

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Lecture-22

Greetings, I welcome you all to this new lecture on materials recycling and we were discussing about zinc recycling, zinc wastes in the previous lectures and before that we had discussed copper and aluminium. We all know that when we are looking at metallurgical wastes, we look at wastes, we look at chemical compositions, we look at why we would like to recycle a given type of waste and here we assume that this given waste is already provided to the recyclers to the people who are interested in recycling. And, these wastes are generally sorted and then we do different types of processing to generate valuable materials.

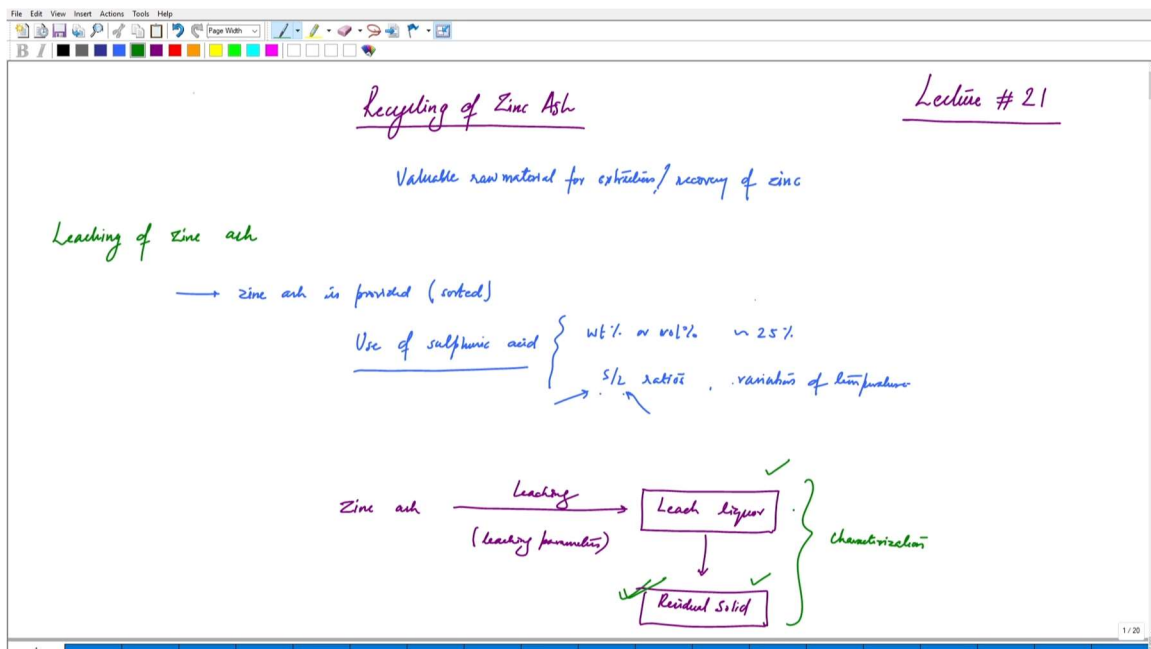
Continuing on what we had begun in the previous lectures. We like to think on recycling of zinc ash. In the previous class, we had discussed the composition of zinc ash and we know that zinc ash is a very important raw material, a waste material that has good quantity of zinc. In order to extract the zinc that is present in the zinc ash, we must subject it to recycling. And we had also discussed that the most common of recycling zinc ash would be hydrometallurgical. Pyrometallurgical routes have also been used, but hydrometallurgical route is also being explored. How do we recycle zinc ash? We all know the hydrometallurgical route of recycling consists of the leaching which is the most primary and fundamental step followed by we will have the purification of solids of the leach liquor where we are removing the solid residue, treating the solid residue and then we go and reuse the leach liquor for making valuable products. We will just follow the same route. And we know that zinc ash is a valuable material. Valuable raw material for extraction/recovery of zinc.

How do we do that? We have zinc ash and again we have assumed that the zinc ash is, we have this zinc ash, the zinc ash is provided, it is pre-sorted and we can go for the leaching of zinc ash. For an example we can just use H_2SO_4 , sulfuric acid. Use of sulfuric acid and we can have various concentrations. Let us say we can have various volume

concentrations, by weight concentrations, weight percentages or volume percentages as per the requirement.

And we can have the zinc recovered into the aqueous solutions so for starters you could have let's say 25 percent of volume we can have different s/l ratios. s/l ratios are basically solid to liquid ratios that are used for leaching, what is the amount of zinc dross that was added to the leach liquor so that ratio is solid to liquid ratio. We can also have the variation of temperature. Not just sulfuric acid, you can have different types of acid right at the beginning you can have HNO_3 or HCl depending upon what we really wish to make but for the starters if we would begin, we could just have sulfuric acid and what does this do actually? This is if you are trying to make a flow sheet, we have zinc ash and we leach it and we follow the leaching parameters. And leaching parameters are just whole set of parameters that include s/l, concentration, variation of temperature, if we provided agitation or not. All these parameters are varied and we would end up in the leach liquor. And we also have as a by-product the residual solid.

This is the valuable material and this is the by-product of this leaching process, the residual solid and one could just go ahead and characterize these both. One can determine what is the quantity of zinc that is present here and here in both the products, the leach liquor as well as the solid residue. What will that do? This will help us in redefining how we should be adjusting our leaching parameters. If good quantity of zinc is ending up in residual solid, we can readjust our leaching parameters such that we can have maximum recovery of zinc at the first stage directly into the leached liquor. And the residual solid will have different phases that are present in it. (Ref. 6:55)

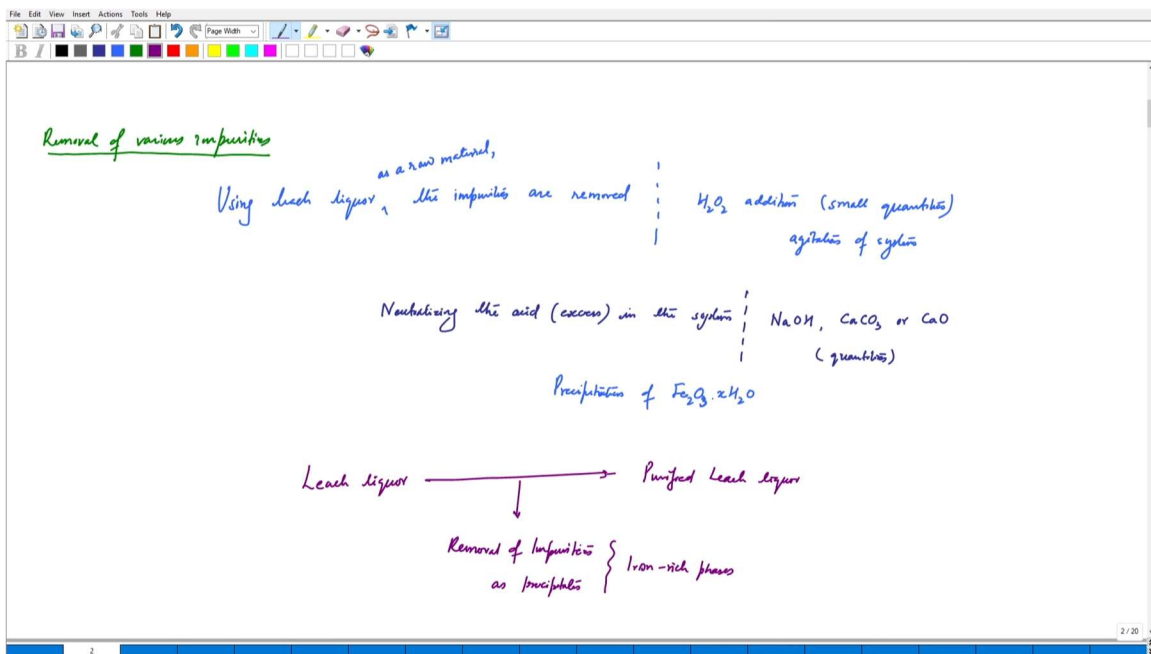


These can be containing some impurities or the materials that could not be leached at the initial hydrometallurgical stage of leaching. This separation is happening only after the filtration. After that we have the removal of various impurities from the leach liquor. Once we have leached, once we have optimized the leaching parameters and we have leached zinc from zinc ash into the leach liquor, it can contain different metallic species that are not required in the upcoming stages of recycling. For instance, iron or aluminum or different other metallic ions that could be present in zinc ash leach liquor which could hinder the process. If you want to remove different impurities you must have different mechanisms.

Using leach liquor the impurities are removed. Using leach liquor as what as a raw material because now as we had already discussed in the previous classes that one process will generate different types of products now that product we will have to treat as a raw material for the next process. If we have the leach liquor as a product now its the raw material for the next process which is purification of leach liquor and this means that we are going to use leach liquor as a raw material for making different types of products.

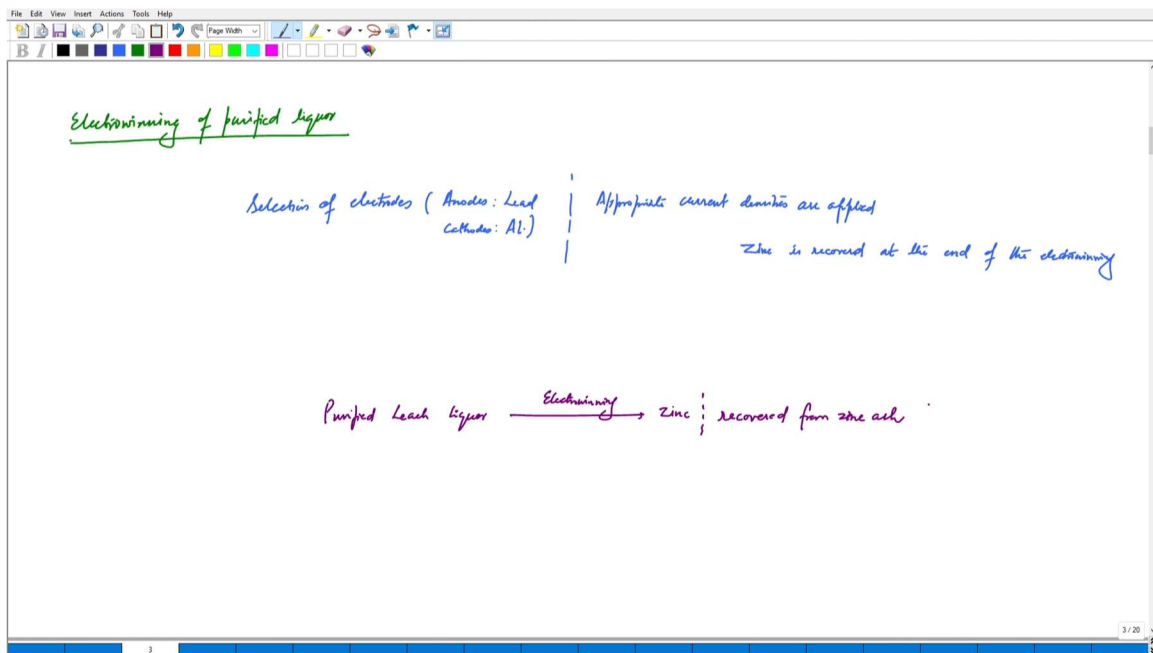
Impurities are to be removed. How do we do that? We can do this by H_2O_2 addition. Hydrogen peroxide addition hydrogen peroxide and this will be done in small quantities as per required and we can also have some stirring in the system so we can have agitation. Now, when we do that, we also can think of balancing the excess acid that is present in the leach liquor. So, this could be the first step and we can have the second step of balancing or neutralizing and the system basically is comprising of the solution leach liquor. How do we do that? This can be done by adding various materials, various reagents, various chemicals that can actually balance then neutralize the excess acid. The common materials that could be added. These are the common materials NaOH , CaCO_3 , CaO . These can be added. One has to think of the quantities. And this is essentially wanting to balance the excess acid.

It has nothing to do with disturbing the whole chemistry of the system. We are not supposed to add excess of NaOH or CaCO_3 or CaO. What we are planning to do when we are thinking of devising such a route is we are trying to remove iron and that will be done by addition of H_2O_2 . But at the same time, if you also want to remove the excess acid, then we can think of adding the reagents that can balance out the excess acid or that can neutralize the excess acid. However we do it, we'll have to monitor the chemistry of the system so that we don't accidentally add excess of NaOH or CaO or CaCO_3 , calcium carbonate. Where are we now, after the leach liquor, so we had the leach liquor in the previous slide, and now we have purified leach liquor. And what were the various impurities that we were actually targeting it helps us to precipitate precipitation of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. Essentially speaking, we have removal of impurities as precipitates. And as an example, we can have iron-rich phases. When we are doing this, we are able to remove iron from the leach liquor. (Ref. 13:30)



And with this purified leach liquor, now we are almost there. We have the purified leach liquor, now we are going to reuse it as a raw material for extraction of zinc. So, this brings us to the electro winning stage of the whole recycling process where we are now going to use the purified leach liquor as a raw material. When we think of electro winning we need to have the selection of electrodes, we have anodes and cathodes. Anodes we could have lead and cathodes you can have aluminium.

We also need appropriate current densities. Appropriate current densities are applied and recovery of zinc is done. This basically is just one step process. You have the electrolyte, you have the electrodes and you will get zinc. Get zinc as the finished product. Zinc is recovered at the end of the electrowinning process. What have we done? We have purified leach liquor and we did the electrowinning. One has to think about various parameters that are present in the electrowinning process as such as what is the distance between the two electrodes or if we have multiple electrode system, how are the electrodes arranged, what is the chemical composition of the electrolyte, did we add anything else into the electrolyte which was basically the purified leach liquor to make it



more useful as an electrolyte in this electrowinning system. What are we doing? These parameters again we will have to optimize and then we can perform the experiments many times to get better zinc recovery. Finally, we get zinc recovered from zinc ash. Till now we have seen and we are able to understand that it is very much important to holistically think about processes from multiple facets. (Ref. 16:50)

What is the first step for zinc ash recycling basically for hydrometallurgical route it is leaching followed that we will have the purification followed that we have the electro winning process. Multiple steps, multiple optimization has to be done multi level, multi parameter optimization has to be done which gives us zinc after these processes and one has to think of optimizing each step to achieve higher zinc recovery.

With this, we are at the end of zinc ash recycling. Now we will be thinking on, we will be discussing zinc dross as the raw material. Just like zinc ash, we are now going to focus on zinc dross. Zinc dross is another valuable waste, valuable waste as in waste that is generated in hot dip galvanization that is considered as this material is considered as a waste.

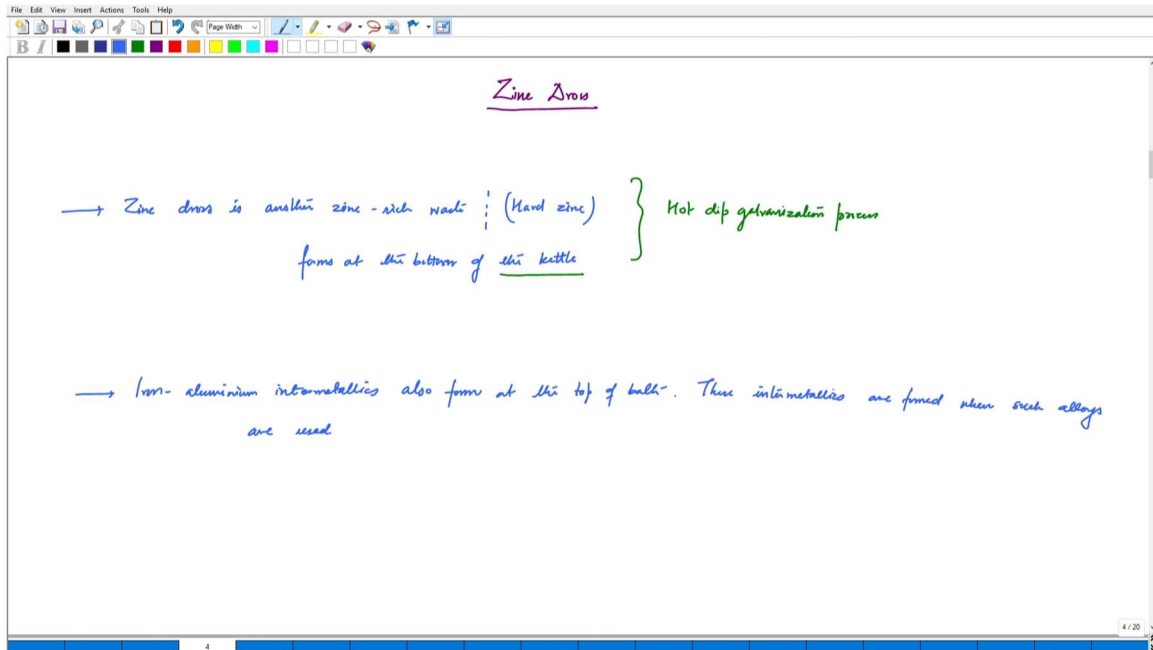
But when we think about the chemical composition we get to know that it is very-very rich in zinc. That is why it is valuable. And zinc we had discussed hot dip galvanization previously. Zinc ash is generated at the top as a skimming. Zinc dross is settling at the bottom of the galvanization kettle.

This zinc dross is basically hard zinc. The other name could be hard zinc. Hard zinc happens to have a significantly larger quantity of zinc compared to zinc ash itself. Zinc ash was formed due to the contact of atmospheric oxygen and it got oxidized and so some amount of oxygen is also present in zinc ash but hard zinc has very less impurities compared to, of course, there are impurities and these impurities are normally present in tracer quantities as compared to zinc ash but it can have a higher quantity of zinc. That is why zinc dross is a very valuable raw material for zinc recycling. Zinc dross is basically another zinc rich waste and it is basically hard zinc also known as hard zinc. It is forming at the bottom. It forms at the bottom of the kettle, which kettle are we talking of, of course, we are talking of the galvanization, hot-dip galvanization kettle and we had discussed in great detail about this in the previous lectures. Hot dip galvanization is giving us two wastes that we can recycle, zinc ash as well as zinc dross. Zinc dross is of course sitting at the bottom of the kettle. It has relatively higher quantity of zinc because it is not getting exposed to air directly.

And the other quantity that can be also counted as zinc dross is basically the intermetallic that is formed between various elements and it can just float up. That can also be accounted as skimming dross. There are different ways of characterizing dross, but essentially we will be talking of hard zinc, the zinc dross. If we just look at the second category, iron-aluminium intermetallics.

This is the classification of intermetallics that can be present when we are thinking of various when we the hot dip galvanization is taking into taking various elements and alloys into the process. If we have iron and aluminum in the system these can form intermetallics and these can just move to the top of the molten bath. Such intermetallics

are also accounted into the zinc dross. These intermetallics also form at top of both. These intermetallics are formed when such alloys are used. **(Ref. 23:16)**



If the composition is available then these intermetallics will form else hard zinc or the conventional zinc dross is forming at the bottom of the kettle. We will now look at the chemical composition of zinc dross because that is how we discuss wastes. We know that it is a very important raw material, but we will see how much zinc can be present or is available for extraction and that gives us motivation for developing the recycling routes for zinc dross. We will make the table. We'll just mention some of the references. We see the chemical composition of these wastes and we see that some of the references have been clubbed to make this table. We see that the most important finding that we should be focusing on is the generation of the zinc dross and how much important it is to recycle.

We see that the composition of zinc is touching 95 % and it means it is very rich it is almost as rich as crude zinc. If it is not refined we can have let us say more than 90 percent of zinc and this is the quality of zinc that is present in zinc dross. There are so many other impurities. These other impurities could be iron and aluminium.

These are present in larger quantities. In some cases, silicon can also be present. And then there are trace elements like calcium, lead, nickel, cadmium. These elements can be present in relatively very lesser quantities. Of course, We always note that there are anomalies in the chemical composition ranges and these values are not supposed to be taken as sacrosanct. But generally speaking, the zinc quantity in zinc dross itself is significantly very large. What are the important key phases that are present in zinc dross? The key phases that are present are zinc as metal, zinc oxide ZnO and if we are looking at intermetallics and if intermetallics are actually present then we can have phases like this $\text{Fe}_2\text{Al}_5\text{Zn}_x$. (Ref. 28:08)

Chemical composition of zinc dross

Elements	Zn	Fe	Si	Ca	Al	Pb	O
	93.9	1.01	0.1	0.08	3.89	—	0.92
	95.4	1.91	—	—	2.59	—	0.08
	97.5	2.2	—	—	—	0.0006	—
	94.5	3.5	0.63	—	—	1.39	—

(Khanjari et al 2008, Sinha et al 2010, Prasad 2022, Wang et al 2018)

Key Phases

Zinc, Zinc oxide ZnO and $\text{Fe}_2\text{Al}_5\text{Zn}_x$

These phases can be present and that is an example of the phases that can be present but essentially speaking we can have zinc and zinc oxide as the major phases that are present and if we have silicon, we can have silica as well. These are the characterization data that we get and we should note that zinc is a very valuable material present in zinc dross. we will think of devising the recycling strategies for extracting zinc from zinc dross. We will be continuing on zinc dross in the next lecture. Thank you.