

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-8

Lecture-37

Greetings, I welcome you all to the next lecture of this course where in now we are going to study about lead acid batteries. In the previous class we had studied about batteries wherein we introduced the concept about how it is so important to understand the various categories that are present in batteries and how it was important to understand that each battery has its own type of recycling strategy. Although it may come under a wide umbrella of e-waste, it still requires its own style of material handling because there can be wide variety of important materials that can be recovered from different battery sources like REEs. In this case now we are going to study about lead acid batteries. It is important to note that lead acid batteries have been widely used as one of the most important powerhouses. Once a lead acid battery has been used, the charging discharging is very much convenient. This has been used for a long spans of time as well.

What we are going to discuss today is we will be seeing the different categories of lead acid batteries based on their intended applications and we'll also see what is the usual life span in years and how it is recycled. We'll just write lead acid batteries. Lead acid are important battery types that are commonly used where where are these commonly used. We'll have some internal classification as well. First, we could have starting, lighting and ignition, then we have backup power supply and uninterrupted supply. Third could be storage unit, other applications. When we look at SLI types, we know that these are used for automobiles, motorcycles, ships, aircrafts, low speed vehicles, tricycles. Generally speaking, two to three years are common life of SLI type batteries. When we look at backup power supply, we'll be using it in internet data banks, banks, hospitals, and internet data servers as well. Things & places where we do not essentially can have any interruption in power supply so there we have lead acid batteries and here it is generally having a lifespan of 68 years. When we look at storage units and what type of storage unit are we talking of, storage unit coming from different sources.

Hydro energy, solar energy, wind energy systems, so we have 4 to 10 years. Other applications where we can have toys, instruments etc. We have also power applications it could be having 2 years. We now know that we even in a lead acid battery category, we have some internal divisions as well. These internal divisions are there because these batteries have been used in different applications and this means that the size, the constructions

and at times the materials as well can change so, these batteries have to be sorted accordingly based on their applications and their intended uses. Why do we need to recycle batteries? Again the same questions. Recycling is important, why recycle lead acid? We can see that lead acid batteries are sources of lead and acid. In this case, it is sulfuric acid. We know that improper handling

or dismantling or even discarding of lead acid batteries can severely pollute because we have lead sitting here can pollute the environment. What we need to understand here is lead acid batteries are to be recycled no matter what is the category of battery and people have found good ways of completely reusing these batteries.

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Recycling of Lead Acid Batteries Lecture # 3.6

Lead-Acid batteries are important battery type that are commonly used.

- Starting, Lighting and Ignition (SLI) : automobiles, motorcycles, ships, aircraft, low speed vehicles, tractors (2-3) years
- Backup power supply and Uninterrupted supply : Internet data banks, banks, hospitals etc. (6-8) years
- Storage Units : Hydro, solar, wind energy systems (4-10) years
- Other applications : toys, instrument etc. Power - (2) years

Why Recycle Pb-acid batteries?

- Sources of **Pb** and Sulfuric acid
- Improper handling / dismantling / discarding of Pb-acid batteries can pollute the environment.

They will be able to separate out the casings. The solution in this case is H_2SO_4 , aqueous solution of H_2SO_4 and the electrode materials and they are reusing it in a very well-defined manner. Conventional method is pyrometallurgical method and people have been now advancing into hydrometallurgical method as well because of various drawbacks that come along with the conventional processes. We will be looking at both the conventional processes and the advanced technologies that have been used for recycling the lead acid batteries. We know that the cathode and anode are two important aspects of the batteries. As cathode we have lead oxide and as anode we have sponge metallic lead, we have fiberglass, a separator and we have of course the aqueous solution of H_2SO_4 acid and all of this is inside a polypropylene casing. The casing is polypropylene. We look at the material distribution in lead acid battery. We have polypropylene, we've just seen casing is polypropylene and the plastics. This amounts to nearly 5 to 12 %, we have H_2SO_4 acid this amounts to nearly 17 to 38 %, we have metallic lead and this is in the grid form so metallic lead grid this amounts to 24 to 30 wt.%.

We have lead oxide or sulfate paste. This paste is amounting to 30 to 40 wt.%. And even in the sulfate paste, what are we looking at. Lead paste. The lead paste can have, we are looking at its internal composition PbSO_4 , we have PbO , PbO_2 , metallic lead. One might wonder we already have metallic lead here. But this is a different composition inside the lead oxide paste. That we are going to look. We see that PbSO_4 is around 50 to 60%. We have 5 to 10% PbO . PbO_2 is around 15 to 35% And 2 to 5% of metallic lead. We see that even inside a battery, we have different categories and these categories can have different chemical compositions and we have different materials. We have a casing, we have an electrolyte, we have the anode and the cathode. The paste can have its own internal divisions, PbSO_4 , PbO , PbO_2 and lead.

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Cathode	lead oxide	fibreglass separator		
Anode	sponge metallic lead	aqueous solution H_2SO_4 acid		polyethylene casing

Material distribution in Pb-Acid batteries	Polyethylene acid plastic (5-12 wt%)	H_2SO_4 acid (17-30 wt%)	Metallic Pb grid (24-30 wt%)	Pb oxide / sulphate paste (30-40 wt%)
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The lead paste can have	$PbSO_4$ 50-60%	PbO 5-10%	PbO_2 15-35%	Metallic Pb 2-5%
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Tan et. al (2019)

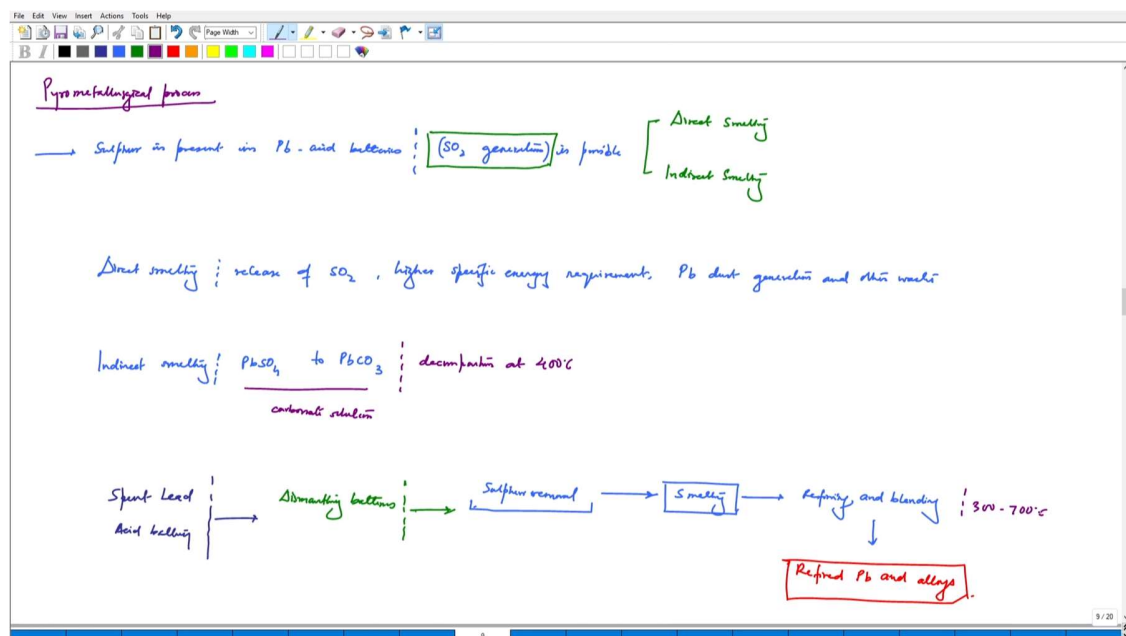
Using this composition, we are going to devise our pyrometallurgical or hydrometallurgical route of recycling. We'll write. Pyrometallurgical process of recycling lead acid batteries. We know that sulfur is present so important points you should note first sulfur is present in lead acid batteries which means there is a possibility, it means possibility of sulphur being released as SO_2 . SO_2 generation is possible. There are two methods of handling such types of wastes. Direct and indirect. Direct smelting, indirect smelting. One has to think about SO_2 generation and then think which route they would like to follow. Is it direct smelting or is it indirect smelting? Direct smelting would mean the release of SO_2 , higher specific energy requirement and dust generation.

Pb dust generation and other wastes. We could also think of direct smelting as a way of giving us the finished lead and refined lead products. But that means we are also going to deal with the release of sulphur dioxide. The other indirect method would be indirect smelting. Indirect smelting would mean what? It means $PbSO_4$ gets converted to $PbCO_3$ and this is done by using a carbonate solution. We are following the decomposition at $400\text{ }^{\circ}\text{C}$. This is a general outline to convert the sulfur and get it out of the system. Lead oxide will be generated.

If we are trying to decompose it at $400\text{ }^{\circ}\text{C}$, we'll get lead oxide and then we can go ahead further processing, general outline looks like this. Spent lead acid battery. We know that will be going for dismantling of batteries. We are assuming here that the batteries are

safely handled. Then again we go for sulfur removal. This means we have done this process and then we can go for smelting. Smelting can be followed by refining. Refining would be required because most of the product that we will be getting is around 85% or more rich. But it's not 100% pure lead. One has to at least approach 95% concentration. For that one has to go for refining and blending. This would give us what? This would give us the finished product, refined lead and alloys wherein we are looking at nearly about 95 or above percent purity. That is the product that we are looking for and this we can be achieving only after refining. A general temperature range is 300 to 700 °C here.

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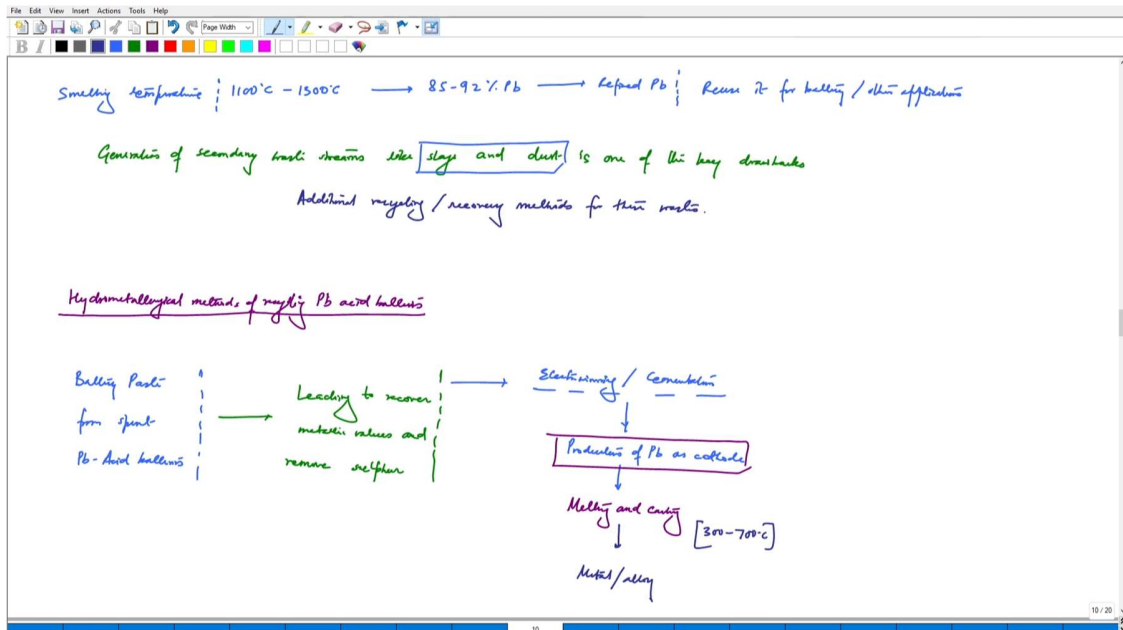


When we look at temperatures for primary smelting, smelting temperature is nearly around 1100 °C to 1300 °C. This gives us actually 85 to 92 % lead which is why we need to refine it. This when we refine it, we get refined lead, when we get refined lead we are actually able to reuse it for battery/other applications. This means we are directly just reusing it. Pyrometallurgy has some disadvantages. We will be observing them. Generation of secondary waste. Secondary waste streams like slags. It is almost inevitable to note that we have a pyrometallurgical process and we are just concentrated in a product that is lead and its alloy. This is really a way of ignoring these byproducts. Byproducts are obviously going to come into picture.

When we look at a pyrometallurgical process we put our raw feed inside it pyrometallurgy has the greatest advantage that it gives us wide range of material handling and good higher productivity. But at the same times, we are also looking at slags and dust generation, which is one of the most important aspects. significant drawbacks if we do not have means of handling these wastes. The secondary wastes that we are talking of, so the secondary wastes like slags and dusts, generation of secondary waste streams like slag and dusts is one of the key drawbacks. One can think of having a recycling strategy for slag and dusts and other connected wastes but it means that one has to have additional recycling or recovery methods for these wastes. We have our pyrometallurgical. We have dealt with pyrometallurgical, we will be now looking at hydrometallurgical method of recycling lead acid batteries.

A general outline that is similar to lead acid batteries when we looked at the pyrometallurgical route, we will now be looking for hydrometallurgical process as well. We have the battery paste from spent lead acid batteries. We have a battery paste material and we know that it is not just lead. Lead in a battery paste is very less. It is basically lead sulphate, lead oxides. When we have material like this, we are now going for leaching. Why do we want to do that? To recover metallic values and remove sulfur. When this is done, we have electro winning or cementation. This is going to give us what? This is going to give us production of lead. In this case production of lead is done and we use it for in the form of cathode as cathode. If we are doing the electrowinning, we have the lead as cathode and then we do the melting. We have lead as cathode now we are going to use it as a raw material for melting and casting. When we do that, we get the based on what we had charged, we get metal or alloy. We do this melting casting at around 300 to 700 °C.

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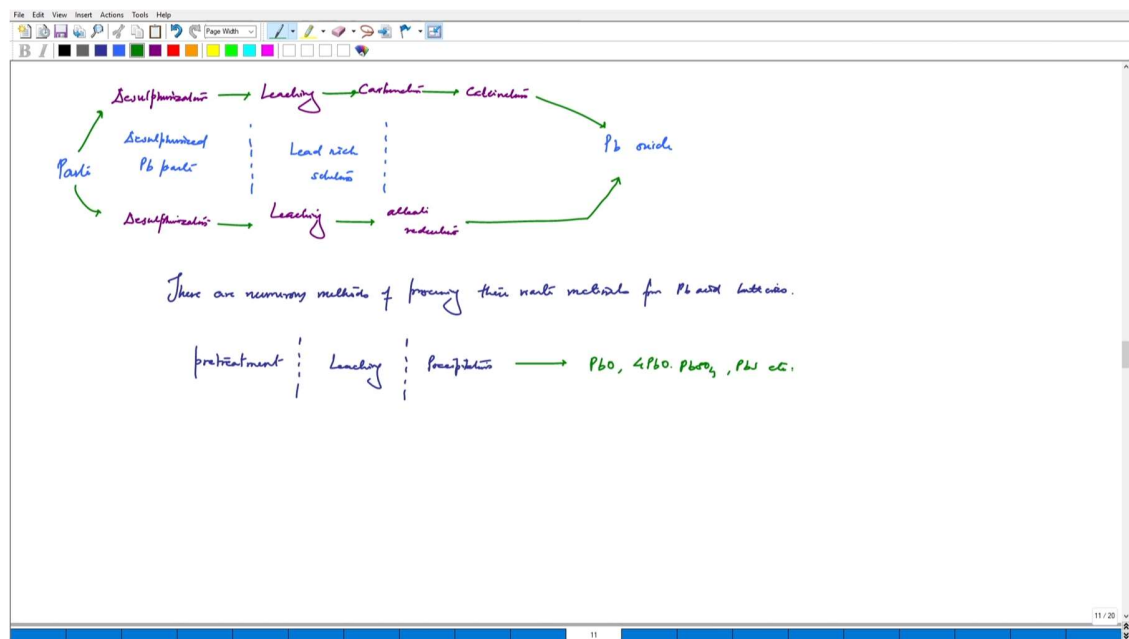


Essentially speaking, we are still using some parts of pyrometallurgy, but the major material recovery has been done through hydrometallurgy and this is followed by electrowinning or cementation and we are able to recover most of the metallic values from the lead waste battery. Another route we can discuss, we have paste and we have lead oxide. There are various ways to move from paste to lead oxide. We will write some of them. Desulphurization, we have leaching followed by carbonation then we have calcination. The other way could be desulfurization then we have leaching then we have alkali reduction. Both these methods look similar but then we have different types of products that are generated at various stages. We will just try to look at some of these stages.

When we are looking at desulphurization, we will have desulphurized lead acid, lead paste and then when we do leaching, we get lead-rich solution and then we do various processes carbonation, calcination. Our target is lead oxide, how we reach there is a way by which we can basically manipulate. This is a chemical route of handling these wastes. what should be added in order to achieve the desired products. In this case it is lead oxide. We could make some other type of products using lead paste material as well. Depending on what we wish to make, we can design our recycling strategy. We note that there are numerous methods of processing these waste materials from lead acid batteries.

They may appear very similar but it's a wide range of products which employs a pre-treatment. One really has to have a pre-treatment stage, a leaching stage of course, when we are talking about hydrometallurgical process and then we will have a precipitation phase. If we are not interested in metal itself, then precipitation or else we will have to go into electrowinning. What type of products we can make? We can have PbO , $4\text{PbO} \cdot \text{PbSO}_4$, PbS , etc.

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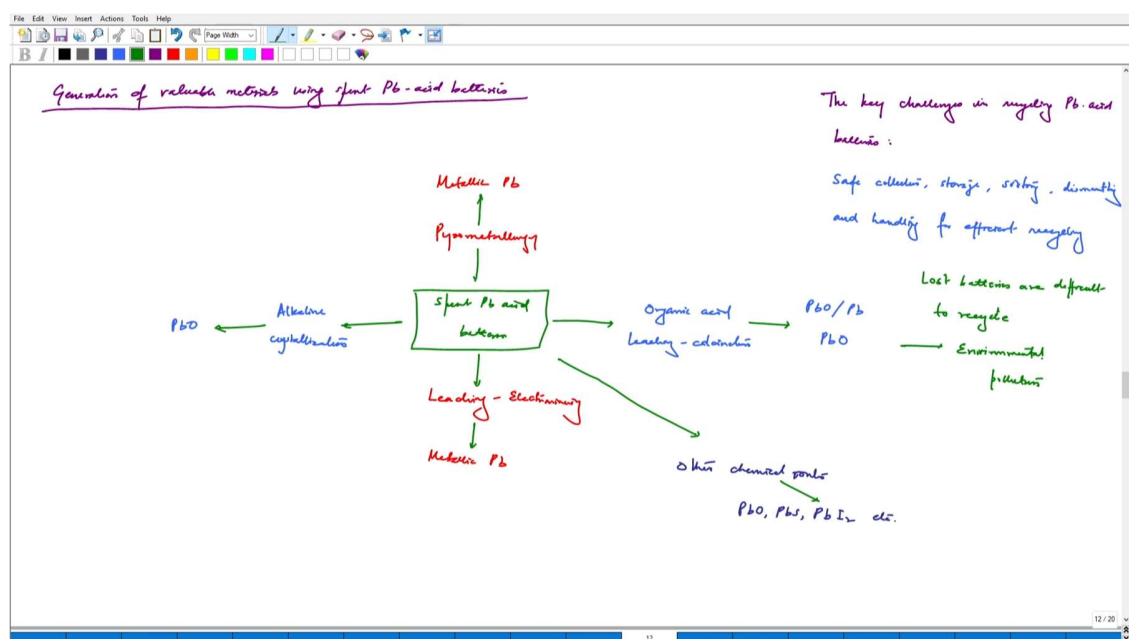


We are going to look at some of the most common products that we will be getting from lead acid batteries. We will just write generation of valuable materials using spent lead acid batteries. We have spent lead acid batteries. Suppose we go for pyrometallurgy we usually will be getting metallic lead. Similarly, if we go for leaching which is hydrometallurgy and we go for electrowinning so leaching electrowinning will give us metallic lead. If we have organic acid leaching and calcination, organic acid leaching and calcination, we will have PbO , Pb or PbO . These types of products. And similarly if we have alkaline system and we have a crystallization. Then we can get PbO . Similarly, if you are looking at some other routes. If we just write. Other chemical. We can get PbO , PbS , PbI_2 etcetera. It is important to note that what are we planning to make and what is the route.

One of the most important aspect is what are we planning to make, what is the route and what is the intended application. In most of the cases for lead acid batteries the most common intended application is applying the recovered materials. In this case it is metallic lead, PbO, PbS and PbO, PbS. These products are basically reused as raw materials for making lead acid batteries. Most common route. When we are looking at lead-based compounds based on chemical routes that are not so conventional then we will be getting valuable products. Those products will be having their own intended applications in their own feeds and these will be directing our lead these materials outside the battery applications. When we have seen the various types of valuable materials, we must note what are the key challenges in handling the lead acid batteries that we will be noting now. The key challenge in recycling lead acid batteries is basically safe collection, storage, sorting, dismantling, handling for efficient recycling.

The most important challenge that people have been facing is the collection itself because some batteries would be lost, lost batteries are difficult to recycle. One really cannot claim the materials back which means it is going to go for environmental pollution. One really has to think about what we should be doing about the lost batteries. This is in general the key challenge because the recycling strategy for lead acid batteries is very well established.

(Ref. 35:15)



People have been exploring the conventional processes, the hydrometallurgical processes, the newer advanced processes, and the recovery of materials in these batteries have been very well. It has been very well studied. People know the how these batteries can be reused to make valuable materials, but we really do not know what to do with the batteries that have not been brought for recycling because tracking of those batteries is very difficult and if those batteries end up in the environment, how they are going to pollute the environment that is a big challenge. We will be continuing our discussion on battery recycling in the upcoming classes as well. Thank you.