

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-2

Lecture-9

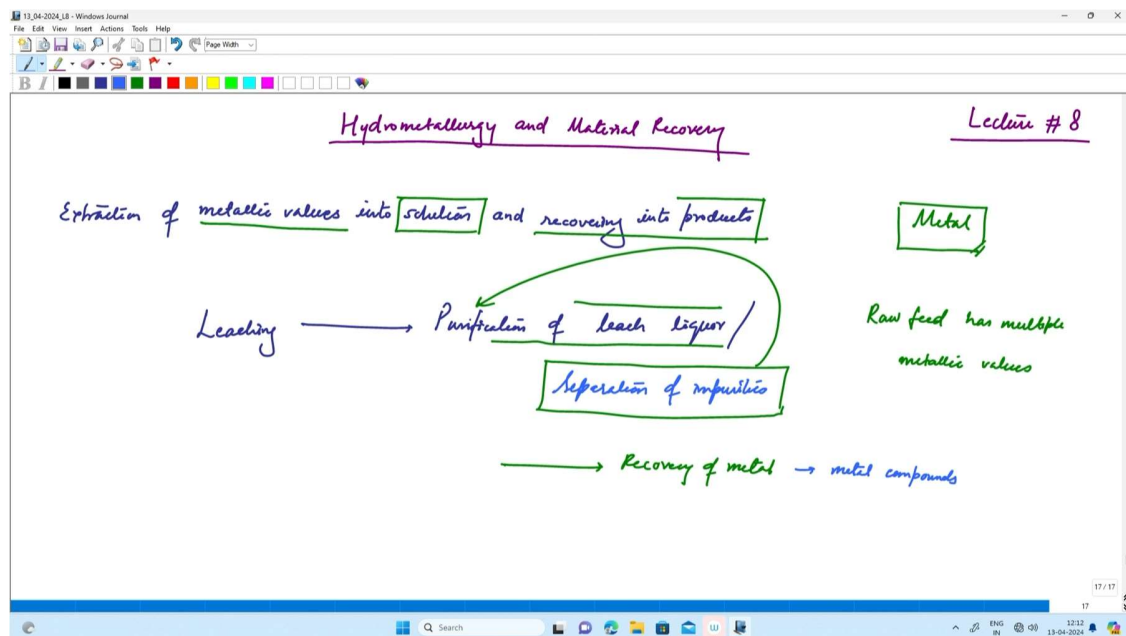
Greetings, I welcome you all to the 8th lecture of this course and in the previous lecture we have been beginning with pre-treatment followed by pyrometallurgical and electrometallurgical processes that can be used to help in recycling the various wastes and of course now we are going to look at the hydrometallurgical route of materials recycling and continuing on the idea of employing these extractive metallurgical principles for our benefit to understand and analyze and enhance the material recovery from various wastes. Now we are going to look at hydrometallurgical processes. What does that actually mean?

We are looking at extraction of metallic values into solution and recovering the products. Now in electrometallurgical and pyrometallurgical system, the resultant product was normally metal. Unless until we are trying to go into some other product but usually it is metal. But in hydrometallurgical system apart from metal itself there could be different types of products based on what is the next process after hydrometallurgical processes. For instance, the most important beginning step of any hydrometallurgical process is the leaching itself.

Leaching is basically the selective dissolution of our raw feed and what we normally do is we choose an aqueous solution and this aqueous solution is going to leach, it is going to react with the raw feed and this aqueous solution is chosen such that the raw material that we are trying to react it with, the reaction tendency should be in our favor. It could be acidic solution or alkaline solution or at times even neutral solutions like water dissolution are also taken as example of leaching. What we are trying to do here is we are trying to use an aqueous solution that can react with the raw feed that we are interested in leaching and what we get is we extract the metal because reaction is going to result in the extraction of metallic ions into the solution itself.

Now, this process is called leaching. After leaching, we can think of purification of leach liquor. Purification of leach liquor would mean that the raw feed as multiple metallic values and which would mean that if the leaching reagent can react with multiple metallic values, the extraction of metallic ions into it would be pretty much observed, multiple ions are coming in so one has to now think of which particular metallic ion we are interested in extracting. That is the reason why we need to purify the leach liquor. When we purify the leach liquor, basically we are trying to target, isolate that single particular type of metallic ion and it also means separation of impurities. When we are purifying, we are actually separating the impurities.

(Ref. 4:55)



After which we can think of recovery of metal or as I have mentioned not just metal, it could be metal rich or metal compounds. Metal rich products, metal rich compounds. Depending on what type of product we are interested in, we can switch from recovering metal to efficiently recovering metal compounds if metal compounds is the desired product again it totally depends on what was the raw feed, what was the leach liquor used, how efficiently the purification of the leach liquor was conducted, and what was the target or desired product if it is metal then one can think of adjusting the process accordingly. Similarly, if it is metal compounds, then different processes could be used.

Now let us go further. What exactly is leaching? Let us just begin with this small reaction that we have written.

We have raw feed and again this raw feed could be, since we are thinking of materials recovery, we could just go into e-waste, electronic waste or metallurgical waste. And of course, we have already assumed that the pre-treatment of the feed is performed and before the pretreatment itself again it is assumed that the sorting, categorization is done because it will ensure in concentrating the raw feed so this ensures concentration raw feed.

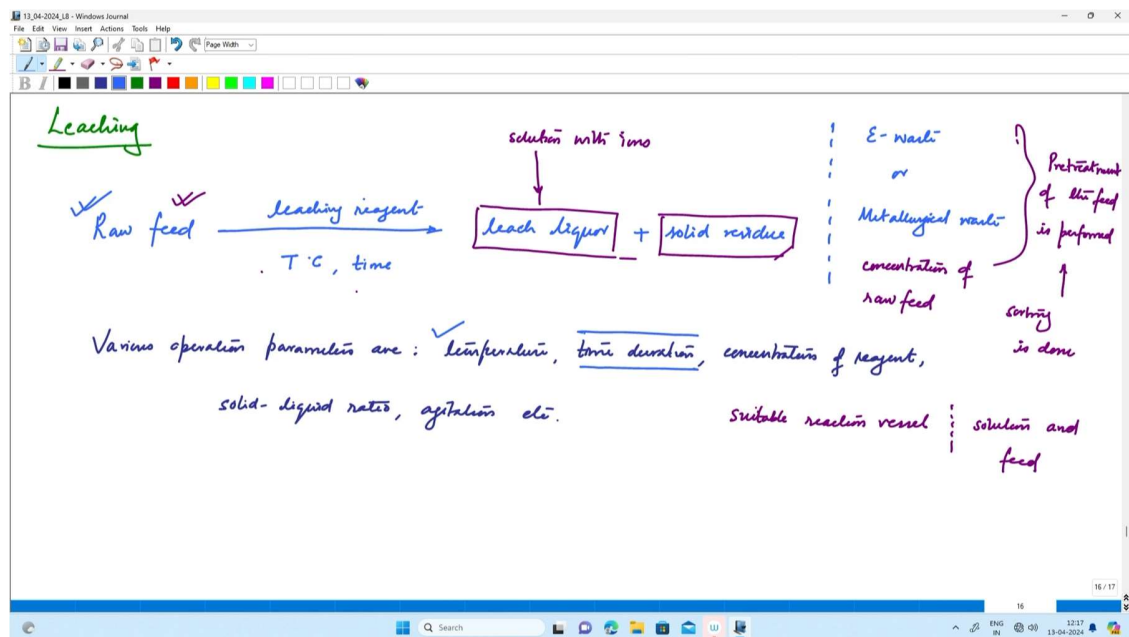
Assuming that we have such a raw feed, we use an appropriate leaching reagent. It depends upon what we are trying to make. It could be alkaline or acidic or neutral based on all of that we have our leaching reagent. We choose the temperature; the time and we normally get the leach liquor and the solid residue. So, we have the leach liquor and the solid residue.

The leach liquor is the solution with ions and the solid residue is basically the raw feed minus the metallic values that have been extracted into the solution itself. What it means is it will be separated after filtration. Right now, we are assuming that it has reacted and we have given it sufficient time for it and after that, the separation is carried out by filtration.

The leached liquor and the solid residues are separated. What are the important operation parameters that are essential in leaching step itself? We must have, of course, a vessel, suitable vessel, suitable reaction vessel that can accommodate the solution and feed. And of course, other parameters that would be applicable for the leaching operations.

These are also taken care of in a suitable vessel. What are the parameters that need to be varied for efficient material recovery? Temperature, we can have heating mechanisms or cooling mechanisms for increasing or optimizing the leaching efficiency. The time duration, how much contact time of raw feed with the leaching liquor was provided. What was the concentration of reagent?

It is normally understood that higher concentration of reagent would be more beneficial. But that's not always the case. Supposing that we are increasingly using more concentrated reagents for extracting some metallic value. It can also lead to the wastage of ions. Because there is only a limitation to which a metallic value can be extracted from the raw feed.



(Ref. 10:31)

As we have seen in the previous lectures as well, whatever process that we do, be it pre-treatment process or recycling process or after this, be it refining process as well, the partition of metallic values in the product and byproduct is always going to be observed. It will be observed almost all the time. Which means there is a fair possibility that even after we are increasing the concentration of the leaching reagent, the metallic values may not be 100% leached. What do we mean by leaching percentage?

It means what was the concentration initially and what was the concentration achieved after leaching. For instance, if we have some grams of metallic value in the raw feed, what was the recovery after leaching? Concentration in the solution upon the initial concentration. And of course, the initial concentration is going to be a larger value.

That is how we define the percentage leaching. Concentration of reagent, indefinitely increasing leaching concentration reagent may not be a very good option. Of course,

optimizing that is essential but indefinitely increasing that is not a good option. Similarly, leach to solid to liquid ratio. What is the raw feed quantity used with respect to the leach liquor volume?

That is very important. And what is the agitation? What is the agitation of the solution? It has been observed that agitating the solution using mechanical paddles or electromagnetic stirrers and such helps in improving the leaching efficiency. Types of leaching.

Types of leaching, so of course there are various types and categories of leaching based on the type of leaching reagent used the reaction vessels used batch type reactors or various types of categorizations can be provided but we'll begin with a simple classification based on the type of the leaching reagent used so acidic leaching and alkaline leaching and of course there is the neutral leaching which is basically using a neutral pH solution preferably it is water leaching and one must usually ensure that the pH of the water is as close as possible to 7.

Such leaching have been described in literature. Acidic leaching is basically utilization of an acid to recover metallic values from a given raw feed. Suppose that we have ZnO. ZnO is our raw material and we added H_2SO_4 and of course, under the required temperature conditions and agitation, we get ZnSO_4 in the solution and water.

This is basically in the solution or it could be written as Aq. ZnSO_4 . This uses H_2SO_4 as a raw material. We can also have other acidic solutions like HCl, HNO_3 and so on and so forth. When we have an acid reacting with a raw feed, so one has to identify here itself, this is the raw feed.

Similarly, instead of ZNO or Al_2O_3 that we are going to see in the next example, we can have some sort of e-waste or metallurgical waste. And we can have a variety of reagents here. H_2SO_4 , HCl, HNO_3 based upon which reagent would react with our raw feed and then the desired product would be formed. Product and of course the byproduct.

Similarly, when we look at alkaline solutions, we have let us say again the raw feed is Al_2O_3 and we have NaOH as the reagent and again similarly we can think of KOH as an alternative to NaOH sodium hydroxide, potassium hydroxide and so on and so forth Al_2O_3 is our raw feed for alkaline solutions what we get is 2NaAlO_2 and water again this is going into the solution and we are able to extract the metallic values from alumina or ZnO in both of these cases and bring this metallic content into the solution so it is

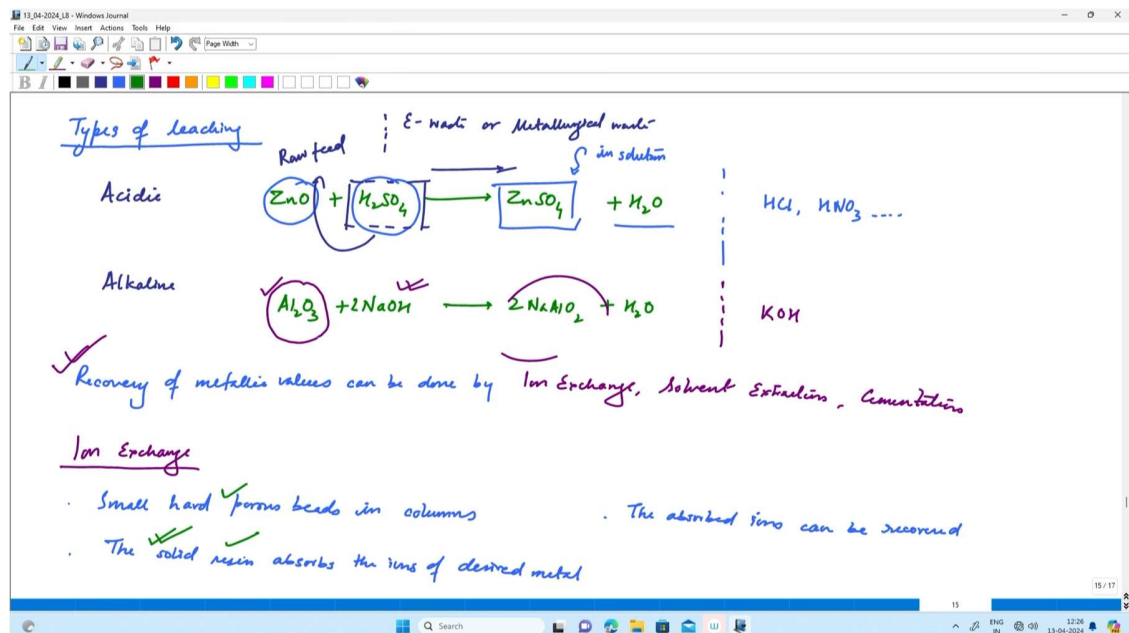
possible to extract metallic values into the solution by leaching but what happens after that so the first step of hydrometallurgy is taken care of. You take the raw material. Again, we assume that it is sorted, classified, characterized and pre-treated.

It has, let us say, smaller particle size so that the reaction itself with the leaching reagents is more dynamic. It is more easily taken care of. After that, we have the leach liquor. What do we do with the leach liquor? Because again, we as recyclers, we are interested in products that are solid, that are easier to carry.

Leach liquor contains the metallic values, but we would be interested in extracting the metal or metal compounds. Let us just discuss some of the possible next steps in hydrometallurgical processes that are essential for metallic values. One of them, these are basically ion exchange, solvent extraction, cementation. Because we are again interested in recovery of metallic values.

Ion exchange, solvent extraction and cementation. Ion exchange means we have a column with small hard porous beads. So, we have porous beads of solid resins. These resins are chemically designed in such a way that they are able to extract, absorb the metallic ions of our choice.

(Ref. 18:11)



The desired metal is absorbed on the solid resins and since it is absorbed on the solid resins, it can be recovered back. The ion exchange on the solid porous beads is possible, which is why this process is called ion exchange. Size and valency of ions are of immense importance. While we think of ion exchange, concentration of ions in the solution, it should have some minimum quantity of ions in the solution that we are trying to extract.

The temperature of the process and physical and chemical nature of the resins and the ions that we are thinking of in the solution these should be compatible. Based on that, we should be able to extract the metallic ions through an exchange. The second process that we will quickly cover is the solvent extraction. We have this schematic diagram where we have aqua solution and organic solvents and organic solvents and aqua solutions.

We will begin with this part of the diagram. This is the leach liquor that contains multiple ions. We have multiple ions here and we take this aqua solution and we bring an organic solvent extractant in contact with it and maintain the pH and temperature such that the metallic ions that we are interested in are preferentially separated into the organic phase.

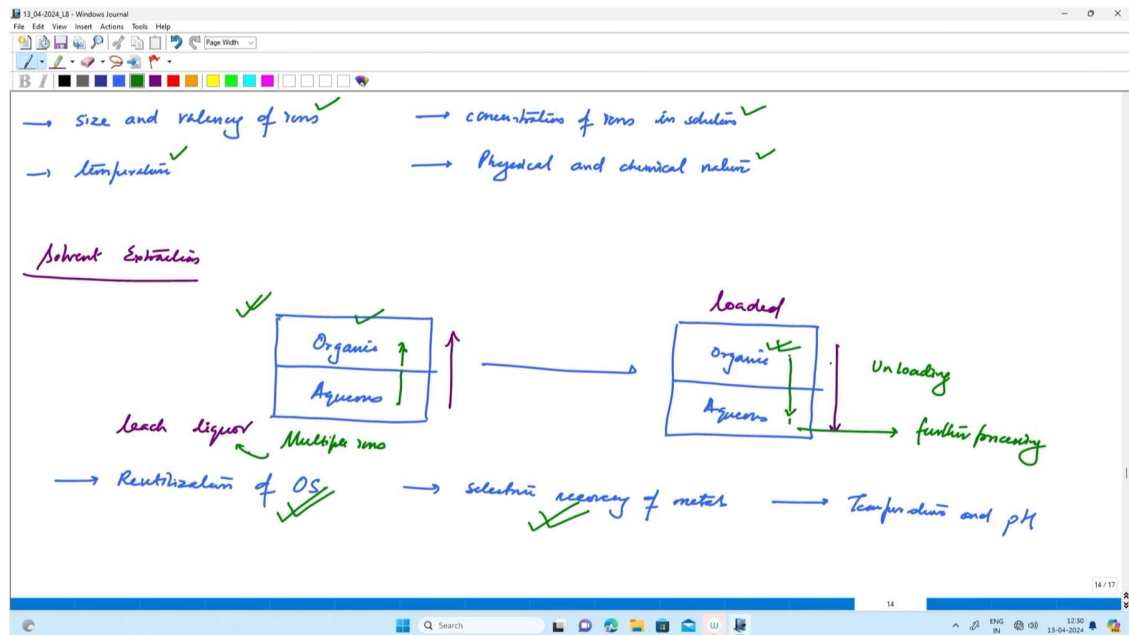
Metallic ions preferentially get taken up into the organic phase and then we separate it out. Aqueous and organic phases are separated. We prepare a separate aqueous phase which could be a different solution altogether. And since this loaded organic phase is what we have, we bring this loaded organic phase in contact with the aqueous solution which is freshly prepared.

Now what happens? The particular metal ion that is present in the loaded organic phase will get discharged into the aqueous phase. The organic phase gets unloaded here. This is basically unloading. Unloading of metallic ions from the organic phase to the next aqueous phase.

And this solution could be used for further processing. Now one might want to wonder we are moving from an aqueous phase to an aqueous phase. In between there is that organic phase. Why is it so special? We are able to selectively remove our metal of choice from this mixture of solution, mixture of ions and bring it into an aqueous phase that has the particular metal ion itself. Moving from a leach liquor that contains multiple ions to an aqueous solution that has the single or desired metal ion. The advantages of this process are we can think of reutilization of organic solvents. Again, since it is unloaded, we can reuse it. The selective recovery of metals is possible from where?

From of course the leach liquor because it contains multiple ions. Temperature and pH are very important for such operations because organic solvents, the interaction of leach liquor with the organic solvent and the organic solvent with the next aqueous solution is dependent on the pH and the temperature.

(Ref. 22:22)



Cementation. One of the most important methods for recovering metals from leach liquor is cementation. What the name normally suggests is basically it is producing cement like products. Cement like products, I mean it feels like cement like powder. When we recover the metallic values from the leach liquor using cementation it is the cement like product.

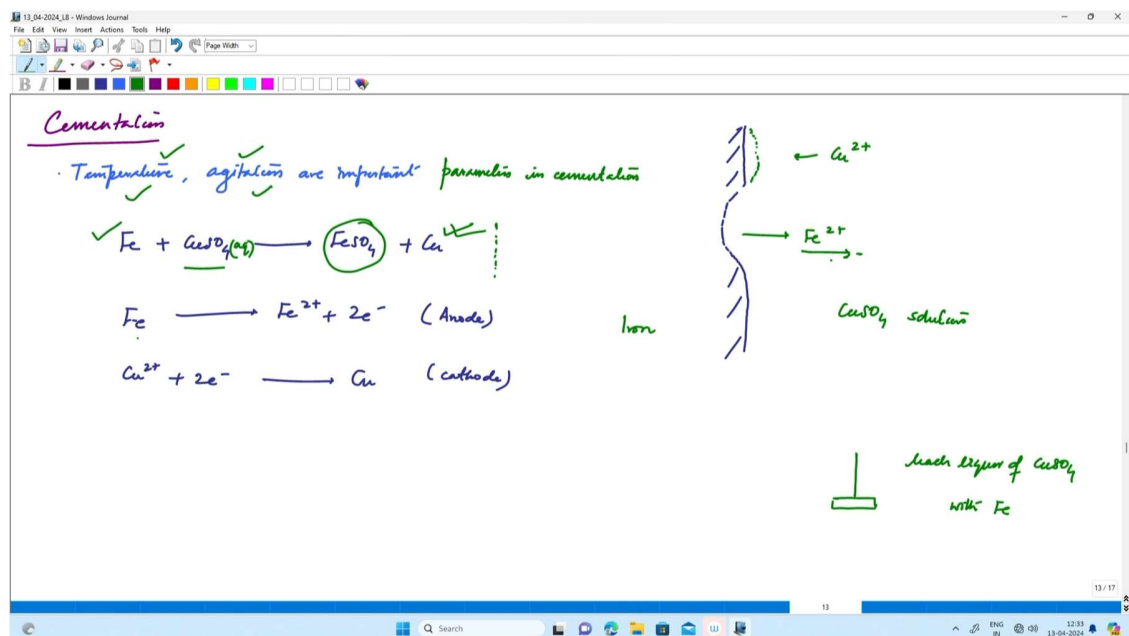
The temperature and agitation are important parameters in cementation. And what normally happens is, basically, we will take an example of iron and copper sulfate solution. Suppose that we have a leach liquor of CuSO_4 and we inserted in it disc of iron with iron. And we have maintained the temperature and agitation such that the reaction between CuSO_4 and iron is taking place.

What normally would happen here is iron would lead to the removal of, at certain spots in iron, the iron would be discharged as Fe^{2+} , iron ions. And Cu^{2+} , from the solution of CuSO_4 would get deposited onto the plate itself, onto the iron disc. The overall reaction

that has been described is $\text{Fe} + \text{CuSO}_4$, of course this is from aqueous solution, gives us copper. Iron is getting transported as FeSO_4 into the solution.

But the main target is basically copper and this copper produced on the iron disk is of cement-like texture. The anodic and the cathodic reactions are described. Iron gives us 2Fe^{2+} , plus 2 electrons. And these 2 electrons are again used for the deposition of copper, Cu^{2+} plus 2 electrons gives us copper at the cathode. What we see here is the recovery of copper from the solution on iron plate.

(Ref. 25:40)



But essentially, we are also losing iron from the iron disk itself and the iron is getting collected into the leached liquor solution. There are multiple other methods by which we can recover valuable products from leach leakers. For instance, we can think of precipitation or crystallization.

These methods are also important for recovering metal compounds actually. In this lecture, we have seen the use of leaching and the leach liquor and we are now able to think of methods of utilizing the leach liquor to the advantage of basically recovering the metal or metallic compounds. Now in the upcoming lectures we will be discussing the refining strategies

and utilizing these processes of all roots of pyrometallurgy, electrometallurgy, hydrometallurgy and of course the concepts we had learnt, the pretreatment. The concepts that we will be covering in the upcoming classes, refining strategies. We will utilize these concepts in producing the desired product from the raw feed and the raw feed could be ranging from any type of waste both in electronic waste and metallurgical waste.

The aim of any recycling process involves the efficient recovery of metals and metallic values in of course in the metallic form or in the compound form and it should benefit the environment. Selection of the process itself is of immense importance. We will be discussing this further in the upcoming classes.

Thank you.