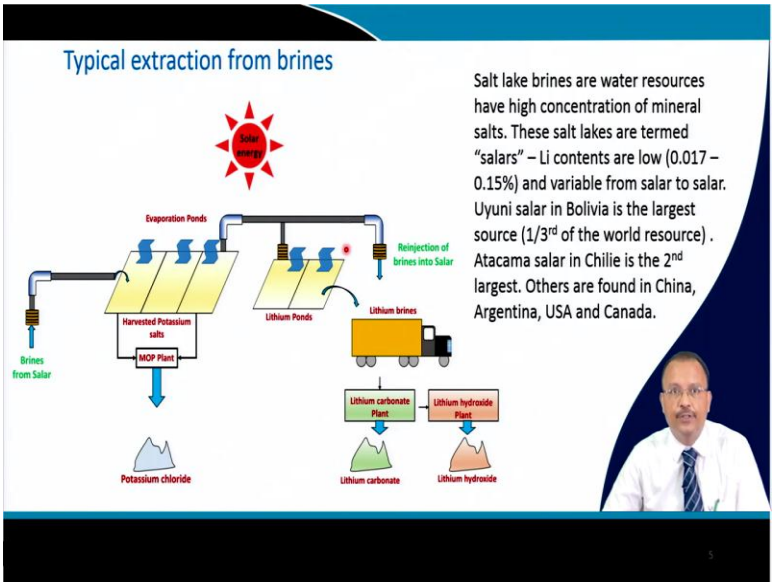

The second popular method is extraction from brines and salt lake brines are actually the water resources which have relatively higher concentration of mineral salts not only lithium, but others minerals are also there. And, the Spanish terminology the salt lakes are termed as salars. So, we call it salars and lithium content here is about 0.017 to 0.15 percent.

But, it is just the lake as you can see it is the evaporation ponds there in series of evaporation ponds are there and from the actual salt lake the brines the salt water is transferred progressively from one brine to others sorry, one this evaporation ponds to other and you need solar energy. So, that is another part because solar and wind that will help for the extraction of the minerals, the water will dry up. So, lithium content they will of course, vary from salar to salar.

So, the Uyuni a salar in Bolivia they are the largest among the global resources about one third of the world resources are there in this salar and Atacama salar in Chile that is the 2nd largest. And, other brine sources are in China, Argentina, USA and Canada. So, you can see that first you can harvest potassium in the form of potassium chloride.

So, these mineral salts they are basically extracted in a MOP plant to get potassium chloride and then they are transferred to the lithium ponds, these minerals are already extracted from the brine sources and then this lithium brines they usually they are transported this brine, which is I mean more lithium contents are there. So, they are transported to the different plants where from the lithium carbonate as well as lithium hydroxide is produced. So, relatively easy process here solar energy is required and the process goes on.

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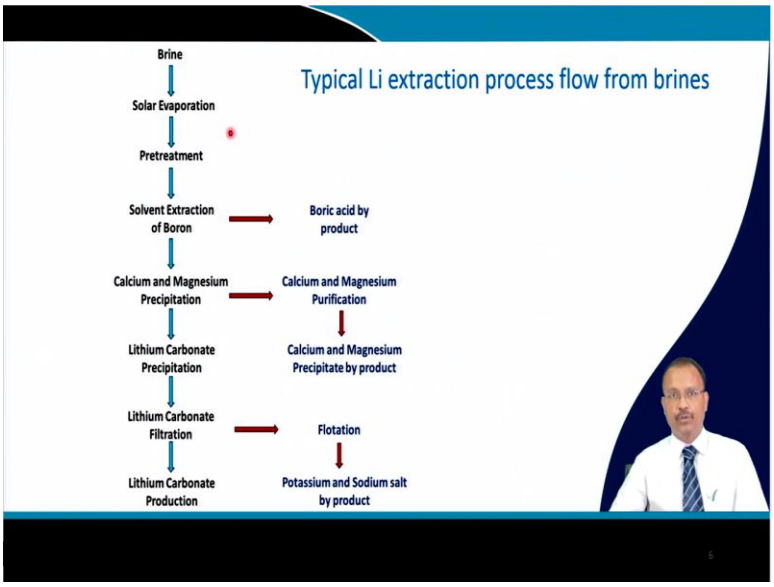

So, the typical extraction from the concentrated lithium containing brines is from the brine you have solar evaporation, then certain kind of pretreatment is there, then solvent extraction of boron and then you get boric acid by product, then calcium and magnesium precipitation takes place and calcium and magnesium they are purified. So, this brines are rich in mineral resources. So, you get other material as well.

Then finally, lithium carbonate precipitation takes place from the concentrated brine solution which is transported to this plant and then lithium carbonate is produced. It is filtered out mostly by flotation this technique. So, potassium and sodium salt byproduct

that is separated and then finally, you get lithium carbonate produce. So, this is one of the simplified version of the extraction process from the salt lake brines.

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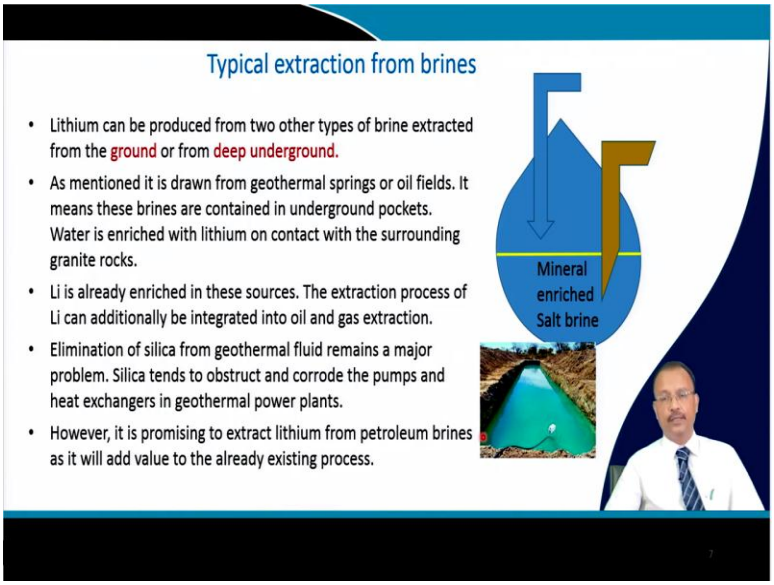

Lithium also one can extract from two other types of brine from the ground or from deep underground. So, it is not the surface type of brines as you can see that there are in depth. So, this type of places where the lake water is mineral enriched salt brine. So, that is also a good source.

So, as I have mentioned earlier so, it is drawn from geothermal springs or oil fills; that means, the brines contained in the underground pockets water is enriched with lithium because it is in contact with surrounding granite based rock here. So, it is enriched lithium, it is more profitable. Although it is not on the surface, but underground. So, you will have to spend money to extract it.

So, lithium is already enriched in this resources and the extraction process of lithium can additionally be integrated into the oil or gas extraction. So, that is also possible because already it is nearby I mean this place is already enriched with oil and gas, it is usually the case. So, this is an additional process and which is which makes it more profitable.

So, the major problem is to eliminate silica from this geothermal fluid and that remains a major problem because silica actually tends to obstruct as well as corrode the pumps and heat exchanger in this geothermal power plants. But, it is promising to extract lithium

from this petroleum brines because as I said that will add value to the already existing oil and gas extraction process. So, additionally you are getting also lithium from this sources. So, that part is that is more profitable.

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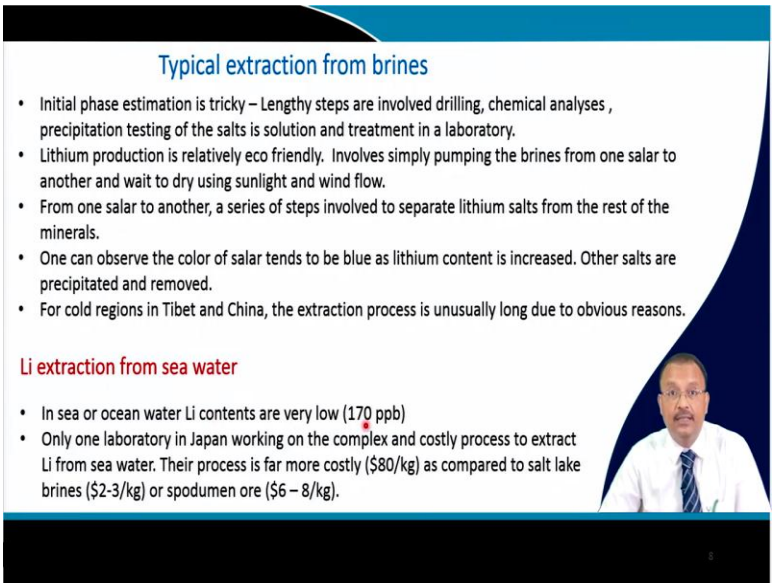

So, in this cases from brine extraction the initial phase of estimation exactly how much lithium content is there. So, that is quite tricky and it is a lengthy step and it involve drilling and then followed by chemical analysis and followed by the precipitation testing of the salt in solution. So, that is usually done in a laboratory. So, that is a lengthy process. It cannot be over by 5 days as we have seen in case of ore extraction of lithium.

And, this type of process is relatively eco friendly not like the ore extraction process which is energy hungry, then transport cost is also involved in it. And for this case it involves simply the pumping of the brines from one salar to other one and wet to dry under the sunlight and also with the wind flows.

So, from salar to salar a series of steps as you have seen is involved to separate the lithium salts from the rest of the minerals and eventually the rest of the minerals gets also extracted. So, the byproducts are also profitable for you to have and one can observe that the color of the salar tends to be blue as lithium content is increase. So, visually you can observe lithium is extracted. So, it turns to be blue colored and other salts as you have seen they are precipitated and that can be removed.

But, the problem is in cold regions even if you have this kind of salars particularly in Tibet and certain part of China, this process is unusually long because of two obvious reason because you would not have enough sunshine to get it dried up. So, that is one problem particular season you can extract it.

So, lithium can also be extracted from sea water, but you can see that the lithium content unlike this brines they are extremely small about 170 parts per billion. So, there is only one laboratory in Japan as far as I understand they are working on this very complex process and this is also another source and particularly in India you have lot of resources sea water resources, but this is costly as compared to 6 dollars per kg the process is very costly about 80 dollars per kg.

So, brines is relatively economic 2 to 3 dollars per kg and spodumen ore as I have shown you about 6 dollar to 8 dollar per kg since compared to both of this you can see that this extraction is very very expensive about 80 dollar per kg. But, as I understand only one company in Japan they are aggressively working on it, probably they can reduce the processing cost and maybe that is also another huge resources of lithium if the extraction can be made economically viable.

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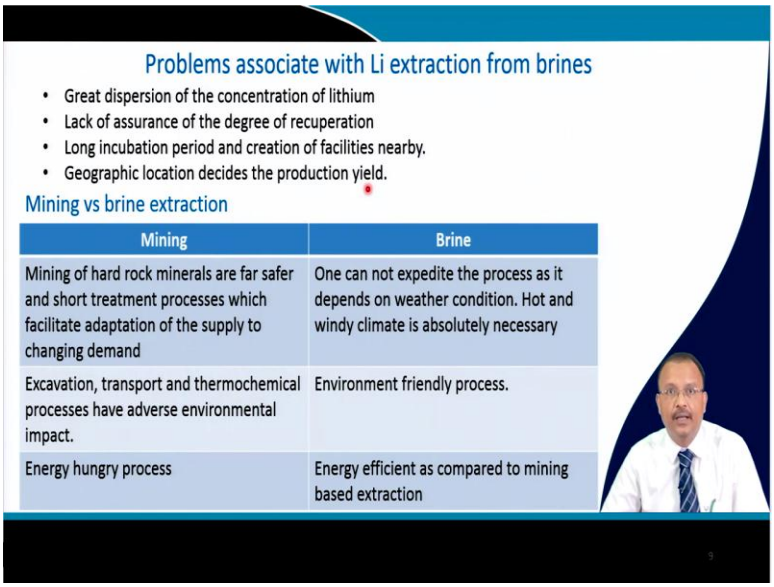

So, there are problems associated with lithium extraction from brines. The first is quite obvious there are great dispersion of the concentration of lithium. So, that is one. So,

brine to brine not necessarily you get same amount of lithium lack of assurance of the degree of recuperation, sometimes it is 60 to 70 percent it may be low also.

And of course, long incubation period and the creation of facility nearby. So, that is also a cost extensive process, but certainly it is more cheaper as compared to the ore extraction and geographic locations that basically decides the production yield due to obvious reason. So, if you compare now between the mining these resources and with the brine. So, mining of the hard rocks are far safer and short treatment process about 5 days which facilitate adaption of the supply to the changing demand.

You may not be in a position to wait for that long and in case of brine one cannot expedite the process because brine will take it is own time. So, depending on the weather condition also the it depends upon the weather condition. So, hot and windy climate they are absolutely necessary to dry it up excavation transport and thermomechanical process have adverse environmental impacts.

So, you have seen it in case of ore extraction first you will have to crush it and then you have to do the acid treatment warm acid treatment de fluorization which I have explained in my earlier slides, but as compared to that this brine extraction is environment friendly process. And, this is of course, energy hungry process and this is relatively energy efficient as compared to mining based extraction.

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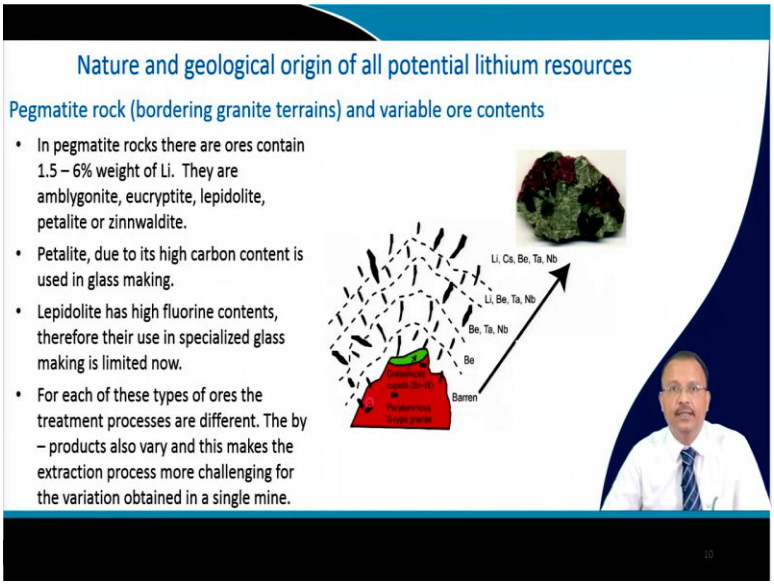

So, if you now consider this pegmatite rock that is actually some kind of bordering of the granite terrains they have very variable ore contents. So, these pegmatite rocks there are ores contain 1.5 to 6 weight percent of lithium which is considered quite high and these are this rocks which is amblygonite, eucryptite, lepidolite, petalite and zinnwaldite.

So, these are the five important variation in the pegmatite rocks and they have variable lithium content and both all of them they are useful not only for the lithium extraction, but for other purposes as well. So, petalite is usually have hard carbon contents and that basically is used in glass making. So, if you consider this lepidolite it has high fluorine contents.

So, therefore, that is used for specialized glass, but this specialized glass nowadays that making is relatively low and for each of these types of force the treatment process remember they are different and byproduct also certainly will vary because the contents are different. And this basically makes the extraction process more challenging for the variation that is obtained in a single mine.

So, today you may have a good source of lithium, tomorrow it is not necessarily that you will have the concentration of the lithium they will start to vary. So, if you see across the depth of this mining, then you can see that at the surface near the earth crust you have the source of lithium and once you start to extract it and go deeper to the earth crust, then you can see that there are no lithium here.

So, your mining is limited to only this part where lithium along with the other rare earth's caesium etcetera that one can get. So, this is one challenge that I consider that to be that should be considered seriously because this is a huge investment and you want to have lithium resources for available for quite some time, so that you can make profit out of it, but as I said that it is also not only lithium, but other rare earths also you are getting from this pegmatite rocks.

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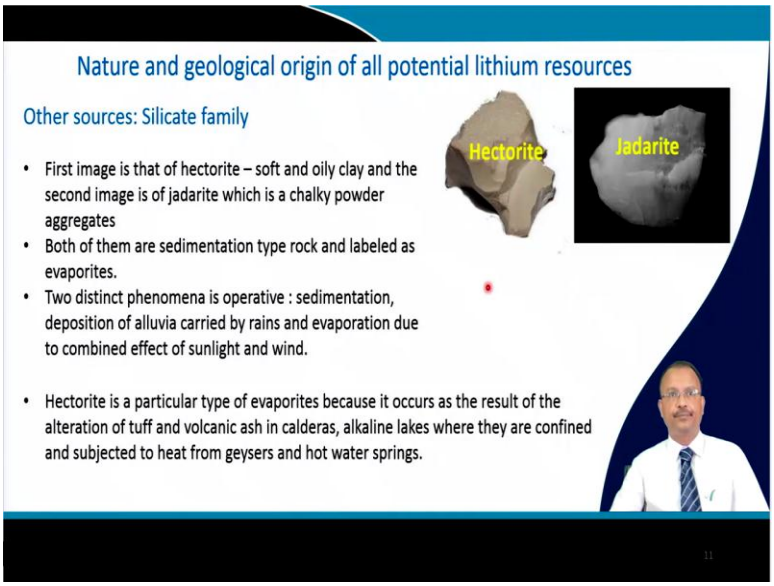

Other resources people are trying that apart from that and those apart from that spodumen and this pegmatite and other ores people have started searching it. So, other sources is the silicate family and the this image is from the silicate type of minerals it is called hectorite it is having a oily and this is basically clay and this is soft and oily. So, that is one advantage that you may not have to use this is not that energy hungry to reduce the size.

And, the second one is jadarite and this is a chalky powder just like the chalk powders of white in colors. So, they are sedimentation type unlike the other one that is igneous type of rock granite based in the terrains this pegmatite is there. But, these are sedimented, sedimentation types of rocks this is labeled as evaporites. So, this is the two types of rocks are different, and here two distinct phenomena is operative one is sedimentation that deposition of alluvia and that is carried by rains and evaporation due to the combined effect of a sunlight and wind.

So, hectorite that is particular type of evaporites because it contains as a result of alteration of tuff and volcanic ash in calderas and alkaline lakes where they are confined and subjected to heat, so that heat is from geysers and hot water springs. So, that that is another source that people are considering now to get lithium extracted from both these two types of rocks hectorite and jadarite and they are all silicate they consists of silicate family rocks.

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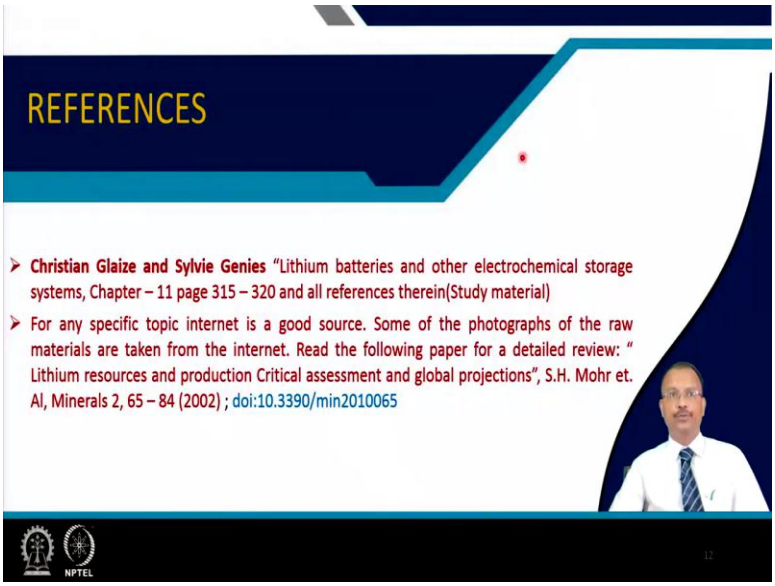

So, this part you can have from the same book and for any specific topic if you are interested then I will consider internet is a good source and some of the photographs that I have used from internet. And this is a very good paper lithium resources and production critical assessment and global projections. So, many of these topics which I have covered here that is detailed in this paper and you can download it if I remember this is you can download it from the internet and this is a good source of the reading material and treated as a reading material as well.

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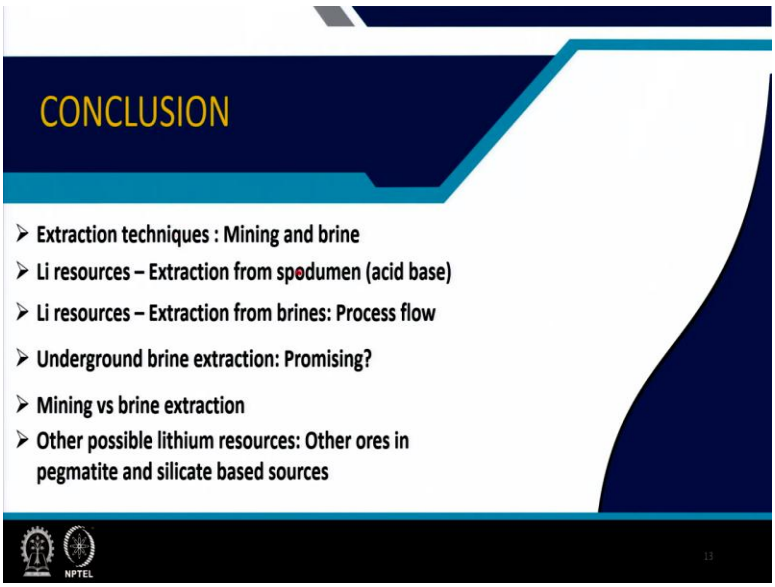

So, in this particular lecture we talked about extraction techniques that is mainly from mines and brine and then lithium resources their extraction from spodumen which is acid base, then lithium resources that is coming from extraction of brines and rough process flow although it is not very detailed, but you can get the idea that how exactly you can extract the raw materials following the schematic process flows.

And, also people are considering now underground brine extraction and we will have to see whether they are promising because if it is with the oil and gas extraction then it will do a value addition, but otherwise it is an expensive process. So, the interest of people to extracted from the surface salt lake surface brines that is not will not be there if you go underground, and then we compared mining versus brine extraction and other possible lithium resources mostly the silicate base resources.

And, also the in the pegmatite ore itself there are other lithium resources and, but they are all confined in the surface of the earth crust and these are the minerals and other resources that is now being used to extract the raw materials for lithium ion rechargeable batteries.

Thank you for your attention.