

# **METALLURGICAL AND ELECTRONIC WASTE RECYCLING**

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**Week-8**

**Lecture-36**

Greetings, I welcome you all to the new lecture of this course wherein now we are going to discuss battery recycling. In the previous classes we have covered metallurgical wastes, then we had covered electronic wastes wherein we discussed different types of electronic wastes and how to handle them. We had discussed the waste printed circuit board recycling. We are going to focus on the battery recycling which is another aspect of the e-waste recycling that we had planned for this course. We will be discussing different categories of batteries, various subcategories of batteries and how we recycle them. It is important to understand that batteries are an essential part of many if not all many electronic devices mostly it is used for electronic devices that are portable. If an electronic device is directly not connected to a power source, then it has to be using, it will be using a battery.

This is a very common concept that fair enough we have an energy source and this energy source is a battery. But what happens when these batteries are completely drained. One answer could be that these could be recharged but then what happens when these batteries are discarded. Suppose that the batteries reach the end-of-life and after these batteries are at the end-of-life we discard these batteries. When we discard these batteries, these would these batteries are no longer fit for their conventional applications. These will again end up just like any other electronic waste in the electronic waste scrap yard, which means that we have another material to deal with. It is not an electronic device. It is not an electronic component. It is a battery and battery needs to be recycled just like any other electronic waste.

We will be focusing on the recycling of batteries and we will see how the recycling is planned for different categories of batteries. We will write, we know that batteries are important components of many electronic devices. We are actually going to look at the categories. We have to study categories. Not just the categories, we will also look at some intended applications, where these are mostly used. We have batteries. We have

applications. And gradually, we'll be studying most of the batteries as far as we can and we'll see how the recycling is carried out for these battery types.

We have lithium batteries. Lithium based. We have lead acid, nickel cadmium, nickel metal hydride, NiMH. We have sodium based, which is sodium ion batteries. Then we have zinc based. We have zinc alkaline and so on so forth. Mostly, EVs have lithium-based batteries, portable electronics, grid storage systems and so on so forth. Lead acid is basically UPS, not just for computers it is. Lead acid is one of the most important type of batteries that gives us uninterrupted power supply for many electronic devices that are used in large scale or the application of lead acid could be thought of supplying a continuous power supply to hospitals or malls or such uninterrupted power supply is actually done by lead acid and not just that we have automotive applications. Nickel-cadmium, railways, aviation and other applications. NiMH hybrid EVs, so hybrid EVs, cameras, so we have digital cameras that may use NiMH. Sodium ion batteries, electric buses. EVs, electric buses or hybrid EVs, they all are using different types of batteries now and again this is grid system, grid storage. Zinc batteries are commonly used in; zinc alkaline batteries may be used in toys or let us say low power, low power application.

(Ref. 7:15)

Lecture # 35

Battery Recycling

Batteries are important components of many electronic devices. | Categories of batteries

✓ Batteries	Applications
Lithium-based	EV, portable electronics, Grid storage systems
Pb-Acid	UPS, Automotive
Ni-Cd	Railways, Aviation and other applications
NiMH	Hybrid EVs, cameras
Na-based	Electric buses, Grid storage
Zinc-based	Toys, low power applications

When we think of different categories of batteries and we now know the various applications, we must note that these batteries can have different types of applications beyond these applications. This means that the source of batteries that we will be getting for recycling will be dependent on where it was used, what was the size, what was the intended application, what were the operation conditions.

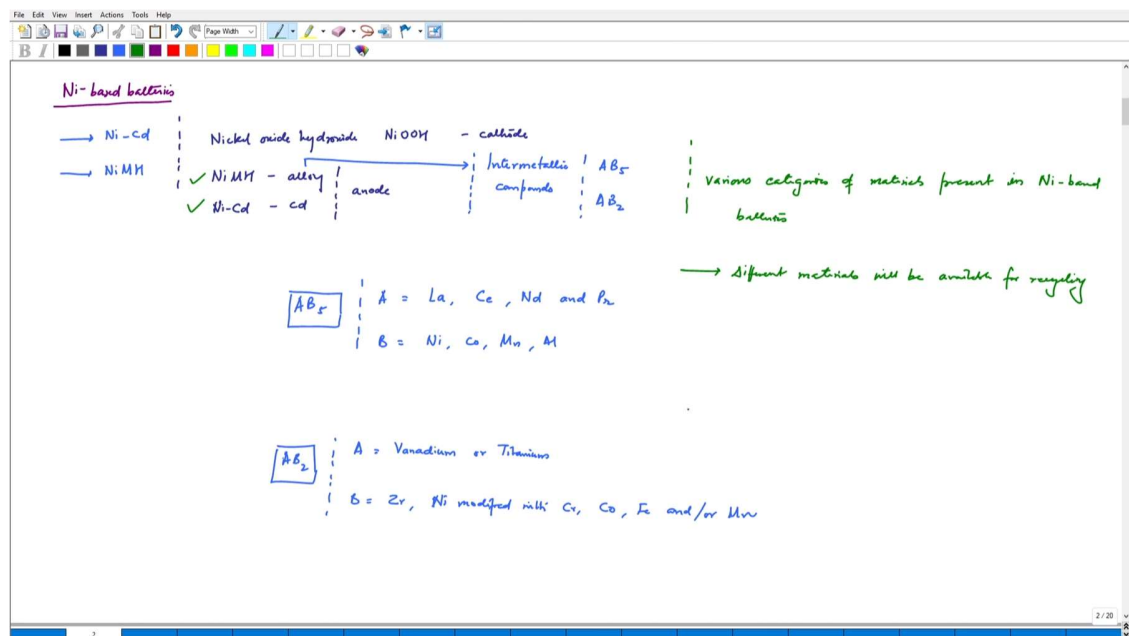
At times it becomes very difficult to monitor these types of parameters for each battery, but a generalized idea at least while we are sorting batteries can really help us in identifying what are the raw materials and how we should approach the recycling strategy. A good idea just like the scraps that we have been studying for metallurgical wastes let's say aluminium waste, copper, zinc or steel waste, sorting of batteries right at the initial stage helps us in identifying the most comfortable and judicious way and there has to be economics behind every process. What is the most feasible process that can be followed to achieve a high metal recovery, high material recovery not just metal material recovery and what is the possibility of reusing these but battery materials for battery applications. If battery materials are directly used for making new batteries, then it's a very good method of reusing these valuable materials. Today, we will be focusing on nickel-based batteries.

Nickel based batteries. Essentially there are two subcategories in nickel base batteries nickel cadmium and NiMH type batteries and we will be seeing how these are different. We know that nickel oxide hydroxide, a many times people just right nickel hydroxide  $\text{NiOOH}$  is the cathode, whereas we have the difference between nickel cadmium and NiMH in the case when we're looking at the anode. When we're looking at NiMH, we have an alloy and this alloy is actually an intermetallic compound and when we look at nickel cadmium, we have cadmium and this is basically anode. A fixed cathode material whereas variation in the anode material can give us different categories of nickel-based batteries. When we look at nickel metal hydride type of batteries NiMH type of batteries, we have some internal divisions as well. The inter metallics, inter metallic compounds that are used for the anode making are basically of two types.

$\text{AB}_5$  type,  $\text{AB}_2$  type. What are A and B and what are these combinations in these two types we will see.  $\text{AB}_5$  will have different A and B combinations. A is La, Ce, Nd and Pr whereas B is basically Ni, Co, Mn, Al. When we look at  $\text{AB}_2$  type of intermetallic compounds we'll have A vanadium or titanium and B is basically zirconium or nickel. That is modified with. It's not pure nickel. It is modified with, so that means the chemical composition is altered, with chromium, cobalt, iron, and/or manganese. This means that

we have various category of materials present in nickel-based batteries. It means if these materials are used in making the batteries, different materials or phases, of course, some conversion will be observed here in the resultant phase will be available for recycling. Based on what type of battery we are looking at. We are looking at NiMH or AB<sub>5</sub>, NiMH AB<sub>2</sub> versus NiCd. We will have different materials for each subcategory of nickel-based battery.

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Some phase transformation can also be observed due to the service conditions or physical conditions, but generally speaking whatever we are supplying in a battery, whatever we are supplying in a battery, we are going to get only those types of materials. A given category of battery will have its limited set of materials. But when we look at a whole stream of e-waste that contains batteries as well. E-waste itself is a part of larger set of waste and within this e-waste we have batteries and when we are looking at these batteries these have multiple categories and nickel-based batteries is a small fragment of it. Within these nickel-based batteries, we have Ni-Cd and Ni-MH.

When we look at these small inter subsections of batteries, we see that they have so much variation in the chemical composition. Devising a specific strategy for these batteries is what we are going to study now. Why do we need to recycle the batteries at all? Why

recycle? We know that the answer is pretty simple that it's a good source of nickel because nickel will be coming in one of the electrodes the cathode it is already there and in many of the cases it can be present in the anode as well and other important elements. Also, we know that REEs, rare earth elements are also safely recovered from nickel-based batteries. Rare earth elements and we know that cadmium is present. The recovery of cadmium is important and this is important from environmental perspective.

How do we really understand what is inside nickel-based battery? We will understand the chemical composition. Composition of nickel-based batteries. We know that there are two categories we will just write type and nickel, cobalt, iron, manganese, zinc, cadmium, aluminium and these are common elements. We will also look at REEs. A different segment for REEs. We have Ce, La, Nd and Pr. Just mentioning Ni-Cd and Ni-MH, we will write let us say 33.5, 0.9, 8.2, 0.04, 0.01, 20.9, 0.002 and this means we are not going to see any REE here because it's a nickel cadmium type of battery.

Similarly, 42.08, 5.9, 0.5, 0.23, 3.86 again the REEs are not present but when we look at Ni-MH we have a different composition. Here, we see cerium is present 11.8, lanthanum is present 7.56, Nd 3.9 and Pr 1.04. Similarly, we have this and this is given in a range. Again, given in a range 0.45, 0.5, 1.4 to 6.6, 0.9 to 4.1, 0.3 to 1.3 and this means that we have a wide range of composition and this tells us that the composition can vary based on not just the type of batteries but also within the type of battery it can depend upon different types of manufacturers and what is the average composition in each of the type of batteries. For instance, if you look at the maximum percentages cerium can vary from 11.8 to 5.5, 7.5 to 8.6, 3.9 to 4.1 and ranging from 1% to 1.3% in Pr. Noting some of the references.

**(Ref. 21:30)**

Why Recycle?

→ It is a good source of Ni and other important elements. → Recovery of Cd is important

→ REE are also safely recovered from Ni-based batteries

Composition of Ni-based batteries

Type	Ni	Co	Fe	Mn	Zn	Cd	Al	REE			
								Ce	La	Nd	Pr
<u>Ni-Cd</u>	33.5	0.9	2.2	0.04	0.1	20.9	0.002	-	-	-	-
	42.08	5.9	0.5	-	0.23	3.85	-	-	-	-	-
<u>NiMH</u>	35.02	6.69	-	2.75	-	-	0.98	11.8	7.55	3.9	1.04
	25-46	2.5-4.3	0.8-3.0	1.6	-	2	0.4-5.5	1.4-6.5	0.9-4.1	0.3-1.3	

References

Tanay (2015)  
 Asif et al. (2018)  
 Yaj et al. (2019)  
 Scott (2009)

We are going to actually see how we are going to plan our recycling. We understand that the internal classification depends on what materials we are using and what is the chemical composition, now we are going to recycle them. Before we go ahead, what is the safest method of handling used battery? Recycling would first require handling of batteries. There are various strategies how we should be handling these batteries. Let us just write methods and observations. What are the methods and what are the key observations that we will be writing now. Electrical discharging, so one can just go ahead and first say let us just go ahead and electrically discharge it this will help us in energy recovery this does not give us any material handling material recovery but gives us energy recovery. We use salt solution we discharge it, it is low cost, but it leads to effluent generation. Cryogenic treatment. One of the most important aspect is that it is pretty safe but it is highly expensive and energy intensive. We can go for wet comminution that means we can just supply some slurry and go ahead for comminution. This process is very cheap, but again the generation of effluent is a problem.

Similarly, then we go ahead for inert gas comminution. It is just a variation of wet comminution. We are going to give inert gas. One has to think about gas supply. Gas supply is required. The inert gas has to be charged in the whole process. Or we could go for thermal process. This helps in binder removal. Every process has its own advantage and disadvantage also. What is a good way of handling batteries? Before we even go ahead for recycling it is important to handle batteries, discharge the battery safely and

then we will be subjecting it to let us say pyrometallurgy or hydrometallurgy or any other combination of these processes. Battery handling is an essential pretreatment that may not be required in different categories of e-waste, but here it is very important because it can cause different process hazards. Some batteries can explode while being recycled. Safe discharging is absolutely important. How do we go ahead for our recycling? The common route of recycling is basically we know pyrometallurgical and the other is hydrometallurgical. We will be covering them now.

(Ref. 26:03)

Recycling of Ni-based batteries

Methods	Observations
Electrical discharge	Energy recovery
Salt solution	Low cost, Effluent generation
Oxygen treatment	Safe, high cost, energy intensive
Wet comminution	Cheap, Effluent generation
Inert gas comminution	Gas supply required
Thermal process	binde removal

(A) Pyrometallurgical  
(B) Hydrometallurgical

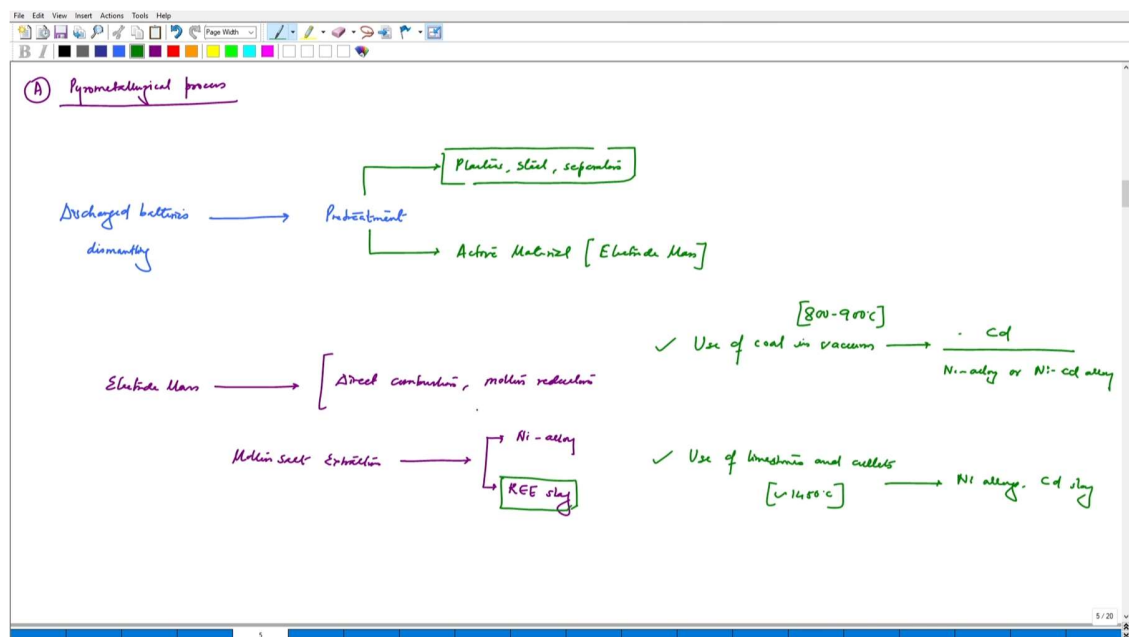
A generalized flow sheet is something like this discharge I am just writing discharge because I did assume that these batteries have been treated, handled properly. Discharge batteries are dismantled. After dismantling we do the necessary pre-treatment. This will help us in separating off plastics, steel separators, steel shells and separators. This is pretty common. This type of waste material generation is very much common in most of the batteries that we will be looking at.

We have the active material which is basically the electrode mass. It is called black mass also. Electrode mass. If we are looking at electrode mass. How do we recycle it? We have direct combustion. Just put it in a furnace subjected to conversion or molten reduction either of these processes can help. If you are going for molten salt extraction, we will be

getting two different sets of products. We will get nickel alloy. We know that different types of elements will be joining in this alloy. It's not pure nickel and we will be getting REE based slags which can be further recycled to get different types of REEs. That has to be discussed separately. One can think of hydrometallurgical route of recycling REE slags.

The ways in which people have tried we will try and write them. Use of coal in vacuum conditions. This is going to give us what? This is going to give us cadmium and nickel alloy or nickel cadmium alloy. The other and this could use let us say 800 to 900 °C that is one way. The other way could use use of limestones and collects and of course, this would require a higher temperature 1450 °C nearly. This would give us what? This would again give us nickel alloys, cadmium slag. These are some important processes by which you can help in treating the black mass, the electrode mass for recovery of various metallic values from nickel-based batteries.

(Ref. 30:00)



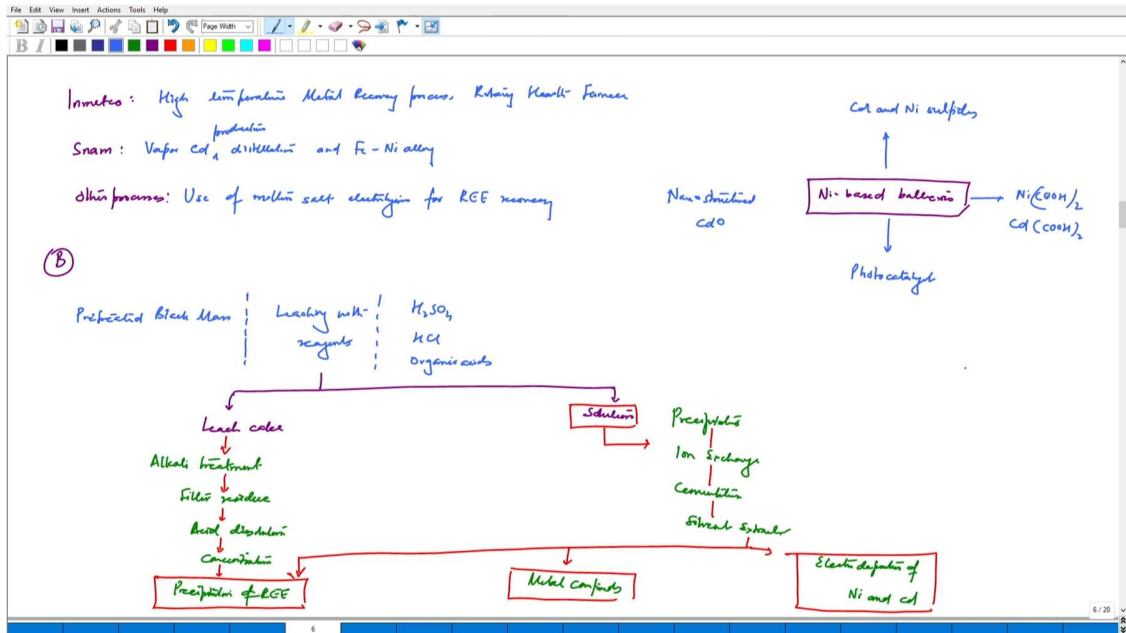


This is a very common way of handling wastes. It has been applied in many industrial ventures as well. We will write those industrial processes and see how they have tried to use these batteries for recovery of these valuable materials. How do we go?

We have Inmetco, Snam and other processes. High temperature metal recovery process, it uses rotary earth furnace. Similarly, when we look at Snam, it is helping in getting vapor cadmium. This is done by distillation. This is nickel vapor cadmium production by distillation and we get iron-nickel alloy. Similarly, we have use of molten salt electrolysis for REE recovery. If we have that REE in the slag, we can go for molten salt electrolysis and get the finished products. When we look at the hydrometallurgical ways, what we see here, just making the same diagram one more time. Pre-treated black mass is leached, and we know that black mass is coming from the electrodes, we are going for leaching with reagents and we know what reagents we will be commonly using  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and organic acids. What we get is leach liquor, leach cake and leach liquor and we know that this is coming the leaching aspect and we have different ways in which we can recover our materials, so let us just write.

Alkali treatment, filter reduction, filter residue we get followed by again acid dissolution we get concentration process. This helps us in recovering precipitation of REE. This is very important. What we get is a precipitate of REE. One way out. If we look at solution. Solutions are actually handled by precipitation and exchange, cementation, we all know this, solvent extraction and finally what we get out of these processes' electrode deposition of nickel and cadmium, you get metal compounds. It really means that in all of these processes we are going to get these products from solution that we have used and not just that we are going to get REE as well. These processes have their own interlocking how they are going to generate various processes and products is it ion exchange, is it cementation, is it solvent extraction or we are going for electric deposition. What are the important products that we get and then we will be closing this nickel-based batteries. What are the important products that we get? It is simple to imagine when we look at the chemical processes, we will be getting cadmium and nickel sulfates, sulfides, we can also get photocatalysts based out of nickel-based batteries. We can also get  $\text{Ni}(\text{COOH})_2$  and  $\text{Cd}(\text{COOH})_2$  or we can have nano structured cadmium oxide. These are the various important recovered materials that we can get from nickel cadmium or nickel-based batteries.

**(Ref. 36:50)**



And we can see that a wide variety of products can be produced using nickel-based batteries. Even though nickel-based batteries comes under the battery section and batteries are a part of e-waste, we still can recover a wide range of materials including REEs. We will be continuing our discussion about battery recycling in the next segments as well. Thank you.