METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-4

Lecture-19

Greetings, I welcome you all to the 18th lecture of this course. In the previous lecture we had discussed some of the wastes that are generated in copper industries and it is important to note that different types of wastes require different types of recycling strategies. Some wastes can be categorized as slags, some can be categorized as liquid wastes, it is important to treat each type of waste within each category differently because decomposition of these wastes can vary a lot.

It happens that a waste that is generated which is categorized as a type of waste can also have different types of chemical composition variation. This variation itself can be possible, can be observed within the industry itself. It again depends upon what was the raw material and what were the operation conditions and what really was generated as the waste. Chemical composition varies on so many different parameters. For instance it is a saying that if we are able to make good quality slag, we are already making good quality metal.

Similarly, one really has to understand different types of wastes. In the previous lectures we had covered the copper smelter slags and copper raffinate solutions. Raffinate solution, a waste that is similar to it is basically copper electrolyte, spent electrolyte that is generated in the electrorefining stage of the whole copper production. We already know that one has to think of the processing of ores in the beginning, the mineral ore beneficiation, the pretreatment, the smelting, reduction process, the conversion process and then finally there is the refining process.

In the refining process, the electrorefining of copper that is done at the end of copper production that stage generates the spent electrolyte and of course, one could really just reuse the electrolyte as many times as possible but at a point of time comes when these the spent electrolyte itself is reused so many times that it has to be changed and a fresh

solution, fresh electrolyte becomes necessary, the bringing in of fresh electrolyte becomes necessary. What happens if we are discarding these spent electrolytes, the solution into the environment just like raffinate solution.

Raffinate solution was produced after the initial recovery of copper was done from hydrometallurgical route. One has to understand that what are the different types of waste generated at different stages. If hydrometallurgical process was used, when we use leach liquor and this leach liquor contains the copper and other metallic content, when we recover these metallic content from the solution, it basically is lean in all of the metallic content. And finally what happens?

This solution becomes a raffinate solution. Similarly, when the electrolyte is used in the electrorefining process, what happens when all of the metallic content is being extracted? One has to think of extracting these metallic ions and some amount of the acid content is also present just like the raffinate, it is the case similar is the case is similar in the electrolyte solution as well. One has to tap in all of the metallic and anionic, cationic ions that are present in the solution so that complete recovery is achieved. A liquid waste is generated. A liquid waste is generated in the electrorefining unit which is basically called spent electrolyte. Why do we call it spent because it has already been used for multiple times and further and of course, it is understood here that further utilization of electrolyte of electrolyte as electrolyte is not possible. One might just want to wonder that the electrolyte itself could be directly used as electrolyte, it is already spent that means, It has served its purpose as electrolyte and we really cannot do much even after changing the composition by some additional additions say, for instance one might want to add some more acid into it or other metallic ions it really is not helping. When the process of electro refining is done and the electrolyte has served its purpose it is discarded.

One is really sure that you really cannot use the electrolyte as many times there is a limit and after that it is discarded. We know that and it is easy to guess that it is rich in wide variety of ions, we will see in the upcoming slides what type of ions we are looking at. Just like raffinate rich in wide range of ions good source of a raw material for extraction. Now we look at the composition of the spent electrolyte.

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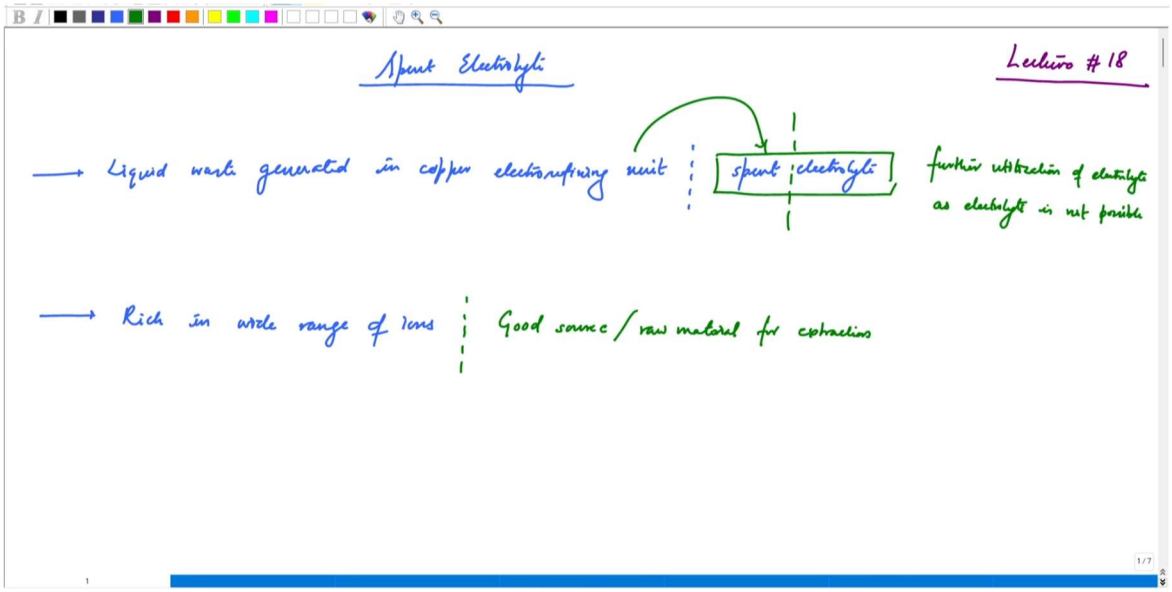

We have different components, of course, all of these metals are in the ionic form the acid is sulfuric acid we can see that at times we have different types of additional ions that can be present. As, Bi and we can also have Sb at times. These metal ions can be present in the spent electrolyte of along with copper and to some extent nickel and iron. The major contribution is coming from copper and H2SO4. It is easy to guess what type of metals are to be extracted.

First it will be copper and the whole acid itself and if it is possible we can recover As, Bi, Sb, Ni if it is present in large quantities or iron and of course, we can have sodium and other metal ions also in the solution and we have always been discussing that these the concentrations that are being described in the present content are collected from various sources and these sources present the whole content in such a way that they are trying to describe the composition, but it is possible that some solutions can have different types of metallic compositions that can be outliers that can be outside the composition ranges. It is fairly possible. We know that the presence of H2SO4 and Cu and such metallic content make it rich source of metal and acid. What should be the first thing that we can extract from the copper spent electrolyte?

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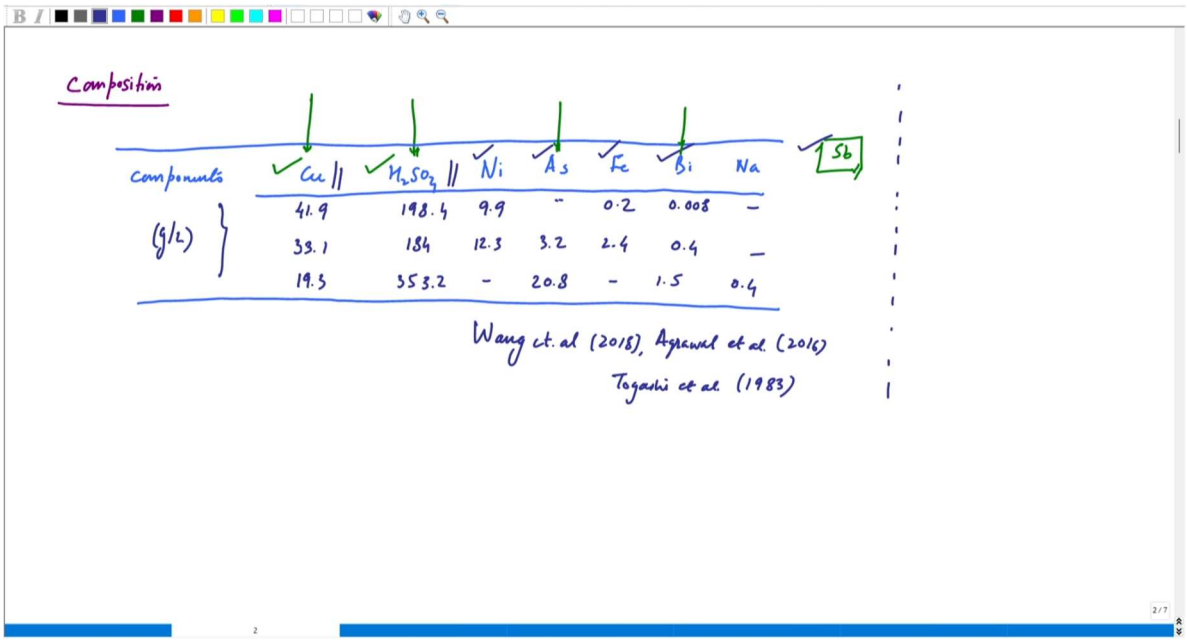

The acid itself, if somehow, we can extract H2SO4 from the solution, it is a good raw material, H2SO4 is a very common chemical that is used in all of the reagents industries. It is a common reagent for adjusting pH to actually conducting the whole reaction itself. The quality and quantity of H2SO4 that can be generated is a question but we can recover acid from the copper electrolyte. And apart from that, there is copper and nickel and iron, As, Bi, Sb, and sodium. These types of metal ions are also present which can be used, which can be precipitated in the form of sulphate and made products, solid products.

Let us just try to look at what we can do with this solution. Various methods of managing spent electrolytes. The two common methods that are easily known and these can be guessed are crystallization process and thermal decomposition. And by crystallization, we already know that we want to have heating and cooling of the solution.

This what would it do? It helps in producing and generating metal sulphates, but one of the major drawback is basically energy consumption of process is large. Energy consumption of process is large and one really has to wonder is this the right way of handling the spent electrolyte. It is one of the most common methods, but it helps in producing metal sulphates and one has to think of devising a method to separate these metal sulphates, separation process. Because these will be crystallized and these will be crystallized as a whole. Whatever metal ions are present these would be crystallized. One has to then think of extracting these sulphates separately. The separation process itself is the next step after the crystallization.

The other way could be high temperature heating basically thermal decomposition done at nearly 1000 °C in furnaces that are capable of the thermal decomposition of the electrolyte. One has to design the furnace take it up to 1000 degrees or so and the thermal decomposition of the electrolyte is done. What normally is observed is that the solution gets decomposed and from the fumes you are able to produce H2SO4. There is the generation of SO2 and SO3 gases and this helps in the formation of H2SO4.

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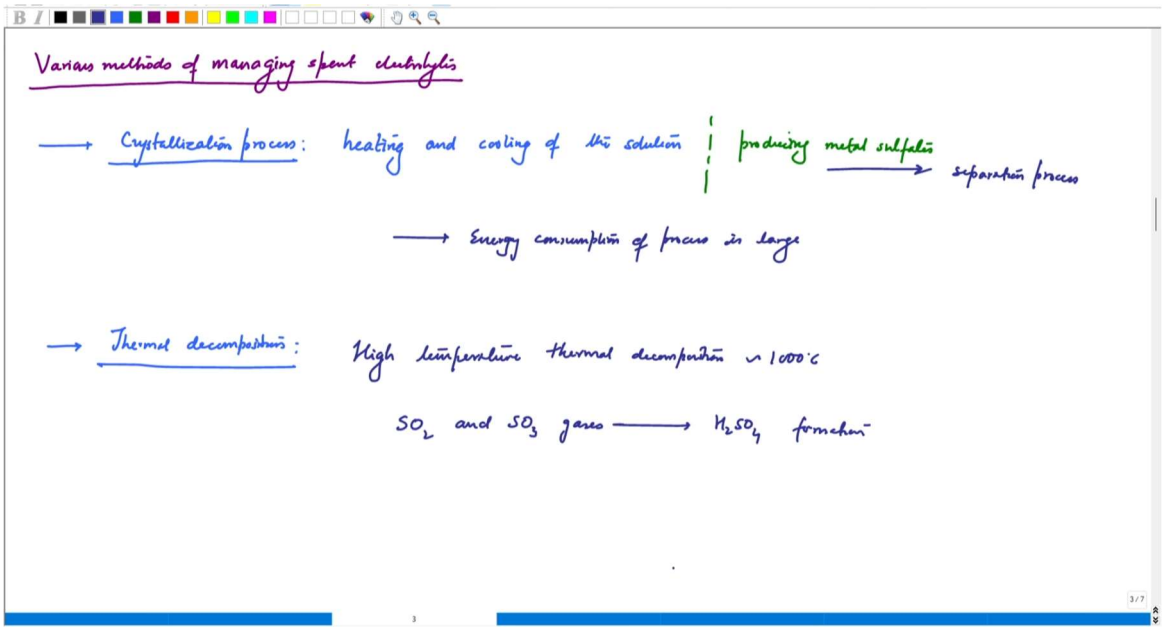


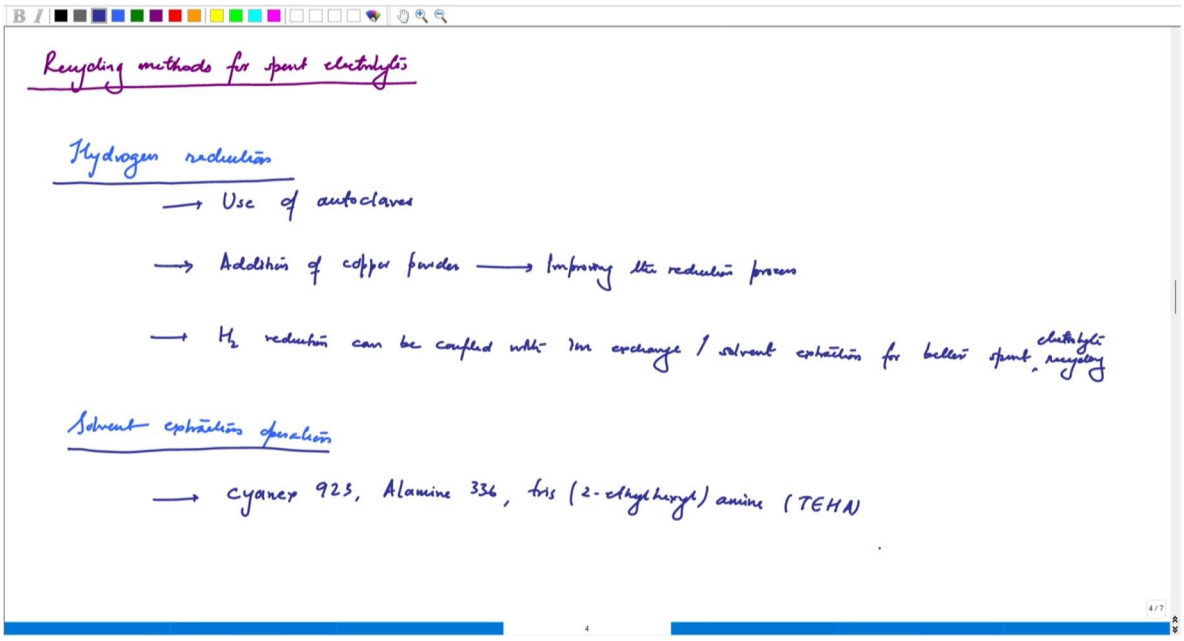
And again this is again energy intensive process consumption of energy. It is corrosive as well because the fumes that are being collected will be converted into acid and it damages the internal lining of the furnace. One has to think about making the furnace that is free from this type of interaction. What are the recycling methods of spent electrolytes? One can have hydrogen reduction.

One will really use autoclave for such a process because hydrogen has to be brought in contact with the spent electrolyte and it has to be brought in with some pressure and some temperature is maintained. Basically it is a process where hydrogen is coming in contact with the spent electrolyte and the reduction process is carried out by hydrogen. We have use of autoclaves. Addition of copper powder can help us in improving the reduction process.

Hydrogen reduction can be coupled with conventional processes like ion exchange or solvent extraction for better spent electrolyte recycling. When we have autoclaves we can insert hydrogen into it due to the pressure and temperature of parameters the hydrogen is being used for reduction and the finished products can be the metallic powders. And we can also have the addition of copper powder separately because it helps along with hydrogen,

it helps in the reduction of the metallic values that are in the spent electrolyte and with this process hydrogen reduction, With this process, we can have addition of other processes behind it. We couple hydrogen reduction with solvent extraction or an exchange for better recycling of spent copper electrolyte solution. If we have solvent extraction operations, people have explored this process extensively. And we know that it is one of the most common routes of recycling basically recovering the metallic values. Hence, it has been explored extensively and people have used a wide variety of reagents for extraction and stripping of the metallic values. Not just the metallic values, but the acid itself. If we want to recover, as we had just discussed, what exactly are we interested in? Is it copper?

Is it As, Bi, Sb or whatever? Or acid itself? One has to direct the process that way. If we wish to recover acid, we can have cyanex 923, Alamine 336, tris(2-ethylhexyl) amine which is actually TEHA. And when we have these types of reagents, solvent extraction becomes lot easier. These reagents have been used for extraction of extraction and stripping. **(Ref. 20:44)**



Extraction of acids, what acid is present in the in the electrolyte? It is H_2SO_4. These reagents help in extraction and stripping of H_2SO_4. The stripping of the acid was observed best for Cyanex 923. Cyan X923 has better efficiency for stripping. But for extraction you can now use all of these three reagents, all the three reagents Cyanex, Alamine and TEHA have been very well widely used. It is just a matter of which reagent is used for what purpose and what type of recovery are we interested in.

The recovered solution, which is basically an acid, can be used for various operations, various purposes. Like, it can be a wash solution. At times we need a solution that can be used for washing, but not essentially with a soap. Washing can be done with acid also. For instance if there are there is a material that is covered with some other coating that requires acid wash.

For such operations we can use these was these recovered acids as wash solutions. Or reutilization in the copper extraction process. Because the whole system is oriented towards reusing the acid itself, so why not recover and reuse the acid that is produced from the solvent extraction back into the copper extraction system. Just as the case for a raffinate solution we had seen the reutilization of raffinate solution as a

raw material for lean ores the same thing can be done for the acid that is produced after extraction from the solvent extraction route. Once generated you can directly reuse it in various operations. Similarly, we can have the recovery of As, Bi, Sb from spent electrolytes. It is observed that if an impure anode is used in the electrorefining operation and it has these types of metal ions associated toward As, Bi, Sb, they have the tendency of self-purification. What does that mean? It means the moment we start the electro-refining process and the anode starts to dissolve, the anode slime that is formed contains these metal ions instantly. It depends upon what type of parameters that are present in the operation itself, what is the concentration of these metal ions, how the electro-refining process was conducted. We can have the recovery of As, Bi, Sb from the spent electrolyte directly. It helps in generation of anode slime and the anode slime has all of these metals. As, Bi and Sb are precipitated in slime.

Process parameters are important. What are the process parameters? Anode composition. The anode if it has As, Bi, Sb, it can be directly converted into the anode slime during the process and we can recover these metals. Metal concentration in the solution of course,

one can change the concentration in the solution deliberately for this process for this removal basically in the solution of course, which solution are we talking of basically

electrolyte and electrorefining conditions. These are the parameters that can help in extraction of these metals from the spent electrolyte.

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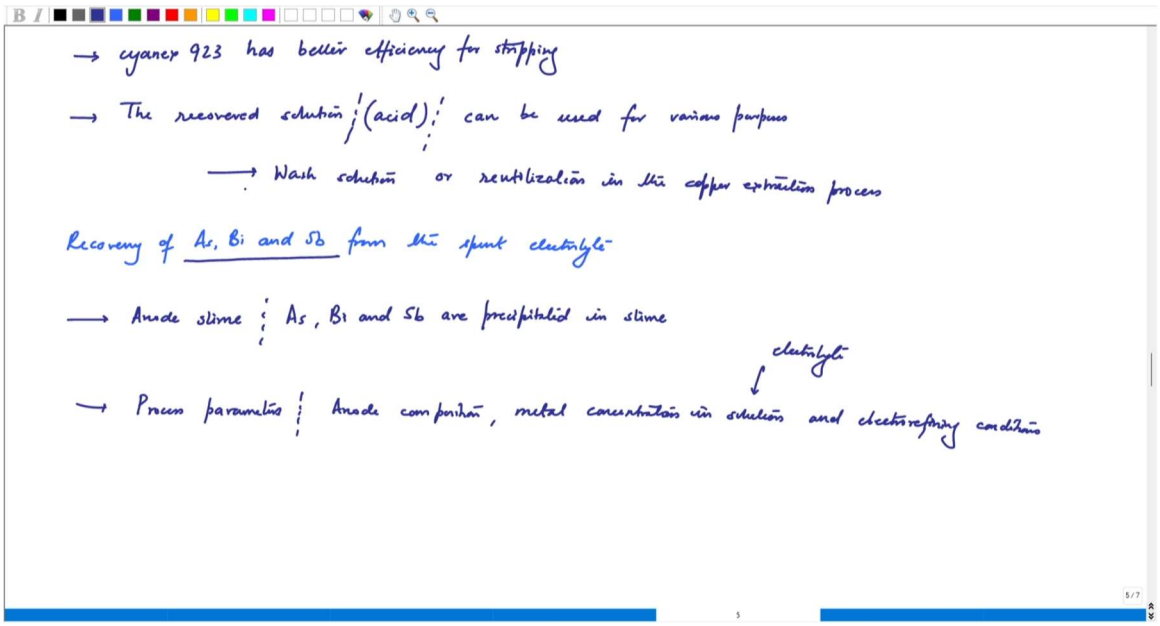

In today's class we have seen different types of processes that can be used for recovery of valuable materials from various solutions of spent electrolyte. We know that spent electrolyte is a waste that is generated in the electrorefining in step of copper refining and copper making basically a bigger stage of copper making the last stage of copper refining. And we know that this waste is rich in lot many valuable ions, H2SO4 and copper, As, Bi, Sb and so many different metallic values. We can think of devising routes that can help in the extraction of these metal ions or acid ions, acid itself and make some valuable products.

In the upcoming classes, we will be discussing more on the metallurgical waste and we will have different routes of recycling these wastes.