

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-7

Lecture-33

Greetings, I welcome you all to this new lecture of this course wherein we will now be discussing on the WPCB recycling. In the previous classes we have gone through the basics of electronic waste recycling where we had first seen what are the classifications of e-waste that was done at the very beginning of this course and we had also very recently tried and explored how we could recycle different waste, e-waste materials, the end-of-life products like let us say washing machines and air conditioners and so many other different electronic devices. And then we move towards the main content of our course which was basically on waste printed circuit boards. And we had also seen the chemical composition, what really is present in a WPCB and what are the common physical processes that are necessary for the recycling of the WPCB. That part is already been discussed.

What are we going to do? We are going to discuss the delamination of WPCBs. Why is that necessary? When we look at a discarded electronic device, we can look at different materials that are associated to it and we start from the exterior and then we move towards the internal components. Exterior components can be dismantled and removed, but one of the most important devices that really govern the operation is the printed circuit board and we know that from materials point of view not just from the electronic operations point of materials point of view, it is like the treasure box of so many different elements and we had seen a very simplistic and generalized overview of what really can be present in a WPCB and we know that there are different types of WPCB so the range of elements and their concentration can vary a lot and we had also seen that it depends upon the manufacturer as well the year of manufacturing the product that we are seeing it there are so many parameters that really govern the composition. But one of the most important central ideas and central operations to recycling of the printed circuit boards is the delamination of the PCBs. Why is that so important?

Because we know that the PCBs can have electronic components that can be soldered and the differences in the soldering operation depends upon the type of PCB and the component itself. If it is through whole component the components are different. Similarly, the other components can be directly attached to one side and the soldering can be done on that part itself. Depending on what type of electronic components we have and what type of assembly is done on a PCB, the delamination process becomes bit more complicated. One of the most important aspects that we should be understanding is how exactly we should be moving towards the delamination, the components need to be removed and then the delamination the layers of the PCB need to be separated out, that part we will be discussing in today's lecture. We know that delamination of WPCB is one of the most important steps in recycling.

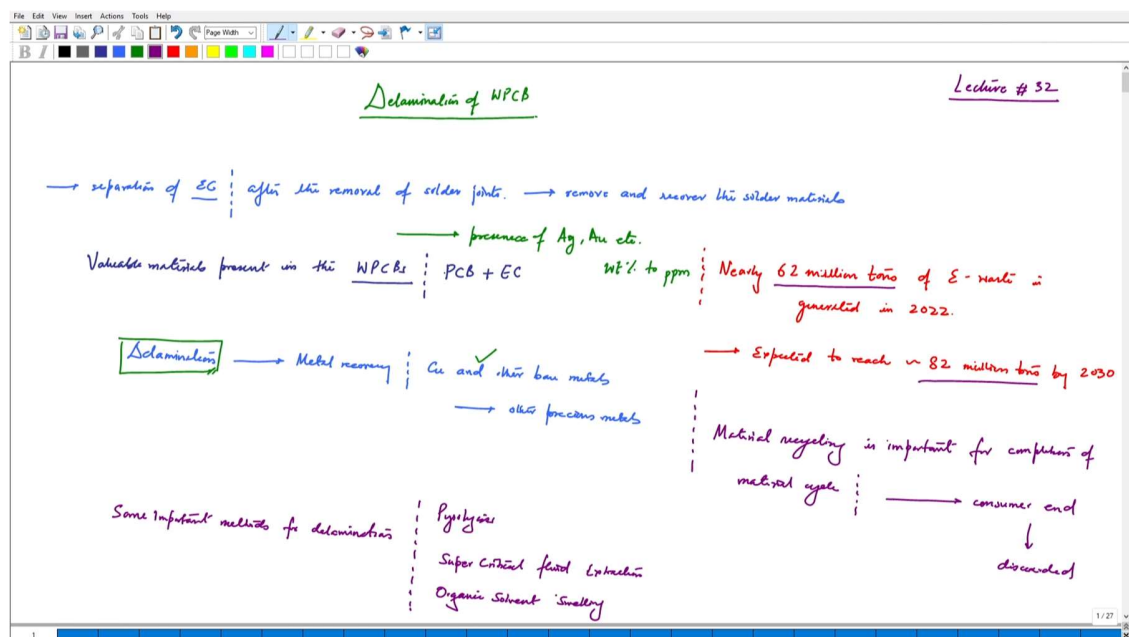
Separation of ECs, electronic components, is done after. This is done and then we can go for the delamination and separation of ECs is done after the removal of solder joints. One can also think of the recovery of solder itself, solder materials itself. We remove and recover solder materials and then we also can have the separation of ECs. After that, we know that we can go ahead for the delamination. A couple of interesting facts before we actually go into the WPCB itself. Nearly, 62 million tons of e-waste is actually generated. 62 million tons of e-waste is generated in 2022 and it is expected to reach nearly 82 million tons by 2030. This is an estimation, but it is projected that it might reach this value and some other projections show that it can reach to about double value of this 62 millions in 2050. Depending on various growth rates that people are able to model, they have this different values that they are projecting. And this is very crucial because if these are the values of e-wastes then delamination becomes very much an important activity to treat the incoming e-waste. This is important for completion of material cycles.

Why? Because we see that just some material is reaching the consumer end and it is getting discarded. We do not really receive this material back. This whole problem of material getting lost is a bit of a challenge. We should be able to isolate the materials from such streams and then bring it back which is why such investigations are important. This delamination and then let us say pyrometallurgy or hydrometallurgy or electrometallurgy and the subsequent combination of these processes for metal recovery for let us say oxide recovery, polymer recovery becomes very important because we are losing materials on all fronts. If it reaches the consumer end and it reaches the scrap yard and we are not able to recover the material from the scrap yard. Bringing back materials becomes very important.

Coming back to the delamination. PCBs along with the ECs have lot many valuable materials, valuable materials. And right now, I am considering PCB plus EC assembly as even without the ECs, PCB is still valuable and we know that gold and silver have been described, presence of silver, gold etc. in varying concentrations. This concentration can be in the range of weight percent to ppm depending on what metal are we trying to look at. If you look at copper it could be in weight percent and some other metals may be in the parts per million or even lesser. When we think of delamination, we are basically wanting to go for towards metal recovery and this is oriented towards copper and other metals, other base metals followed by other precious metals.

The first option would be to recover the base metals and then we go ahead for the precious metal and we know that this is possible only when we are doing delamination properly. What are the methods by which we can do delamination? Some important methods for delamination. These are pyrolysis which we will be discussing in pyrometallurgical route of PCB handling in the upcoming classes as well, Supercritical fluid extraction, and organic solvent swelling. Somebody might want all to rewrite it as organic swelling as well. Both the terms can be used, organic swelling or organic solvent swelling, we are going to use organic solvents.

(Ref. 12:40)



What exactly are we trying to note when we are thinking on pyrolysis? The temperature range can be very large. The range itself can range can be from 300 to let's say 1300 °C. The common range could be till 800, 850 depending on what exactly we are trying to do. But beginning temperature is around 300. The end temperature could be let us say 850, 900 to 1300 as has been described. What we do here is basically heating the WPCB in inert atmosphere. Why? Why do we do that? Because we don't want oxygen to come in and react with all of the metals. This leads to generation of gases and oils. Oils. Chars. And there is the mixture of products that we can get after we remove these. We can have fuels, chemical fuels whereas, we can have solid residue which is basically glass fiber and metal mixture.

This is the solid residue and this can be further processed. One of the key drawbacks for delamination itself is that we have generation of hazardous gases and we have brominated organic compounds which are difficult to process and these are really hazardous. Why does this happen? Because we have epoxy resins, this we had discussed previously as well. We have epoxy resins present in it and these contain bromine. It has also been seen that if we are looking at 270 to 280 or odd temperatures, this generation of hazardous gases is observed.

(Ref. 16:00)

The image shows a digital whiteboard interface with handwritten notes. The notes are organized as follows:

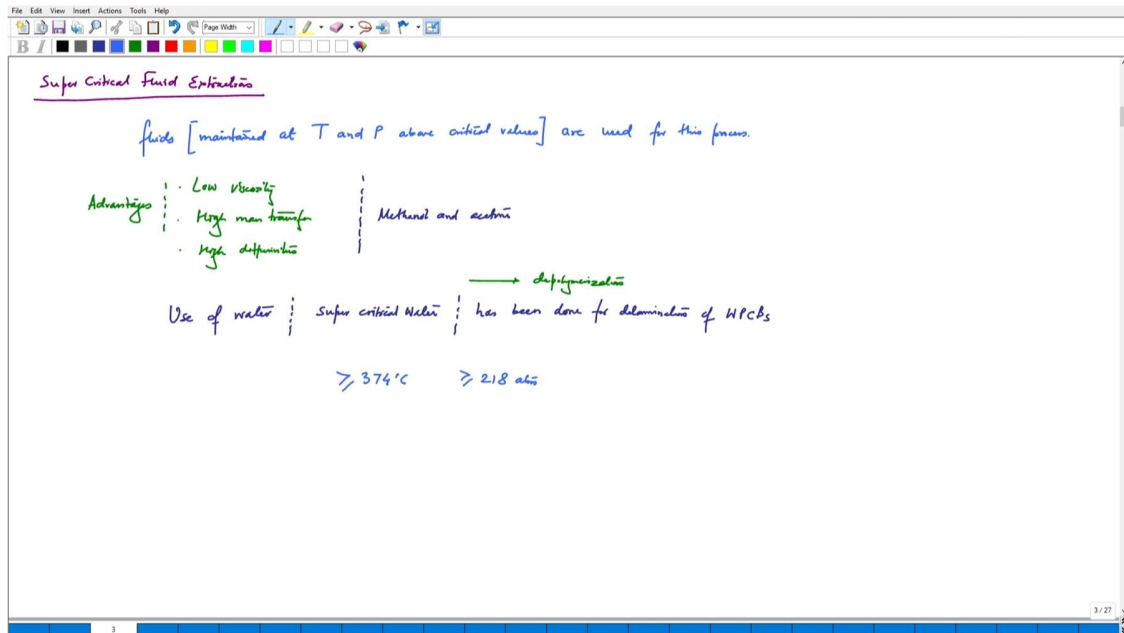
- Pyrolysis | Temperature range | 300 - 1300 °C
- Heat the WPCB in inert atmosphere | generation of gases and oils / chars
 - chemical fuels
 - solid residue : glass fiber and metal
- generation of hazardous gases
- brominated organic compounds | ER contains Br

The whiteboard interface includes a menu bar (File, Edit, View, Insert, Actions, Tools, Help), a toolbar with various drawing tools, and a status bar at the bottom showing the page number 2.

One might want to optimize the process of pyrolysis, but then again at times we want to want the epoxy resins to be removed and at times it is very difficult to control the generation of these hazardous gases. This is a good method if you are looking at large scale WPCB processing, but it comes with its own drawbacks we have just discussed. We will now be looking at other routes of WPCB delamination. Supercritical fluid extraction we are going to discuss now. We can have fluids that are maintained so these are maintained at T and P, temperature, and pressure well above critical values. Basically, bringing this these types of fluids in contact with the PCB. What it does is basically have, so we have advantages. Some of the key advantages are low viscosity of the fluid, we have high mass transfer and then we have high diffusivities which means we have good control over what we are doing. Now what are this examples of fluids that can be used so we have methanol and acetone. These are the fluids that have been used and one of the most common examples of apart from methanol and acetone is water itself. Water is one of the most common fluids that is easily available to most of the industries and having this fluid as the raw material it makes the operation cost really very low, at least from the materials point of view. But we will see that the pressure and temperature requirements to maintain the supercritical properties that we have been discussing. These are very demanding parameters.

One has to have high temperature and high pressure and this really adds to the cost of the operation. We see that the use of water. The process is called supercritical water. The use of water has been done for delamination of WPCBs and this is possible due to depolymerization. Depolymerization, the temperature requirement is very large, so we can have let us say, above 374 °C and above 218 atmospheric pressure. These parameters are very large. Having such high temperature and high pressure one has to have that investment that can maintain the temperature of water and pressure in the given conditions and then we will have to charge this fluid into the PCBs so that the delamination is possible. What happens is this temperature and pressure helps in the conversion of the resins into the finished products, the hydrocarbons that are being taken up by water and the depolymerization is happening simultaneously. What happens is the layers are finally getting delaminated.

(Ref. 21:30)

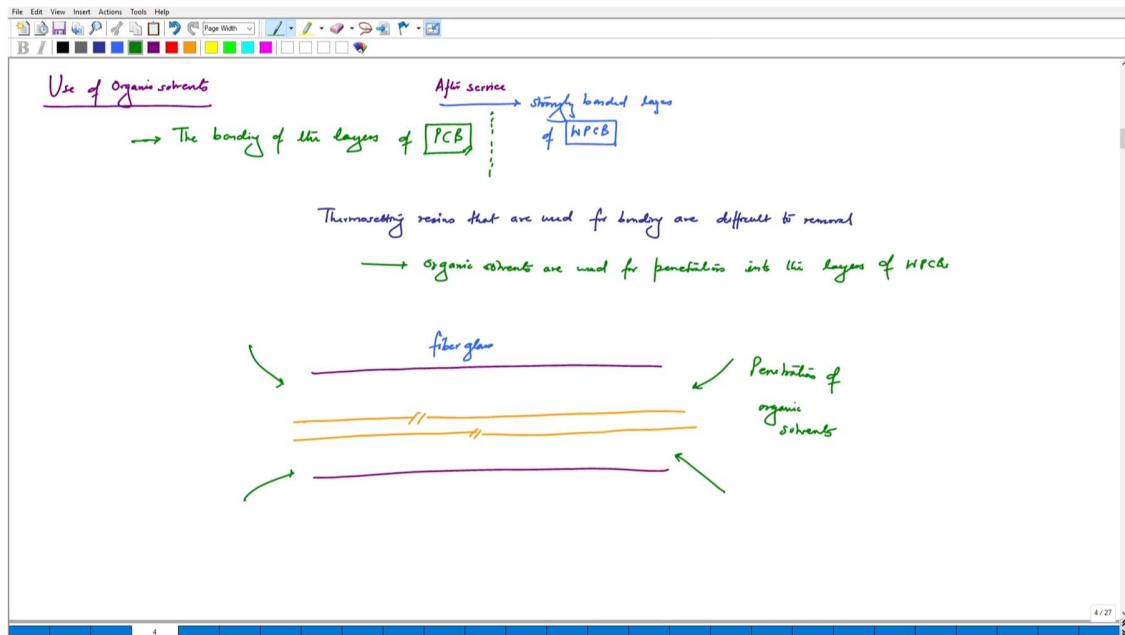


One another route that we are going to discuss is the use of organic solvents. This process is going to lead to the swelling of the WPCBs. One has to really understand what we are trying to discuss up we need to understand the bonding, so we'll discuss about bonding. The bonding of the layers the bonding of the layers of PCB now, we are actually writing PCB because we assume that this is actually in context of the manufacturing stage. When we are talking about bonding of the layers of PCB, we must expect that it should survive the operation conditions and it should not get damaged due to physical or other various forces that it experiences during its service. Unless until somebody is deliberately destroying a PCB it should, the bonding of the layers should be intact. It is engineered in such a way that it should stay constant. This itself makes the whole disassembly delamination a bit of a challenge because these are strongly bonded. Strongly bonded layers of WPCB.

We are writing WPCB because it has reached its end-of-life. We can just write after service. We had this is basically during manufacturing and this is during after service when we are trying to recycle what happens. What we are facing is basically the thermosetting resins, thermosetting resins that are used for bonding are difficult to remove and these thermosetting resins basically provide the strength. And which is why now we are thinking of organic solvents are used for penetration into the layers of WPCBs. We'll draw the diagram to understand this better. Suppose that we have and we have and then we have these. This is fiberglass and suppose that this one is metal and we

are trying to involve the penetration of organic solvents. It goes something like this and then what happens? The epoxy resins that are present inside here, inside the space, it will get a chance to react with the organic solvents and it swells. This leads to the delamination.

(Ref. 25:50)



We are going to discuss some more properties that can affect the delamination. Many times, the WPCB can be reduced in size what does this do? It helps in delamination. How do we do this? One can do crushing or shredding. This can be done and it helps in delamination but this is just a clause, one can also directly charge WPCB for organic solvent delamination. One assumes that we have removed the ECs and we are directly charging the whole PCB inside it. We look at some of the key examples of organic solvents that have been used for delamination. We have organic solvents, parameters and WPCB size, this is in mm^2 , so I'm assuming that they have that times they have just directly charged it or at times they've just crushed it and reduce the particle size. In case we are using DMF, we have let's say two cases 135°C for 4 hours s/l basically solid is to liquid ratio is 3:10, we have 100 mm^2 , 50°C , 32-68 hours, s/l is 1:5. It is not necessary that we are all always sticking to 3:10, the ratio can change. If we write for DMA or somebody might write DMAC as well basically dimethylacetamide, 60°C , 420 minutes nearly 420 minutes, s/l of 1:3 or 140°C , 180 minutes, s/l of 1:3. It can be around 100-

1600 or 225 and so the references we'll just. These are some of the references that have been used to collect this data.

We see that DMF, DMA, NMP, DMSO are some of the organic solvents that have been extensively used for delamination and we know that this makes the delamination lot easier. These chemicals and these parameters have been used. We charge the PCBs either these are chopped or shredded or sized according to the size is mentioned, 100 mm², 15 mm² or whatever is the size and then we just charge it inside the organic solvent bath. We may have different other parameters also that help us govern the delamination some at times we can have higher temperatures or agitation and then it helps us in delaminating the layers and then we can peel off the layer of epoxy resins and glass fibers and finally, we are able to get the metal clads. What are the important parameters that help us in understanding the whole process. It's we have tried to see the Hansen solubility parameters, which people have been writing in short as HSP. These are the various parameters that govern it.

HSP have three different components. This is the total value of HSP and we have δD , which is the contribution of dispersion force, dipolar interactions, hydrogen bonding and then finally there are these parameters when combined help us in understanding why really some organic solvents are good at delaminating the epoxy resins and the metal fractions are then separated. Some other routes that are being investigated are and we are just highlighting them because these are being investigated. These are co-heating swelling wherein we are just heating the organic solvents while they having the PCB assembly inside it.

(Ref. 33:50)

Organic Solvents	Parameters	WPCB size (mm ²)
DMF	- 135°C, 4h. S:L = 3:10	100
	- 80°C, 32-68h S:L = 3:10	100
NMP	- 100°C, 90 min S:L = 1:5	16
	- 200°C, 10 min S:L = 1:3	25
DMAc	- 160°C, 4-10 min S:L = 1:3	100 - 1000
	- 140°C, 180 min. S:L = 1:3	225

The WPCB can be reduced in size
→ helps in delamination

Directly change WPCB
for OS delamination

crushing or shredding

HSP

$S^* = \delta_d^2 + \delta_p^2 + \delta_h^2$

δ_d - dispersion forces
 δ_p - dipolar interactions
 δ_h - hydrogen bonding

co-heating swelling
microwave assisted delamination

[Verma et al. 2016, 2017
Tafaviant 2017,
Monteiro 2021
Mortola 2024]

Co-heating is basically we have a bath, we have organic solvents and then we are heating it it helps us in having that action of heat transfer and the action of organic solvents and it helps in the removal of the components lot more quickly and we also have microwave assisted delamination. Again similar, to co-heating swelling bearing, now we are supplying microwaves to container that contains organic solvents with the PCB pieces and then it helps in the delamination. We have understood the delamination process, we will be now going into pyrometallurgical and hydrometallurgical operations and other routes for the recycling of WPCBs. We will continue later. Thank you.