METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week- 7

Lecture-35

Greetings, I welcome you all to the new lecture for this course. And we have been discussing till now the methods of recycling electronic waste wherein we have been discussing some general electronic wastes and our main focus was on waste printed circuit boards and we have discussed the delamination and the pyrometallurgical route of recycling the WPCBs. In this lecture we will be sort of concluding our investigation and we will be discussing the hydrometallurgical route of recycling WPCBs. We will be emphasizing on what are the general important aspects that one must take care of while designing a holistic route of recycling WPCBs. What are the challenges that people have faced. Some of the important laboratory investigations will also be highlighted in the end and gradually we will be then moving towards the next aspect of electronic waste which will be focused on the battery recycling. Coming back to the hydrometallurgical route of WPCBs, we know that in pyrometallurgical route we have the pyrolysis and the different processes that are involved in pyrometallurgy. They have their own advantages; they these processes can lead to the generation of pyrolysis products apart from what we get as the mixture which can be further processed to get the metals. We know that there are different advantages of pyrometallurgical processes. But at the same time, when we are looking at the generation of hazardous gases that can cause health hazards, we think about hydrometallurgy which does not have these hazardous implications. We will begin on that. Hydrometallurgical recycling of WPCBs. We know that similar to pyrometallurgy we already have the hydrometallurgical route and we have discussed it for metallurgical basis as well. The same concept will be applied for the WPCB for recovery of valuable materials.

Recovery of valuable materials, but here in actually we are supposed to ask a couple of questions. The questions are what are these valuable materials that can be extracted? A probable answer could be, we have metals, base metals, precious metals and hazardous metals. We do not wish to use hazardous metals, but we need to extract this to keep the whole environment safe. Then we have refractories, these refractories are oxides and polymers. These are the valuable materials that can be extracted. The next question could be what are the appropriate procedure steps involved in this process. A generalized outline can be made. We need pretreatment which is again appropriate suitable for hydrometallurgy then we need the leaching of reagents leaching with reagents again choice of reagent is a good thing to consider then we need to purify, purification of reagents of, in this case, it would be leach liquor and then it will be recovery of valuables from liquor and residue and finally we will have development of products. Pretreatment followed by leaching followed by purification and then we get the development of products. This is the appropriate procedure that we can think of when we are having a generalized outline of WPCB recycling which appears pretty much similar to any other hydrometallurgical route that we have been discussing so far. It means that in general the outlines remain the same.

It is just that we are going to change the raw feed, similarly we are going to change the reagent, the operation parameters might change, the recovery that we might get for various reagents and operation parameters are going to change and then we should be gradually optimizing them to get the best fit and then further recovery can be done using the leach liquor. The same will be followed for WPCBs. What are the key parameters? The next question could be what are the key parameters that basically govern the efficiency of the process. What are the key parameters of the process? We know that for hydrometallurgical processes there are there is the choice of reagent, we have temperature range, duration which is time of reaction, we have solid-liquid ratio, pH of solution, feed size, particle size, agitation at times it is very important and if we are looking at bioleaching, we might also need aeration and so many other parameters that are important for bioleaching and for such leaching operations which use the microorganisms.

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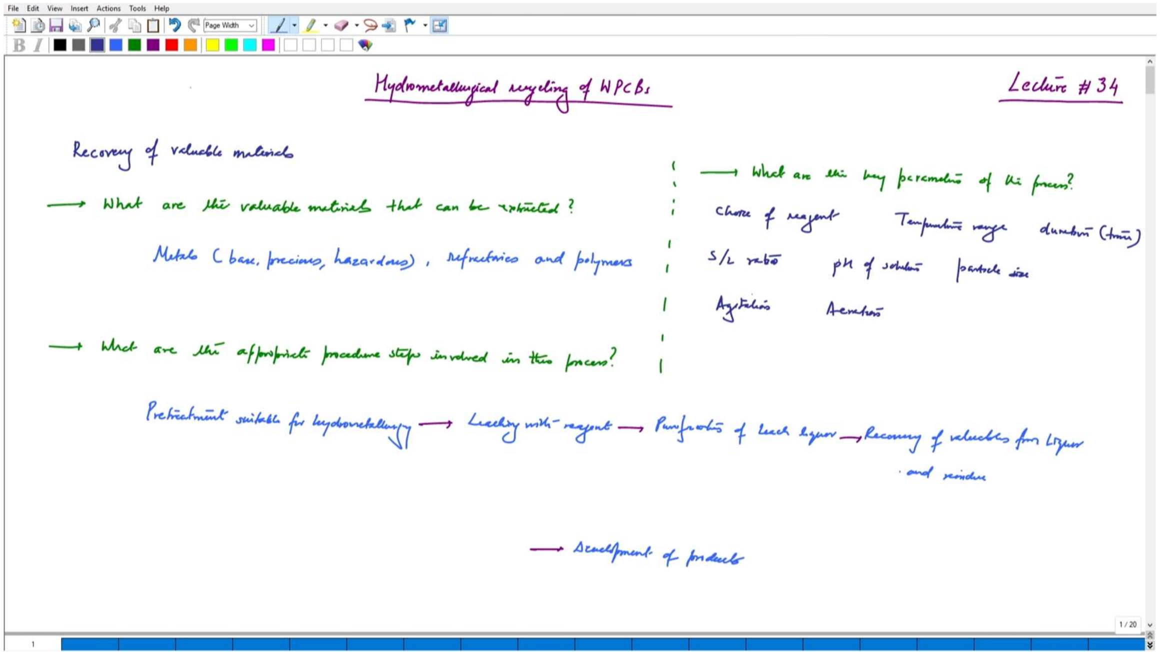

These are the key parameters that are involved in optimizing the overall efficiency of the process. We are now going to discuss specific processes that are involved for WPCBs. We know that WPCBs can be subjected to disassembly or dismantling and then we can go for damaged ECs and WPCBs and if we have usable ECs, we separate them out. What we are actually trying to do here is mechanical and chemical processes. We know the different types of pretreatments that are generally used for these operations and then we also know that we are going for separation. After separation, we are having the metal fraction and the non-metal fraction which can be further processed as in hydrometallurgical route or pyrometallurgical route. We are assuming that it has followed a path line starting from WPCB collection to disassembly to damage ECs for further separation and then going into the separation of the metal fraction and the non-metal fraction and then another classification between hydrometallurgy and pyrometallurgy. We are going to discuss hydrometallurgical route assuming all of these processes are already done.

Another important aspect that we should be considering before we jump here is importance of EC removal before hydrometallurgy. Why? Why should we focus specifically on EC removal? This is very important because it interferes with the hydrometallurgical process. What are the reasons? There is a risk of or chance of explosion during reaction. This is possible if the EC somehow react with the reagent itself or the risk of chance of generation of hazardous chemicals or it can also lead to the various hydrocarbons, which can be very much hazardous to the humans. Generation of hazardous chemicals, this will be formed due to leaching of epoxy resins or any other hydrocarbon that is present. The third one, excessive use of reagent excessive use and of course, unwanted use of reagent for leaching because it is going to get partitioned. Suppose, I have some leaching reagent it will be partitioned into various end results and the leaching efficiency that we expect will not be achieved because it is getting consumed by various ERs or hydrocarbons, etc. This is something that we do not wish to entertain. What we wish is we should be using the leaching reagents for leaching purposes only.

The splitting of or excessive consumption of reagents for unnecessary reaction and that to that reaction is going to render our leach liquor hazardous. It should not be encouraged what we can do is just remove the ECs directly go for the WPCB leaching and this is how we should be approaching our raw material. There are some important ways by which we can remove these ECs by hydrometallurgical route as well. One can think of use of KBr as a reagent. That is possible. People have tried using it for metal recovery and it has given some good results. The other option could be. If we have let us say solder alloy, so solder alloy, solder alloy leaching, where is solder alloy? Solder alloy will be attached to the soldering joints where we have attached our ECs. If we wish to approach the solder alloy recovery then we can and we wish to do it through hydrometallurgy then such reagents can be opted for.

Right now, we are assuming that the ECs are already removed, but in case if we wish to remove it through hydrometallurgy, then it becomes an alternative. This process becomes an alternative to the conventional desoldering process. Solder alloy leaching has been projected and this can be done by using methanosulfonic acid and what can be done along with methanosulfonic acid is you can have additions of H_2O_2 as well. This really helps in the solder alloy leaching. We will directly jump into the important flows of WPCBs. We have let us say WPCBs and right now I am assuming that important pretreatment has been done as discussed here. After that we have primary leaching. One can have let us say H_2SO_4 plus H_2O_2 this is just an example we can have so many numerous examples coming in here in as a choice for primary leaching and then we can have decoppered material because this can actually lead to copper recovery.

This is just an example. And then we can go for, using decoppered materials, we can go for, HNO_3 leaching which is basically the second stage leaching. If this is primary stage leaching. We can have a secondary stage leaching here. The second stage leaching. Which can give us silver recovery. This can again give us, let us say, if it has gold, then gold residue, if at all it is there, and then this can be further processed for gold leaching and recovery. This could be the last stage. Again, it depends upon what type of metal are we targeting.

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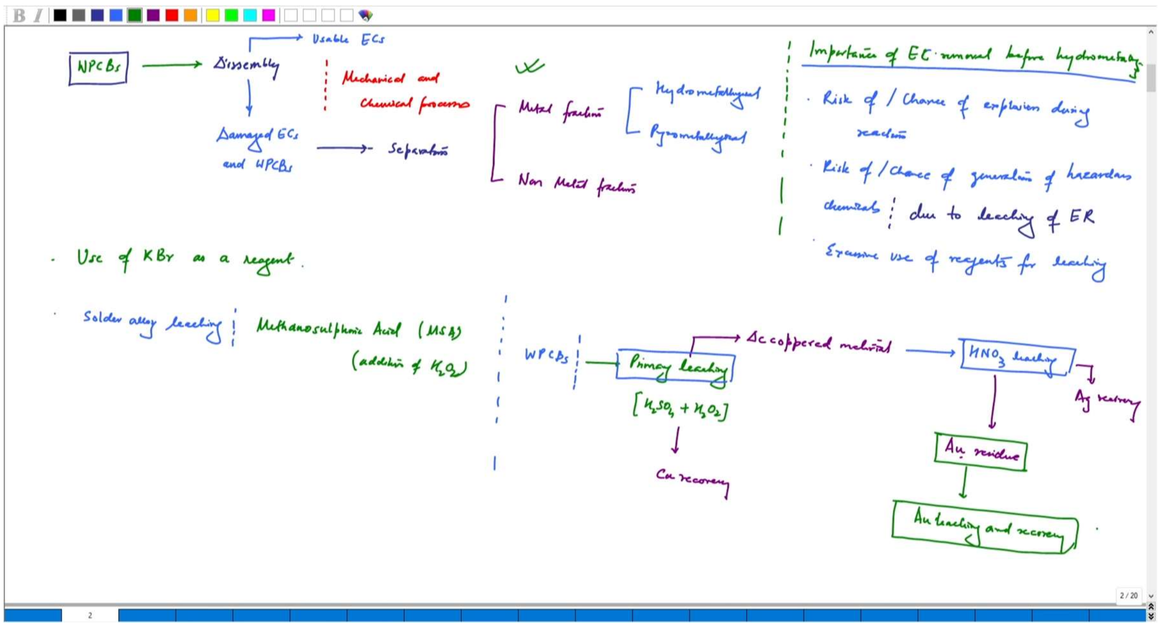

In this very simple flow sheet, we have assumed three elements, copper is the waste metal, gold and silver are precious metals. This the complexity increases when we are having numerous metals in the picture and we know that in reality WPCBs have numerous elements with varying concentrations and the sample tends to change, which means the complexity of the problem is very high and one has to design how we are going to extract the base metals, how we are going to extract the precious metals, what are the elements that we can extract first or later. That really governs our choice that what is the reagent that we will be using as a primary leaching reagent then our secondary leaching reagent or if there is a third stage leaching then what should be using in what should be used in the third stage.

It depends on the complexity of the process and what is the final target of the whole recovery procedure. we can have a different route. If we have processed WPCBs, again we are assuming that some pretreatment procedure has been done and along with PCBs, we have ICs. Again, the complete of WPCB is considered which has been pretreated, then we can have leaching with reagents, you can have adsorption wherein we can add let us say activated carbon. Because we are thinking of adsorption so we need to have some means for some material that we need to use for adsorption. Let us say activated carbon is that material and then this can give us gold recovery. After adsorption we process it to get gold. Or at the same time, since we are using this, we can have ion exchange, we can perform elution and then this can also give us gold. We have gold recovery by precipitation,

or cementation. This means we have so many different routes by which we can recover our materials and, in this case, we have just focused on gold and right now we are assuming that we are able to recover our base metals as well. Thinking on gold recovery from WPCBs. Gold recovery is usually performed by using cyanides.

Cyanide leaching is one of the common routes and this applies for WPCB as well. Leaching with reagent one of the most common reagents would be cyanides. If we do not wish to go into cyanides, so non-cyanide reagents include, there are non-cyanide reagents. Thiosulfates, thiourea, halogenates and so on so forth. These also have good recoveries. The leaching parameter changes. One should really mind whichever process we are trying to follow leaching parameters vary with the reagent. There is the addition of H_2O_2 and Fe^{3+}, $Fe_2(SO_4)_3$ to basically improve the leaching in case of let us say thiosulfates or thiourea. All additions can be done to improve the process.

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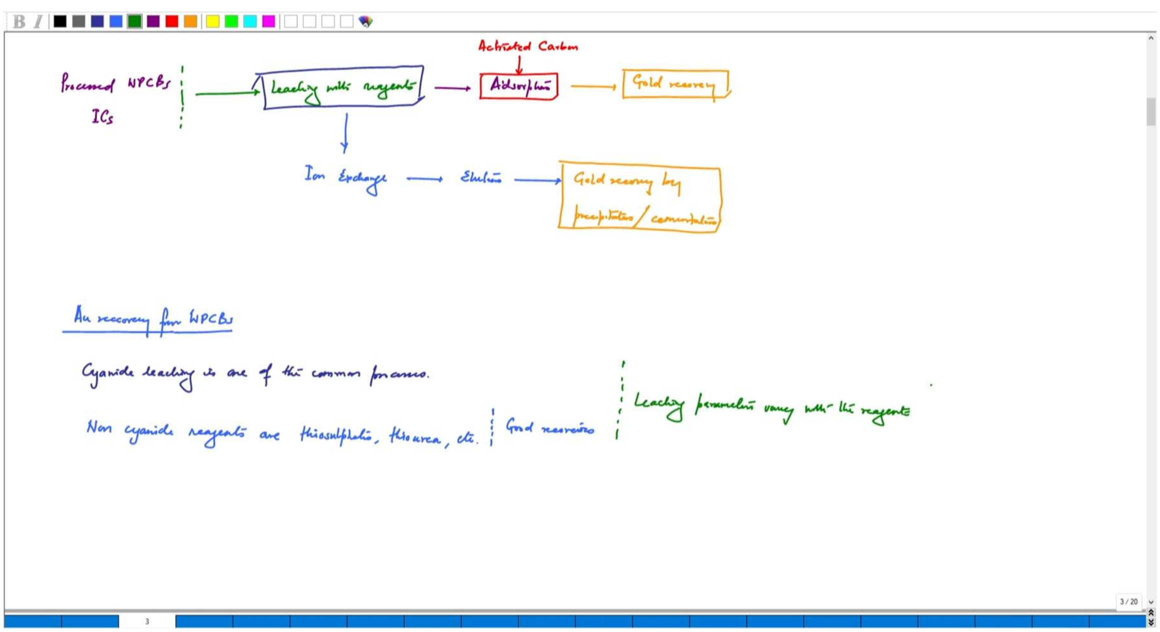
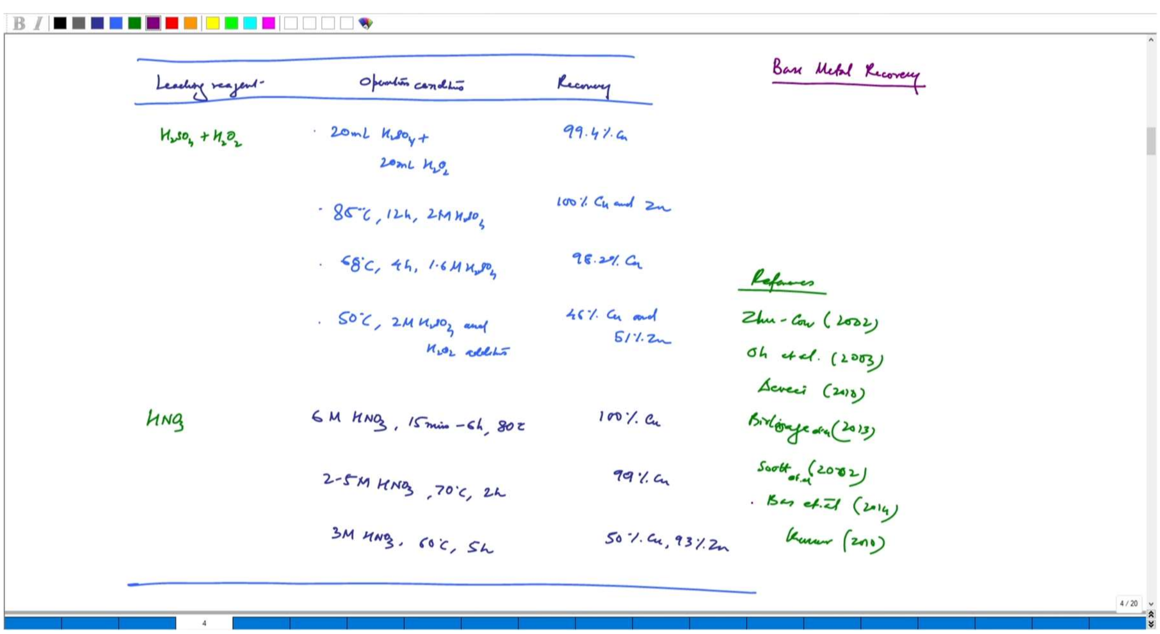


But again, it is just dependent upon what reagent we are trying to really use. We are going to discuss some of the most important findings that people have described in their work and how it really impacts the whole leaching procedure. These tables are going to help us understand how the leaching procedure is done and we already know that the recovery after leach liquor is going to be either through ion exchange, solvent extraction, precipitation or electro winning or cementation Different routes are already available with us the most crucial step actually is the first step itself how we are conducting our leaching experiments. We will discuss on this and we will make these tables and these are this table is specially for the base metal so we will write base metal recovery and we have leaching reagent conditions and then recovery. If you are using H_2SO_4 just as an example we have added this. So, we have let us say 20 ml H_2SO_4+20 ml H_2O_2 we can get let us say 99.4% copper. Similarly, 85 °C, 12 hours, 2 molar H_2SO_4, we get 100% copper and zinc. 68 °C, 4 hours, 1.6 molar H_2SO_4, we can have let us say 98.2% copper. Then we have 50 °C, 2 molar H_2SO_4 and H_2O_2 addition.

We can have 46% copper and 51% zinc, we have let us say HNO_3 so this was for H_2SO_4. If we write for HNO_3 we have 6 molar HNO_3, 15 minutes the reaction duration is 15 minutes to let us say 6 hours and at 80 °C, we see we can reach nearly up to 100% copper. 2 to 5 molar, H_2SO_4, HNO_3 70 °C, 2 hours, 99% copper. 3 molar HNO_3, 60°C again, 5 hours, 50% copper, 93% zinc. This tells us that a wide variety of recoveries can be described. Let me just quickly highlight some of the important references. Zhu-Gow, Oh et al. **(Ref. 30:40)**



We see that this is already giving us a wide range of information and we see that copper is just getting recovered very quickly just by using very common reagents. What happens if we are going to go ahead and switch our reagent for a different metal altogether? What happens if we are going for bioleaching? We see that H_2SO_4 and HNO_3 are good reagents. One just has to think about increasing time at times or increasing molar concentration or at times one can think of increasing S/L ratio or agitation. This might help. When we look at the case of precious metals, we will have. We will have again the same leaching reagent, operations, what are the operation conditions, recovery.

In this case, we have NaCN, sodium cyanide, we see that 4 grams per liter sodium cyanide is taken for 15 days. This can give us let us say gold of 46 %, silver 51 %. If now we are taking thiourea then we can say let us say 20 grams per liter. This thiourea is taken and I have mentioned we need to add let us say Fe^{3+} ions or some other additions and 0.5 molars H_2SO_4.

This type of addition is at times important to help us increase our overall metal recovery. Suppose, that 121.1 milligrams per liter of silver is recovered and this could be having 24 grams per liter, Fe2+ addition and then we use room temperature also. This can give us 90% silver, 90% gold. Finally, thiosulfate, so in this case it is ammonium thiosulfate, ammonium thiosulfate.

If this is the case then we have 0.1 molar ammonium thiosulfate. In this case we are going to use 40 millimoles of $CuSO_4$, 10 grams per liter pulp density which is basically S/L and this case we need 8 hours and they mentioned RPM also so 250 RPM and this gives us 56% gold. Mentioning some of the references we have. Similarly, and this was the case for what? This was the case of precious metal. This is precious metal recovery.

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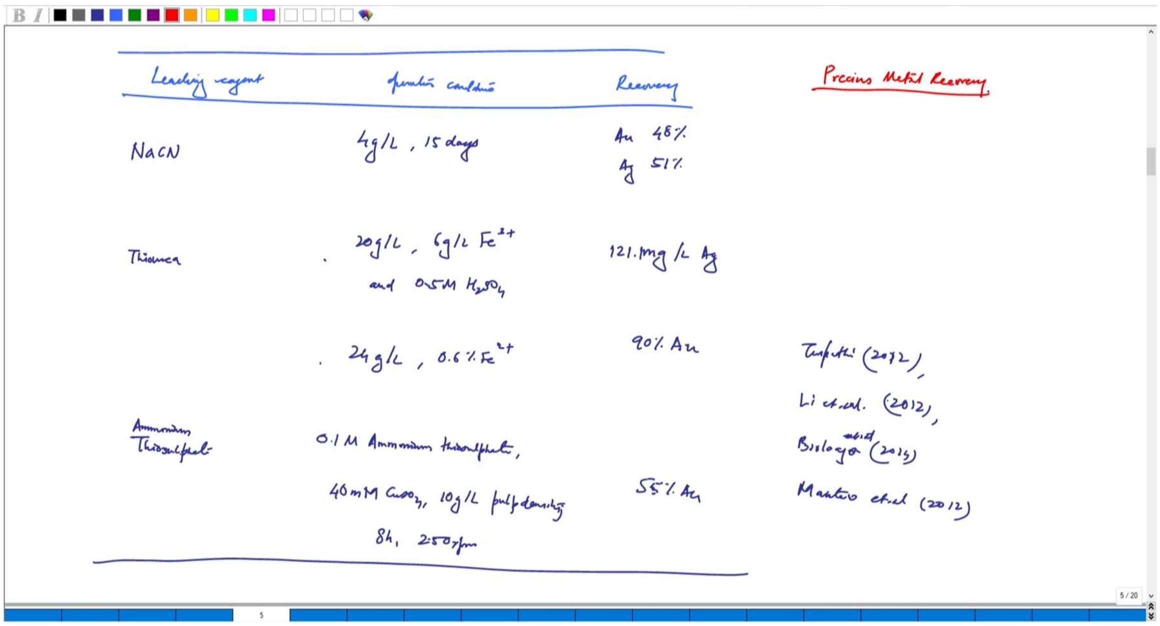

The last one that we are supposed to discuss is basically bioleaching. Bioleaching because it is a one of the most important advancing technologies that people have been exploring for material recovery. In this case we are using microorganisms and then biology conditions and then recovery. *A. ferrooxidans, ferrooxidans*. In this case one has to actually mention as much as possible what is the size of WPCB. This is the size of the WPCB actually. 93 micrometer, pH is 2, 17 to 20 days because one has to keep it for a very long period 80% copper recovery. Similarly, if you have 0.178 to 0.250 millimeter size, pH again is 2.25, they kept it for 183 hours and Fe^{2+} addition is 9 grams per liter, you get 92% copper. If we have a different microorganism. We have *acidophilum*. *A. acidophilum*. Then we can have 60 ml A. acidophilum, supernatant. This is supernatant and then we have 15 ml H_2O_2, 60 °C kept for 2.5 hours this can give us nearly 100% copper. Putting up some references here.

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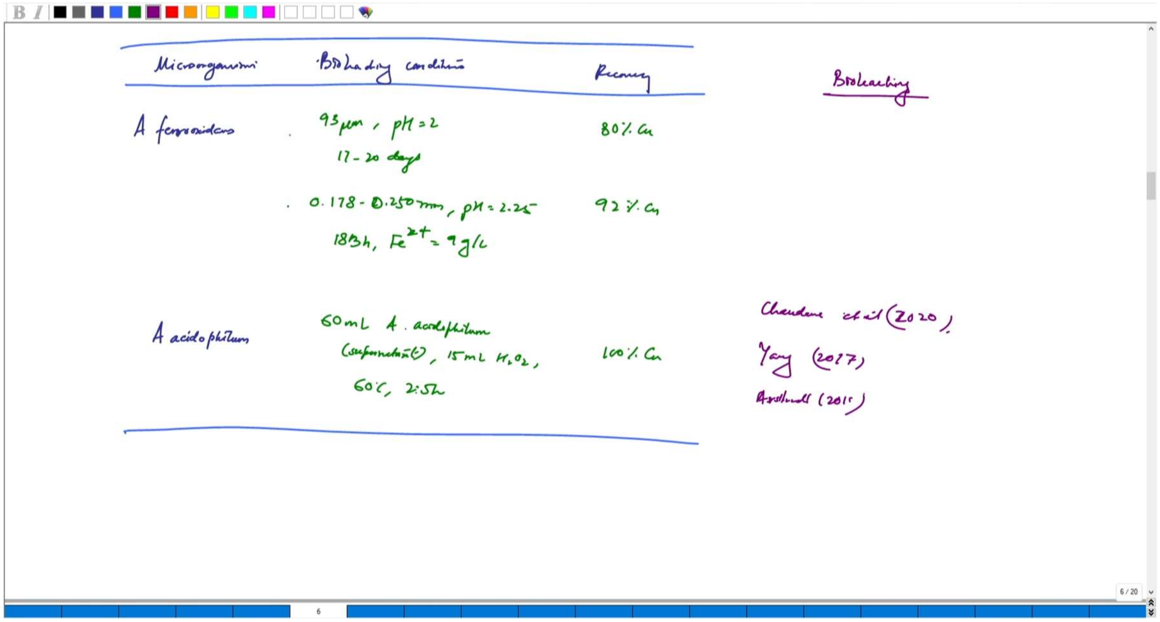

In all these three tables that we have seen, this one is for bioleaching, the previous one was for precious metal and the one before that was for base metal. We see that there are different types of parameters that people have described in their research and different overall recoveries. We know that these parameters can vary depending on reagents and the raw feed that they have. The values may not appear to be very much consistent. The reason behind that itself is because the PCB compositions are not consistent. We have already emphasized that e-waste is a waste that can vary from sample to sample, from source to source.

The recoveries can change and people have been exploring wide variety of reagents for their overall recovery. I like to mention two important strategies for final recoveries that people have explored, one is polymer inclusion membrane and, the other is the organic solvent displacement precipitation strategy. When we think of organic solvent utilization it helps us in precipitating out the solutes that are present in the aqueous medium and polymer inclusion membranes are those membranes that can help us in isolating the specific metal ions from the leach liquor. These are really new strategies that have been utilized for metal recovery from WPCBs and other complex leach liquors that have been explored. Till now, we have covered extensively the delamination, the pyrometallurgy and the hydrometallurgy. In the upcoming classes we will be discussing about the next segment of e-waste which will be on the recycling of batteries. Thank you.