METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-8

Lecture-38

Greetings, I welcome you all to the new lecture of this course wherein now we will be discussing about zinc battery recycling. Zinc based batteries is what we are going to discuss in today's class and we will be focusing on lot many batteries that use zinc as one of their primary elements. We have been discussing a lot about how we should be approaching various electronic wastes, different categories of e-wastes and we had also discussed the WPCB and we have also been discussing about batteries. Along with zinc batteries will be focusing on lithium-ion batteries and then we will be focusing on the environment aspects of materials recycling. When we think about zinc battery recycling the most common or commonly used battery comes to our mind. When the common equipments that we have with us the ah electronic devices that use AA or AAA batteries, they are mostly zinc based batteries. Alkaline batteries or zinc carbon batteries are those batteries that are being used very commonly. What do we do to these batteries when these batteries run out?

We will note that most of these batteries if they are not rechargeable, they are usually single use batteries. What it really means is we have a device, electronic device, that consumes low energy, lower energy, we put a zinc-based battery. It does not require high amount of energy. Zinc battery can provide consistently the required amount of energy and the device functions for a given period of time let us say 1 year or 2 year. Suppose that we are putting a battery a set of batteries in let us say remote controls. These electronic devices do not require high energy output, but then if there are devices that require high energy output, we just change the type of battery and our function basically goes on. Single use batteries is what we are going to discuss in today's class. One of the most widely used. Because it is being used in almost all of these common electronic devices.

Zinc alkaline and with it comes in carbon as well. In terms of US dollars, we are looking at 8.3 billion that is the market share in 2023 and this market share is projected to grow.

Because zinc alkaline batteries are not going to get replaced very soon by us. Another common type of battery because we have just said it is most widely used battery. Commonly used in simple electronic devices. What we are looking at is simple electronic devices with not so high-power energy requirement. Not so high-power requirement. Single time zinc-based batteries, single time use, single time use zinc-based batteries are classified as zinc carbon or at times it is also written as carbon zinc batteries or alkaline zinc batteries which can also be written as alkaline zinc manganese dioxide. Dioxide Batteries.

Why are we so focusing so much focusing on the categories? because these two are different categories of batteries altogether. Zinc carbon batteries also actually uses manganese dioxide but it looks like the name is more focused on carbon itself instead of manganese dioxide. Essentially zinc and manganese dioxide are present in both the categories of batteries Just that zinc carbon batteries uses a different type of electrolyte as compared to alkaline we will be looking at that. We look at various materials. Why are we discussing materials? Because materials that are used to make a battery are the materials that we are interested to recover. Materials present in batteries are stainless steel can, which is basically the cathode collector, cathode current collector. We have graphite particles and MnO_2 powder. It is a combination graphite particles and MnO_2, manganese dioxide powder which is also termed as electrolytic manganese dioxide, electrolytic manganese dioxide and this is actually the cathode. When we think of the separator it is basically a porous separator. We will have zinc powder with KOH. If you are looking at alkaline batteries KOH is here. We must have the anodic current collector also and this is brass, we also need plastics for casings or coverings. We know that we have a wide variety of materials stainless steel can, graphite particles with MnO_2, this is the cathode, porous separator, this is the anode, we have the anode collector, we have plastics.

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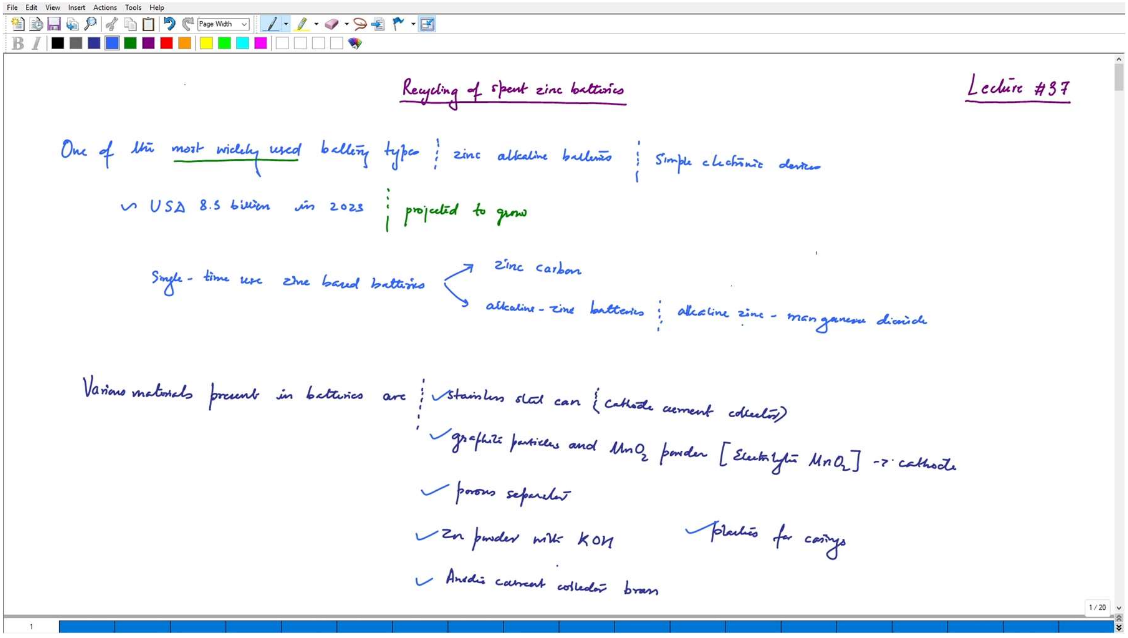

What is the key difference between zinc alkaline battery and zinc carbon battery. The electrolyte in alkaline batteries, we have alkali as an electrolyte whereas for zinc carbon batteries which are going to use a different electrolytes basically it is ammonium chloride, NH4Cl. Those changes need to be observed and these changes apparently are changing how the batteries function. It is just the composition that we are interested because these compositions govern how we are going to recycle a given type of battery. What are the key reactions that we are supposed to expect? We will just write some common overall reactions. Zinc carbon. Zinc alkaline.

Look at anode, cathode again we'll anode. Release of two electrons, $2MnO_2$ gain of two electrons here, NH_4Cl giving us $2NH_3$ $2Cl^-$ ions here. But, if we look at how zinc alkaline battery's function, we have zinc hydroxide production, $Zn(OH)_2$ and again just the release of two electrons which will be consumed at the cathode end so we have MnO_2 single electron, that is how it is. We can just put up the balancing to complete the whole reaction series. We see that this is how it becomes different. We have NH_4Cl here and we have KOH here. OH, is coming from KOH and that is how it becomes different. Why are we going to recycle zinc batteries?

So, let us just write why recycle zinc based? Sheer number and sheer quantity of zinc-based batteries. Because we know that it is a single use battery, so it will be generating waste. Sheer quantity of zinc-based battery waste due to large utilization of batteries.

This also means that we are looking at the overall worldwide market share. We already know that 8.3 billion USD is the market share of zinc-based battery. We know that it is going to dictate the total number of zinc-based batteries and those battery wastes. It is interrelated and we also know that recovery of zinc and manganese because we know that the two elements that we can see that are clearly playing important role is basically zinc and, in this form, it is manganese dioxide. Manganese also. Recovery of zinc and manganese from spent batteries can complete material cycle.

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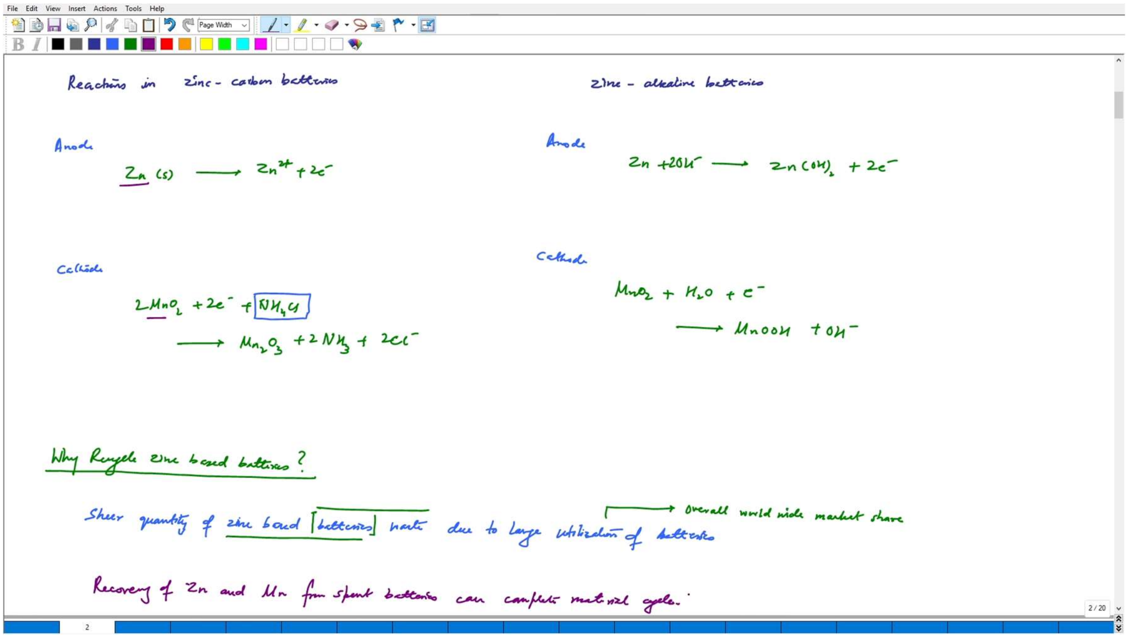

We know what is the key reason, why we should be focusing on zinc-based battery recycling? We will be now looking at some of the chemical compositions that are observed, some generalized chemical compositions and then we will be focusing on the routes of recycling the batteries so pyrometallurgical route, hydrometallurgical route and some apparent products that we can form using the using the zinc-based batteries. Chemical composition. We have the type of batteries, we have elements zinc, manganese, potassium, iron, lead, chromium, aluminum, chlorine, titanium, silicon, nickel, and others.

If we have zinc manganese dioxide dry powder that is one. The other one is mixed type batteries, mixed battery waste, mixed battery powder and we have alkaline battery powder. It comes to be something like this If we have 15.4, 0.27, 0.49 12 to 21 so 26 to

33 manganese, we have 5.5 to 7.3 potassium, 0.17 of iron, and 0.005 of lead, and then it is just looking at nickel, so nickel is somewhere here 0.01, 0.01 that's it. We see that in a battery if you looking at different categories and we are just looking at some very simple generalized compositions of the powder mass. We are assuming that the pretreatment required for such battery has been done.

The batteries have been safely discharged and the batteries have been properly treated and the electrode mass is what we are characterizing. We see that zinc and manganese and some other trace elements are present. Zinc and manganese are our two primary targets. Apart from that we can have let us say potassium, iron, lead, chromium, aluminium. At times you can also have chlorine, titanium, silicon, aluminum also or nickel or any other trace elements. These elements are present, but these are present in very small quantities. The main focus will be on zinc and manganese. We will write some of the references before we leave.

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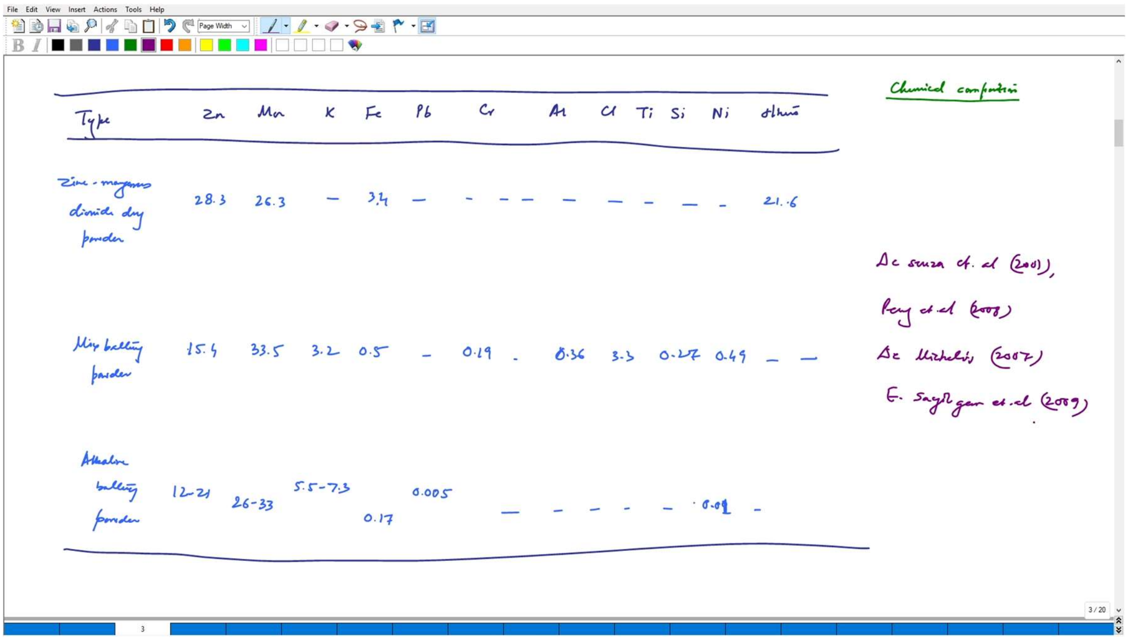

We will now be focusing on the pyrometallurgical route of recycling. We understand that our target is zinc and manganese and every other metal is since it is present in lower quantities will be focusing on zinc and manganese recovery. How do we do that? When we look at conventional pyrometallurgical routes, these are basically the selective valorization, selective valorization of metals. What are those metals? Primarily zinc and manganese. If at all, some iron is present or any other metal at high temperatures followed by condensation. A generalized scheme looks like this, we have alkaline batteries, these will be put into a shredder and then we have the main pyrometallurgical unit. We are going to add flux and reducing agents. and what we usually will be getting out is dust. When we do the dust cleaning, we will get ZnO. This is what I was talking about when we talking about condensation and dust cleaning and all of that but the key product here is iron-manganese alloy.

It will be a manganese-based alloy. In case we have iron, we will have iron-manganese based alloy which is the key product and along with that we will have slag. One has to think about recovery of valuable materials from slag as well. Manganese from electrode mass is alloyed with steel casings. One might want to wonder why is iron coming into picture, so we added steel casings to form the iron-manganese alloy. We can think of adding some other raw material also.

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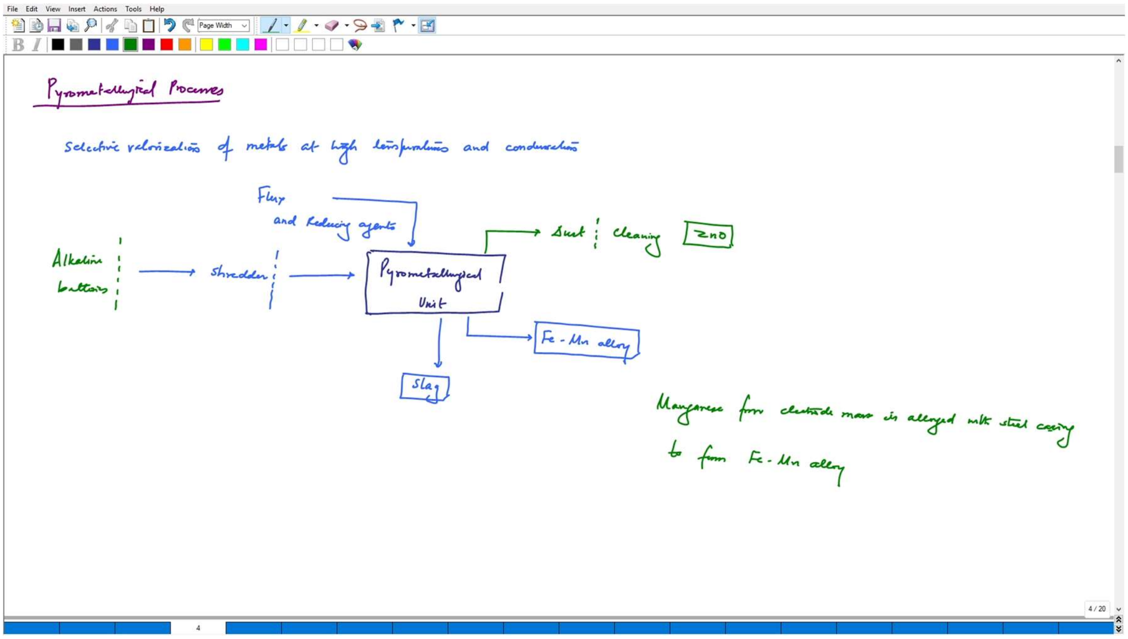

But in that case, the composition of the final master alloy will be changing. We shredded the batteries, put it in the furnace, let the zinc dust get released. We have the iron manganese alloy and of course, we will have the slag. This is one route. The other way could be if we are using let us say a Kaldo type of furnace, kaldo furnace. Use of Kaldo furnace, which is basically top blown rotary converter, so TBRC type of furnace, and if you are using this then we have some Schematics that we can follow one after the other. If we have step 1, pretreatment and TBRC will be using propane or oxyfuel as burner for the operation. If we have pre-conditioning step as stage 1, pre-conditioning stage, second, we could have oxidation stage, third we can have reduction stage. We can have 500 to 700 °C and this generates some porous product, we actually wish to remove moisture and graphite. The next range 700 to 115 °C, we have removal of unwanted toxic materials and retention of manganese and zinc. Retention or retaining manganese and zinc but removal of toxic materials. This is very important that oxygen to fuel ratio is over 1, so we have more oxygen than fuel. When we are going beyond this when we are going beyond this, we have 1150 °C to 1300 °C. In this case we are going to have the reduction of zinc oxide. Many things are happening first reduction of zinc oxide to zinc then we have the evaporation and recovery as zinc oxide. Essentially, we are moving from zinc oxide to zinc oxide just that zinc oxide was first present as a battery mass. It is getting converted to zinc and then again it is getting collected as zinc dust and this time zinc dust is zinc oxide. When it gets evaporated again it is getting in contact with oxygen and forming zinc oxide. From zinc oxide to zinc oxide, but this time the zinc oxide that is forming is relatively purer. This is what is happening when we are looking at this. Then we have the formation of manganese alloy from the residue. Here, oxygen to fuel ratio is under 1.

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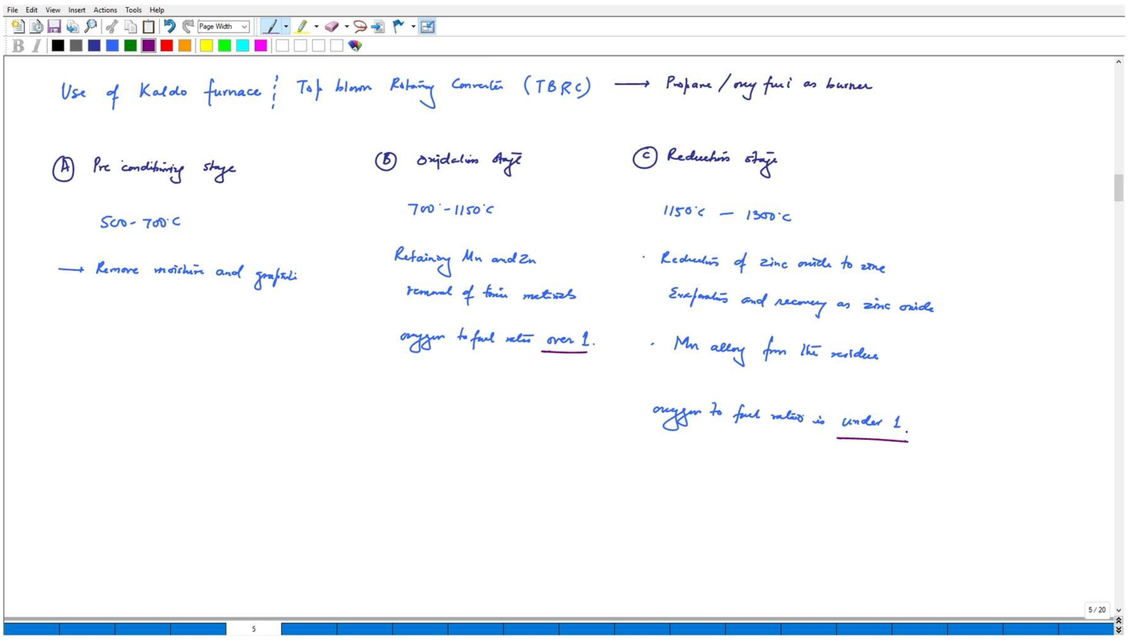

In this case it was over 1 and this is case it is under 1. And this is what we are looking at when we are looking at pyrometallurgical processes. We can have lot many different ways of handling batteries and the electrode mass and we can do some sort of optimization to recover our desired products. In this case it was zinc oxide and manganese alloy and in the previous cases if we are using casings also, we can make iron-manganese alloys. When we are looking at hydrometallurgical processes, we will be focusing on the leaching. A schematic about how to handle batteries before hydrometallurgical process is what is we are going to discuss first. Batteries sorting plus shredding plus sieving coming all under common comminution, so all of this is taken into one single step what we get is let's say a coarse fragment and we get a fine fragment, fine fraction. Fine fraction by is actually going into either pyro route or hydro route of recycling. However, the coarse fraction will go into magnetic separation and we can get metal this is ferrous and we can here we get non-metals and non-ferrous metals. We are looking at the next step which could be eddy current separation, pneumatic separation, or any other type to remove non-ferrous metals and non-metals altogether, plastics and other materials.

When we look at a hydrometallurgical route, a general schematic would look like this. We have again the pretreated mass. This is why we are discussing this. Pretreated battery mass, black mass. That will be first it could be subjected to water leaching. Why? Because we would like to let us say remove potassium or chlorine and then we can go for leaching with acids. If you are going for acids will get $ZnSO_4$ if you are using sulfuric acid or $ZnCl_2$ if you are using hydrochloric acid. This also means impurities are removed. Some common metals that can react with acids will react with acid and these will be removed following which we will also have the next stage. Most of the materials will react but some will not suppose manganese dioxide or other forms of oxides of manganese may not react. In that sense we are going to have leaching with acids and reducing agents to get manganese sulfate. Manganese oxide is difficult to react that would require reducing agents and we have a plethora of valuable metal recovery options. We have precipitation, solvent extraction, ion exchange, cementation and so many different methods. These are the ways by which we can recover valuable materials through hydrometallurgical route.

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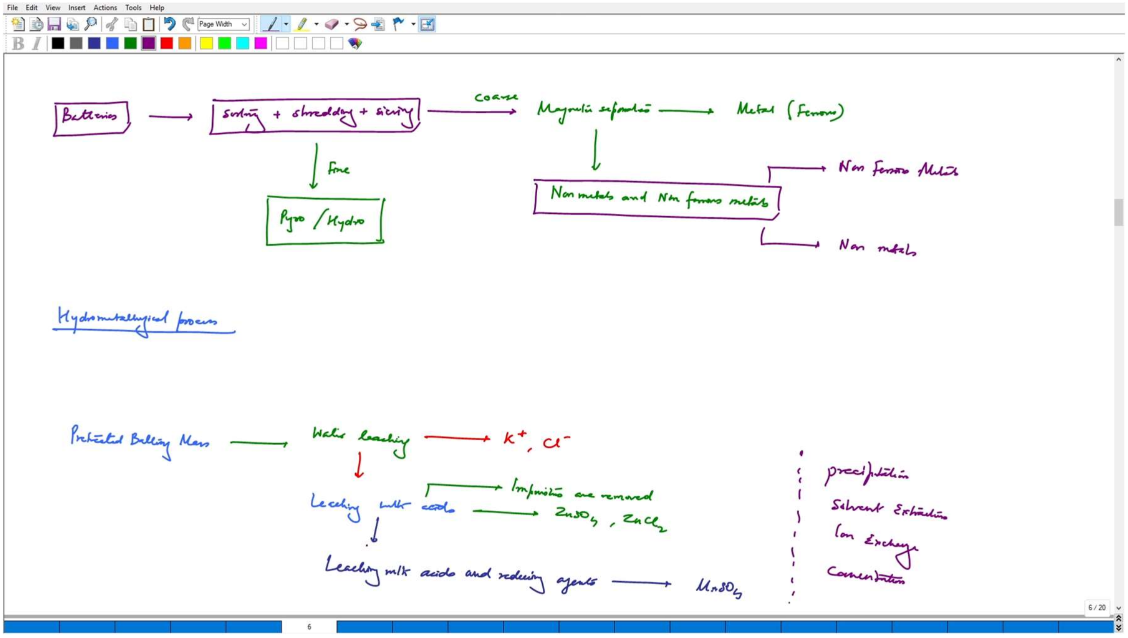

In the end we are just going to discuss what are the key materials that we can produce or generate using hydrometallurgical processes from these battery masses. When we look at leaching of spent zinc-based batteries. We have alkaline leaching which could be using, let us say, NaOH and this is a very generalized observation 6.5 molar, we can have 64 to 82 % of zinc recovery. We can have complexing or complexation leaching where in we are going to use different chemicals such as $(NH_4)_2CO_3$, this could be of 2 molar solution or NH_4Cl, this could be 5 molar solution we can get 72 to 83 % zinc recovery. When, we look at acids we've just seen that acid leaching works so if you are going to use H_2SO_4, we will be getting 1 to 2 molar solution or HCl again 5 molar solution, we can get 35%. It is not always that we will get a good recovery. But we may get some recovery in manganese also. 92 to 100% zinc can be recovered. If you are using reductive acid leaching. Basically, using reducing agents also. We have H_2SO_4 of 1 to 4.5 molar solution and H_2O_2 or oxalic acid or any other reagent.

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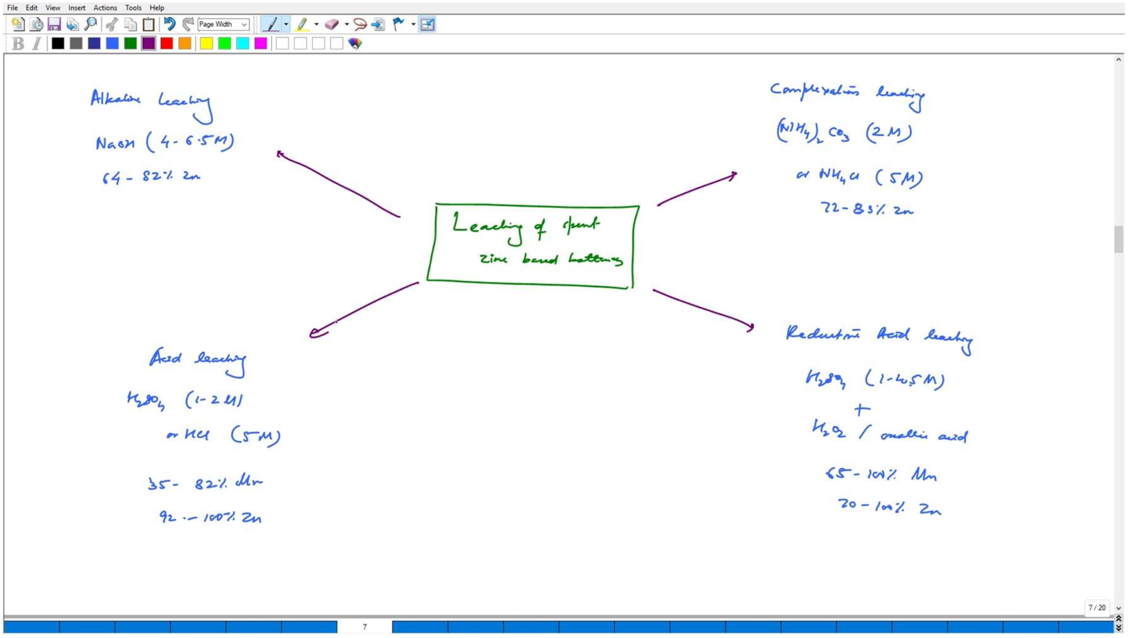

Then we can have let us say 65 to 100 % manganese and 70 to 100 % zinc recovery and these are some valuable routes by which we can produce some valuable materials from battery masses just by flipping our method of leaching. In this class we have covered a wide variety of processes for zinc-based batteries. In the upcoming classes we will be focusing on lithium-ion batteries and its recycling. Thank you.