METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-2

Lecture-10

Greetings, I welcome you all to the 9th lecture of this course. So far, we have understood lot many aspects of materials recycling and we have understood the importance of sorting, characterization, initial characterization, classification, followed by the essential pre-treatment, followed by various extractive metallurgy strategies that can be used for efficient material recovery. Now, in addition to the three routes that we have discussed, the pyrometallurgical route, the hydrometallurgical route, electrometallurgical route and the separation techniques that is associated with the hydrometallurgical route.

We will now be looking at the essential refining strategies that can be used for producing the desired composition of the recycled metals. Now, this is the reason why refining finished products is essential. While the raw materials of the recycling process can have variety of compositions, the finished product that is desired at the end usually having very strict composition demands. Composition control is to be achieved during the recycling process, which can be done at the refining stage.

Let us now discuss the refining processes which can be applied after having decided on the recycling strategy. Metals produced need to be refined to achieve the desired chemical composition. Why do we need chemical compositions? And of course, desired chemical composition because the applications require these compositions. At times you might find an application where high purity copper or aluminium or zinc or iron is required.

A recycled metal may not be of the desired composition. One has to refine these metals further just like refining metals in the conventional extractive metallurgy processes. It's just the same. What we are trying to do now is we will try to employ the raw materials from various waste sources and then apply these refining strategies so what it does is basically it adds value to it value addition to the metal and again it means that we'll have to invest additional investment in resources because All of the refining processes consume resources. There are various types of refining strategies that we will be looking at. In today's lecture, we will be looking at electro-refining, zone refining and to some extent, fire refining. There are other strategies also.

But all of these refining strategies will consume resources in form of energy and raw material and investment in the facilities also. The additional investment is required. When we think of electrorefining, which we will be discussing at the very beginning itself, we normally see that it is just similar to the electrometallurgical processes that we have discussed previously. Like the electrometallurgical processes, we will have anodes, we will have cathodes, we will have electrolytes, we will have the cell that is required for conducting these operations and based on temperature we will have high temperature operations or low temperature operations. We will be looking at the electrorefining of aluminium that is commonly described as the three layer process for aluminium refining and we'll see how electrorefining is conducted for aluminium. So, for aluminium we will have the composition of electrolyte and it is aluminium fluoride is nearly around 36%, cryolite which is Na_3AlF_6 is around 30%, barium fluoride 18%, calcium fluoride 16%.

Impure metal is alloyed with copper and used as anode. We have discussed the composition of the electrolyte. And of course, we know that in an electrometallurgical system, even electro-refining system, electrolyte will play a very important role. It helps in the refining of the impure anode. What is the anode itself?

Impure metal, in this case it is aluminium, is alloyed with copper and used as anode. We will see the composition of anode as well. Impure aluminium is alloyed with copper and used as anode and we know the composition of electrolyte. The temperature required for the operation is around 950 degree celsius. We know, just now we have mentioned that the temperature for the operation of refining is very crucial.

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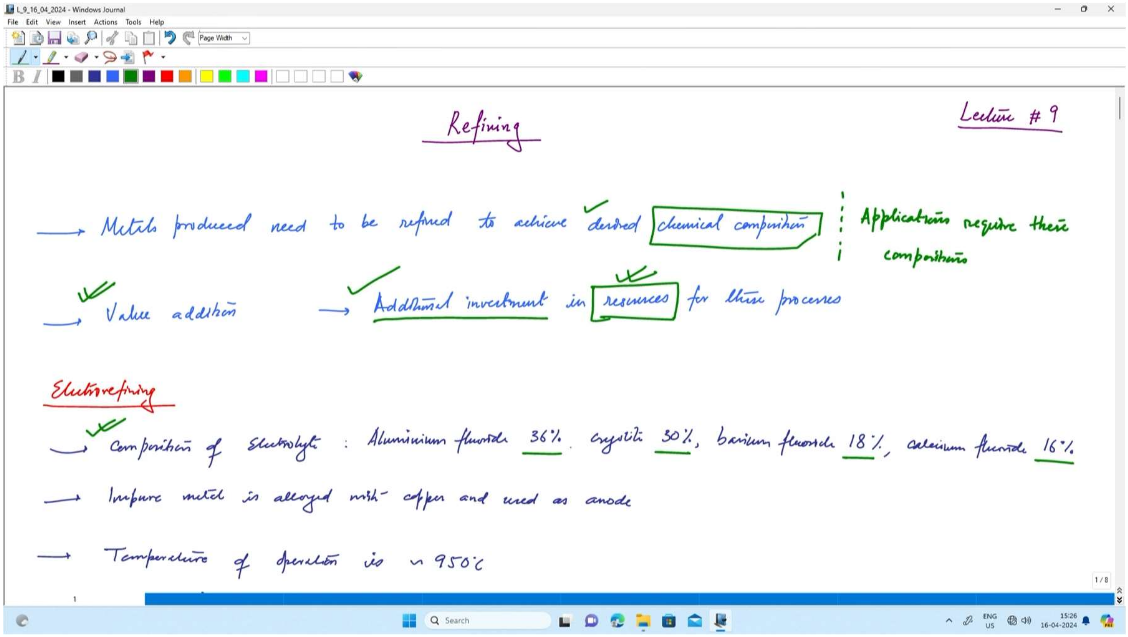

It may appear that it is pyro-electro refining. But essentially temperature is just assisting the whole electrodefining process. We need to supply electricity as well so as to recover pure aluminum by this process. We see that. Nearly 99.99% purity metal can be produced by this process and a capacity of a typical cell could be around 100 kg per cell per day.

We see that these are very well established processes with very high production rates and these are very well accepted processes in the industries. We also should look at how exactly this process works. We have graphite electrodes and we have aluminium copper anode and of course this graphite electrode is the cathode here. We have seen the composition of electrolyte. As we have mentioned, we have aluminium fluoride, cryolite, barium fluoride, calcium fluoride and we know that the anode is aluminium-copper alloy which has around 28 to 30% of copper. The rest is aluminium. We try to keep anode composition with copper and we try to avoid different types of impurities, especially magnesium, else it would render the process unfruitful. Because it can react with the electrolyte and it may disturb the process. This type of chemical composition is achieved.

Now, what happens is, we have the temperature maintained at high temperatures. This is around 950, as mentioned, 950 degree celsius is required. And what we see here is the passing of electricity between the electrodes and the formation of pure aluminium towards the graphite electrode.

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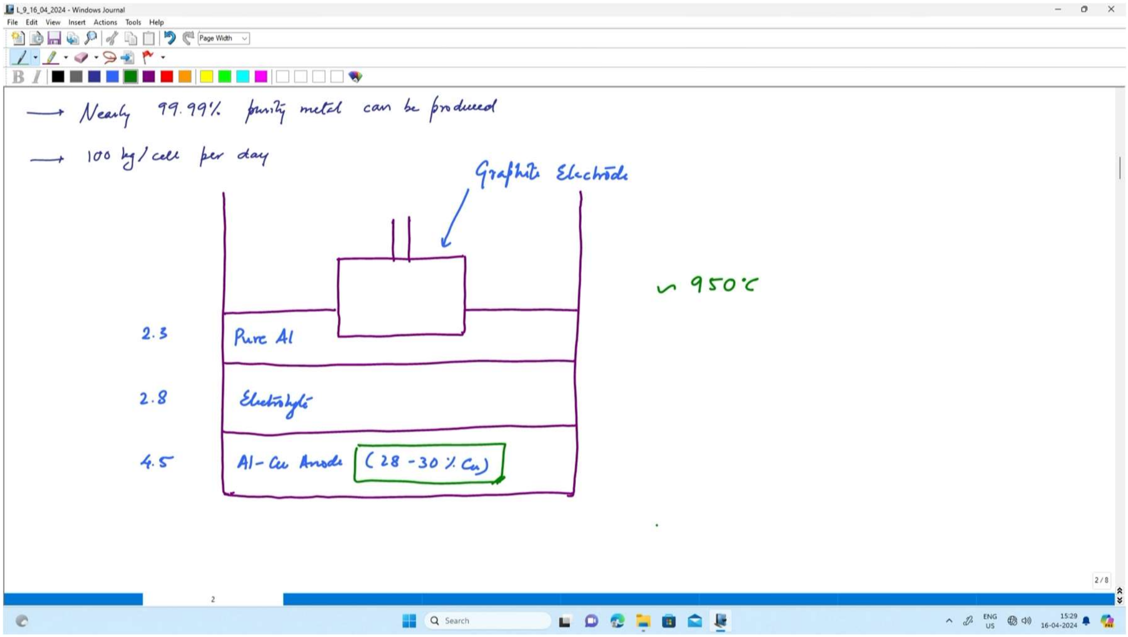

This is one way of refining which is basically consuming electrical energy and therefore the name electro-refining.

We are now going to look at zone refining. Before we actually go into the process, how exactly zone refining takes place, we have to look at a concept in phase diagrams, we see that suppose we have a composition P which is being solidified. Initially, it was in the liquid state and now it is going into the solid state. What we see here is the distribution of composition of liquid and solid.

We see that when it reaches a given temperature, when the solidification starts, we will have two compositions marked A and marked B. Of course, for the point P and Q on the composition axis and of course, we also need to describe that this is the component A rich end and the B rich end and here we see the composition change from

this point to that point, we see 100% of B at this end and 0% on that side. We see that at equilibrium. Assuming that the cooling is done very slowly and we are again assuming that each step is achieving equilibrium. Normally, it does not happen but a very steady and slow cooling is expected. And at such cooling rates, the equilibrium distribution coefficient is, let us say, K0. It can be described as A on B, where A is the composition shown here and B on the side.

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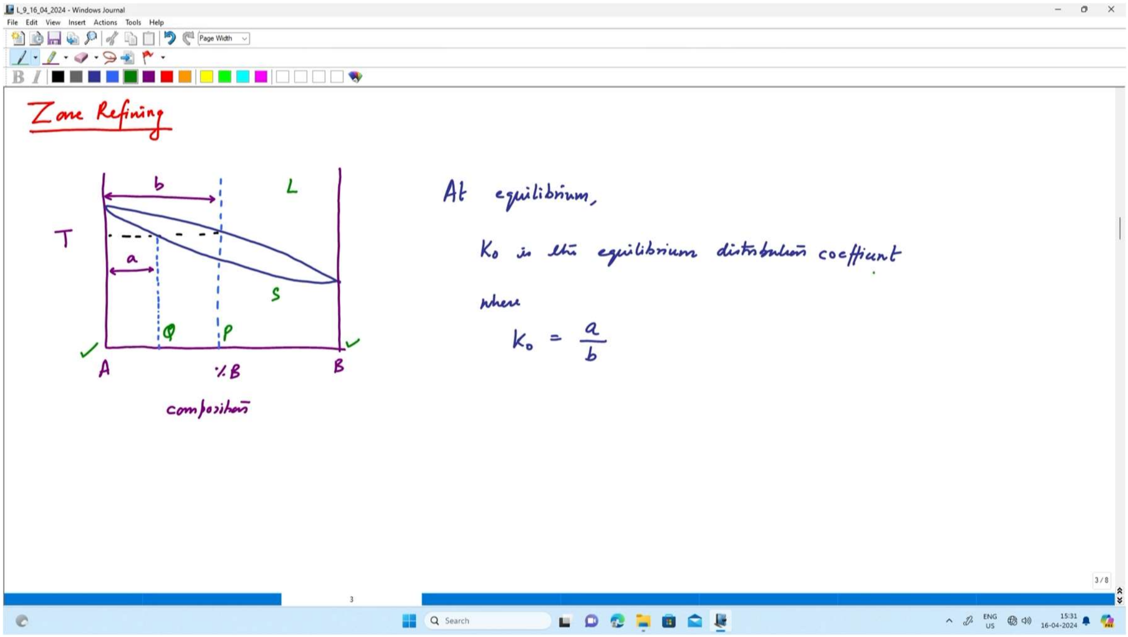

With this, we are now going to describe how zone refining really works. Suppose that initial composition was C0 of our raw material. If the initial composition is C0 of the feed, raw feed when and let us assume that at this end at this end the refining is beginning. The melting is beginning at one end and gradually the next layer is melted, the next layer is melted of the solid and gradually it starts melting the whole solid and simultaneously the cooling and re-solidification is also taking place. What happens is, we have unmelted zone and somewhere in the middle we have the molten zone. This is the zone in which, we have the molten metal as well in contact with the unmelted zone and the solidified zone. What we see here is when solidification begins the concentration of B where B could be referred to as impurity.

When B is the impurity we see that the concentration of B is K0*C0 where K0 was A upon B. Basically, the difference in the composition as observed in the phase diagram and C0 was the initial composition. What gradually is observed? When the zones tends to move further concentration gradually increases with distance so at this end suppose it was K0

and this is the reason why we have drawn this concentration versus distance profile and we see that at the end we have K0*C0 and gradually the concentration is increasing with distance so we have the increase in distance and we also have the increase in concentration. Why is that happening? Gradually, B is B, that is impurity and right now we are assuming that there are only two components in the system,

A and B, where A is the material that we are interested in and B is the impurity. At the beginning itself, we have K0*C0 and gradually as the distance is increasing, more of B is getting rejected into the liquid front. And gradually what happens? After some distance, C0 becomes unchanged.

We will look at it one more time. Concentration gradually increases with distance due to further rejection of B, further rejection of impurity. After some distance... C0 becomes unchanged, which is basically this part of the graph. After each pass, and of course, at the end, what happens?

It is getting increased. The impurity is getting concentrated at the end. And this happens after every pass. At this end, we will have K0*C0, but at the other end, we will have an increased composition of B. Now, after each pass...

the rod becomes purer at one end and the impurities accumulate at the other end. What gradually is happening is the collection of impurities from the whole of the sample and accumulation like we have said and impurities accumulate the other end accumulation of impurities at the other end this is happening at the other side finally what happens after multiple passes, when we are very sure about the removal of impurities

from the raw feed we can simply remove the end that is impurity rich. That is in the sense B rich if A and B are the components A rich is the end that we are interested in and B rich is the impurity so we can detach, remove the part where B is accumulated and this process is essentially very much useful for removing impurities down to parts per million

and zone refining has extensively been used in refining germanium which is used in many of the important industrial sectors.

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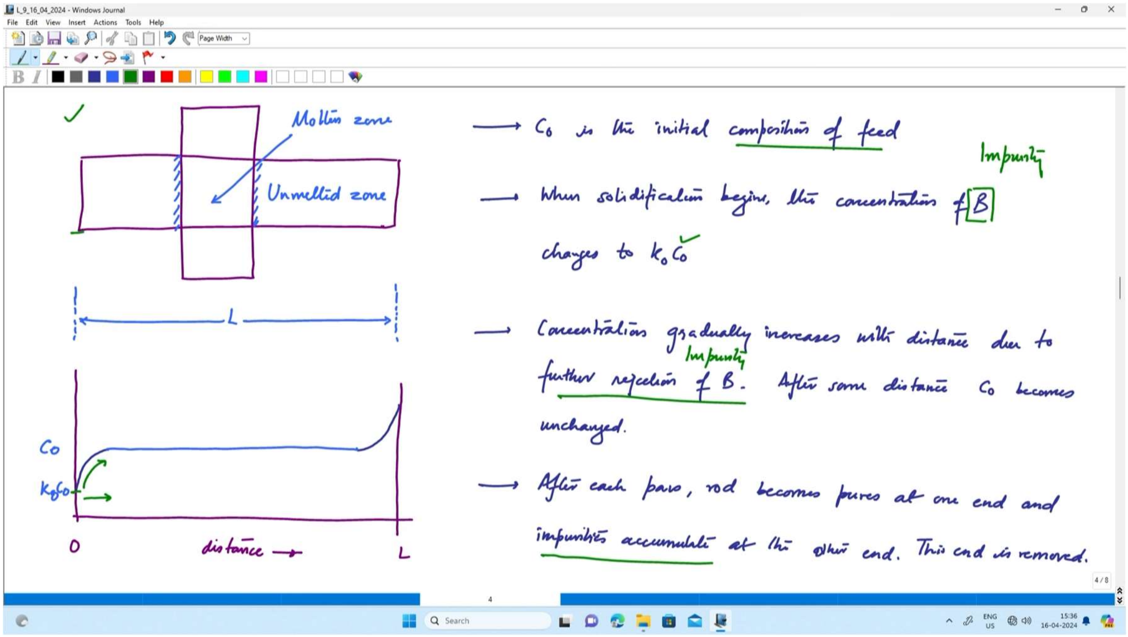

So, we see that if we want high purity metals which have very specific applications, we can go into various refining strategies. Of course, we have discussed electrometallurgy, electrometallurgical process, that is electrorefining, and zone refining, which is basically a pyrometallurgical process

that takes into account that one has to go through the solidification slowly, gradual solidification so that impurity is rejected into the liquid phase and gradually these impurities can be separated out at the other end of the raw feed. The last example that we should be looking at is the fire refining. When we look at refining strategies,

one of the most important requirements that come to mind is the capacity of the refining unit. Pyrometallurgical processes in general have higher processing capacities and such refining units are also having the same characteristics. When we look at fire refining, what exactly are we targeting? We are targeting the removal of impurity elements that can be preferentially removed by oxidation.

More reactive elements from molten metal. The prerequisite is the metal is in the molten state and it has impurities impurities present in it. Now more reactive elements compared to the molten metal itself,

they are supposed to be removed by preferential oxidation. When we think of oxidizing the impurities, we must think of ways by which these target elements are being oxidized.

And the most commonly used refining processes are for iron, lead and copper. Fire refining is common for these elements.

Also, how do we do that? We supply atmospheric oxygen into the system. We can have the vessel in which we will have the molten metal and we will have the oxygen supply being blown at various flow rates. Also, flux is added to remove the impurity oxide as mixture of liquid oxides.

At times it is possible that the impurities will be removed from the molten metal but they have to be separated out from the molten metal itself so the impurity oxides have to be removed from the molten metal this is possible if we are forming a layer of slag and that is possible when the flux addition is done so the addition of flux here is to help, is to help

the removal of impurities, the flux addition is done to help the removal of impurities as impurity oxides from the molten bath. We must note that there is the oxygen supply and the oxygen supply can be done by either blowing oxygen or addition of chemicals that can supply oxygen to the system. Normally, oxygen blowing is general method of fire refining that is used in fire refining. Flux addition is done to remove the impurity oxide as mixture of liquid oxides

and a common example of that as we have seen is for iron, lead and copper refining. It is done in a reverberatory furnace for copper. The copper refining can be done in a reverberatory furnace.

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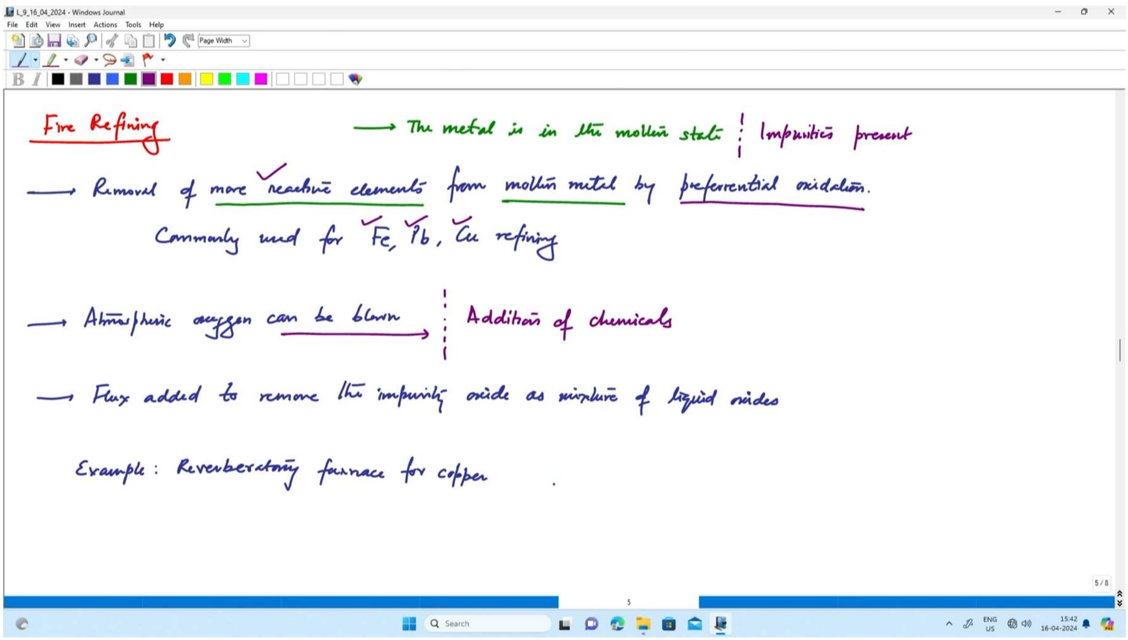

Similarly, we will have iron. We have the steel making processes. The LD converter is a good example where we can remove various impurities including carbon and further processing can be done as per the desired composition of the resultant product. We have seen in the present discussion what are the important refining strategies that are essential for materials recycling. It is essential to note that not just the three basic roots of materials processing, metallurgical processing like pyrometallurgy process, hydrometallurgy process and electrometallurgy process.

Not just these three routes, it is the pre-treatment and refining that help us in defining the complete recycling process. So, when we think of developing a strategy for recycling a given waste, be it metallurgical waste or electronic waste, one has to start with the characterization of the raw material, initial sorting followed by pretreatment and then comes the selection of the process whether pyrometallurgical process is good or hydrometallurgy or electrometallurgy and do we really need to be isolated in these strategies or a combination of these strategies would be beneficial.

When all of this is done, let us say we have the combination of pyrometallurgy with hydrometallurgy or hydrometallurgy with electrometallurgy or hydrometallurgy combined with multiple separation strategies, it becomes easier at the other end. And of course, after all of the recycling processes, there is the refining strategy. There is the refining that we have discussed. We can have electro refining, fire refining and zone refining. These are some common refining strategies that are normally used and after that when we are satisfied with these refining strategies we can end up with our desired product. At times, metal recovery is not the target.

It can be possible that we can think of producing some valuable compounds. Suppose that we have a leach liquor which can be used for extraction of metal. At the same time, the same leach liquor could be used for making the metal compound by let's say precipitation method or crystallization method. These are methods by which we can produce the desired chemical product and again the refining strategies would follow. We will be now discussing on the metallurgical wastes in the upcoming lectures where we would be going into various metallurgical industries and we will be discussing their industrial wastes and we will discuss some of these strategies that have been described in literature and how we can improve in the overall metal recovery.

Thank you. Bye.