

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-4

Lecture-18

Greetings, I welcome you all to the 17th lecture of this course, where we will now be discussing and continuing on what we had started in the previous lectures. So, when we started discussing metallurgical waste recycling. And, we started going into the metallurgical wastes, we have covered aluminum dross and aluminum slag and the aluminum industry wastes including red mud. And, we were discussing on copper wastes, and we have covered copper smelter slag and we were discussing copper raffinate solutions. Now, we will continue on our discussion on raffinate solution recycling.

We had seen that in the previous lecture that there are a wide variety of ions that are present the metal ions, the ions that are present that contribute towards the metallic content as well as the non-metallic content, the sulphates that are present. These ions are basically making the solution hazardous and the recycling of these solutions is of utmost importance. So, what do we mean by developing a good recycling strategy. We have already discussed that it is important to understand the raw material itself.

When we have seen the composition of the raffinate solution, we understood that the metallic content in the raffinate solution can be safely extracted. Similarly, the sulphate ions can also be somehow extracted. Let us now look at some of the important strategies that can be used for recycling the raffinate solutions. Before we go there, we would now try to look at some of the environmental impacts that are associated with improper disposal of the raffinate solutions. It is very well understood that industries are oriented, industries have invested on the methods of utilizing the raffinate solutions.

But one must also think what actually happens when we are trying to discard and when we try to dispose of these raffinate solutions without any pretreatment. Without pretreatment, without any mitigation methods where if we just release these solutions into the environment what can happen. We know that a variety of ions are present in the

solution and these are some of the metals and metal ions that can be and the sulphate ion that are present in the solution and we have seen the composition. If this type of composition is present, these metal ions are commonly present in the raffinate solution.

We know that a major chunk can be iron and sulphur and to some extent since we are actually looking at a copper solution. We know that copper can also be present to a good amount of extent, iron and sulphate. The safe disposal becomes necessary. If it is present then it's an opportunity to recycle and it is a good source of metallic values. The question comes is it possible to extract some material from a solution?

We already know that the good methods that are present are basically solvent extraction, we have cementation, precipitation, ion exchange and if at all, we would like to include we can also have crystallization. In today's class we are actually looking at raffinate recycling. A similar solution that we will be discussing in the upcoming classes is basically the spent electrolytes. When we look at spent waste electrolytes and where are these electrolytes coming from electrorefining.

These electrolytes are basically electrorefining waste of electrorefining process. When we know that these types of solutions are present and these electrolytes are also in liquid form and we know that the raffinate is also in liquid state, then the recycling process is pretty much common. Solvent extraction, cementation, ion exchange, precipitation and crystallization, these processes are roughly used one after the other or standalone and these can be used in both of these types of wastes.

And we will be discussing on spent electrolytes or waste electrolytes in the upcoming sessions. Various processes are developed for safe disposal and extraction because we know that it is a good source of metallic values and disposal of these ions directly into the environment really is hazardous. Because we have cadmium, we have iron, we have the sulphate ion itself and these ions are really hazardous when we are trying to dispose of without reducing the concentration of these ions. Safe disposal and extraction is really important.

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Raffinate Recycling

Lecture # 17

Environmental Impacts

- Variety of ions present in the raffinate
- Safe disposal necessary
- Various processes developed for safe disposal and extraction

commonly present in the solution

SO_4^{2-}

Fe

$, Zn, As, Cu,$

Cd

Good source of metallic values

Solvent extraction, cementation
precipitation, ion exchange
crystallization

spent / waste
electrolyte

electrorefining
process

What are the methods of recycling? Recovery of iron from raffinate, as we had just discussed, it's either precipitation, solvent extraction, cementation, ion exchange or crystallization. The methods of recycling would like to include these in one form or the other. Chemical precipitation and coupling it with or making it standalone with ion exchange. If we are making a phase called jarosite and the iron can be entrapped in the jarosite phase, we have seen that the precipitation becomes lot easier and it generates higher percentage of iron. It has been reported that nearly around 70% of iron can be recovered by jarosite precipitation.

When we know that the precipitation process is being carried out, temperature and pH are important parameters. We know that in every step of recycling process there are important parameters that govern and direct the overall efficiency of process. We know that pH and temperature are important parameters here. A range of temperature that has been observed for chemical precipitation of jarosite that entraps iron from the raffinate solution is basically, it's around 70 to 90-95 degree Celsius and pH could be of the range of 2 to 3. These ranges can differ, but it is seen that these are important parameters and it helps us in achieving the desired product. Using this precipitate some other valuable product can be made. This is not the end, basically we would try to recover metallic values from the precipitated phase.

(Ref. 11:05)

Methods of Recycling

Recovery of Fe from raffinate \rightarrow chemical precipitation
(A) and (coupling with) ion exchange

Jarosite precipitation \rightarrow Higher Fe recovery
 $\sim 70\%$
 \downarrow
Recover metallic values from this precipitated phase.

These are important parameters that direct the overall efficiency of process

70-95°C 2-3
Temperature and pH
are important parameters

The next method that can be understood is formation of nanoparticles using the raffinate solution. What type of products are we making depends upon the processes that we are employing and it is the other way around as well. Many a times we are more oriented towards developing a process for a fixed type of product. So, it can be thought in both the ways. We can think of devising a process which can give us some sort of product or we can go the other way around as well. For instance, if we have a product in our mind and then we can insert the necessary processes so that we can achieve that type of product. If we wish to make nanoparticles. How do we go about with this? Magnetite (Fe_3O_4) nanoparticles using copper raffinate solution.

We take the raffinate solution and we have the reduction stage where we are reducing iron(3) ions to iron(2) ions, the change of valency basically and then we have the precipitation stage where we are removing aluminium from the solution. One might wonder do we have large quantities of aluminium in the solution? The answer is no but it affects the formation of nanoparticles.

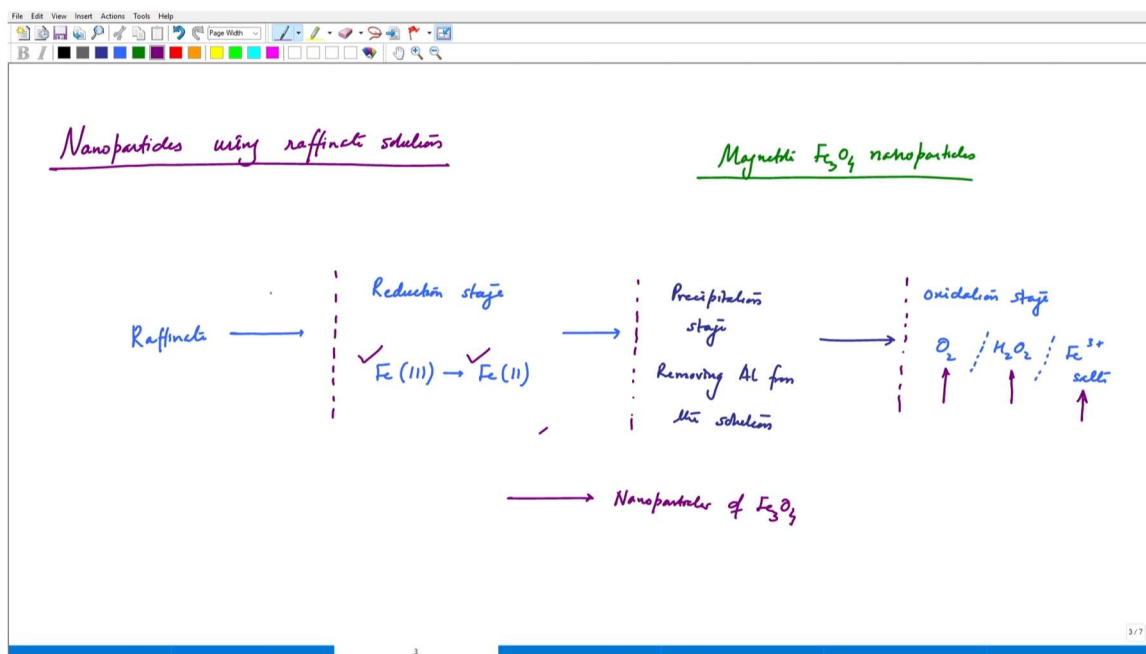
If during the process of making nanoparticles, some amount of aluminium is present, then it can affect the whole process itself. Multiple stages are being performed in order to achieve higher efficiency and quality of the finished product. In this case it is

nanoparticles. Magnetite (Fe_3O_4) nanoparticles is the required product and the hindrance that people have found is the presence of alumina/aluminum.

One has to avoid that. The necessary step that becomes a part of the process is removal of aluminium from the solution so that the formation of nanoparticles becomes easier. And finally, the oxidation stage where one can use different types of reagents & finally we get nanoparticles of Fe_3O_4 . Let us just understand what exactly is happening. We have the raffinate solution. The first thing that we would like to do is change as many Fe^{3+} ions to Fe^{2+} ions. This is reducing stage. We are trying to convert Fe^{3+} ions to Fe^{2+} ions.

The oxidation stage has its own set of parameters like pH, temperature and all the related parameters. So, it is necessary to have those ions converted beforehand. After that, we have the precipitation stage. We have already discussed. After this, we need to remove aluminium because it can cause hindrance and after that, the actual oxidation is being carried out. We have Fe^{2+} ions which will be converted to Fe_3O_4 . The last step is basically just oxidation and during the oxidation the formation of nano particles is taking place. What type of oxidation processes are available? We can use the addition of oxygen or we can have the addition of H_2O_2 or one could simply just increase the concentration of Fe^{3+} by introducing Fe^{3+} type of salts into the system and this helps in the generation of the nano particles that are the required finished products.

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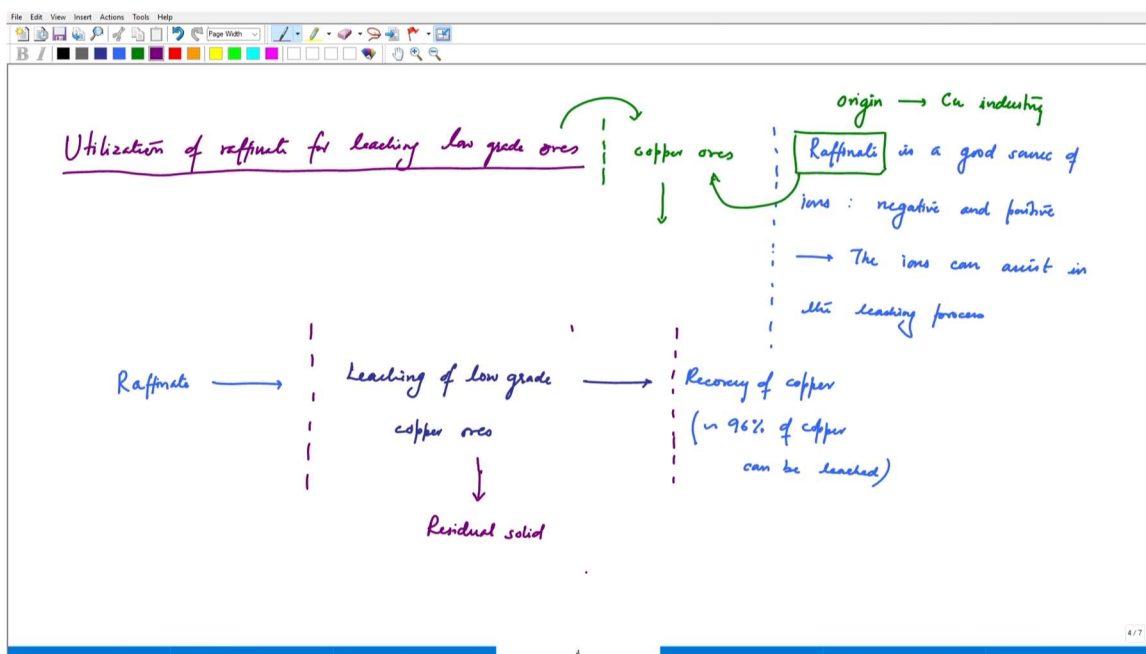
We will now look at the utilization of raffinate for leaching of low grade ores. What does that mean? It means that it is just as simple as it is written. The raffinate as we have seen is a good source of ions and all types of ions. It can have negative ions as well as positive ions and anions and cations. We have both types of ions present in the raffinate solution. It is a good source of ions which means it can still react. The ions can assist in the leaching process.

And raffinate is in the aqueous medium. One really just needs to adjust the acidic content. One can think of adding some more acid into it if it is required. Low grade ores which can have relatively lesser quantity of copper because this raffinate solution originated from copper industry. We know that origin of raffinate is basically copper industry.

One would really like to use this raffinate solution in leaching of low grade ores of copper ores. If the concentration of copper in the ores is relatively very less, this raffinate solution can be used as a raw material for leaching these ores and would get the metallic content. Let us just redraw, we have the raffinate. We have taken the raffinate and we leached it with low grade copper ores.

And what exactly are we doing? We are bringing this raffinate in contact with the low grade ores allowing it to react with it and tapping out the leach liquor. It will also lead to the generation of the residual solids. And some amount of copper mist will be left in the residual solid. But it has been reported that as high as 96% of copper can be leached.

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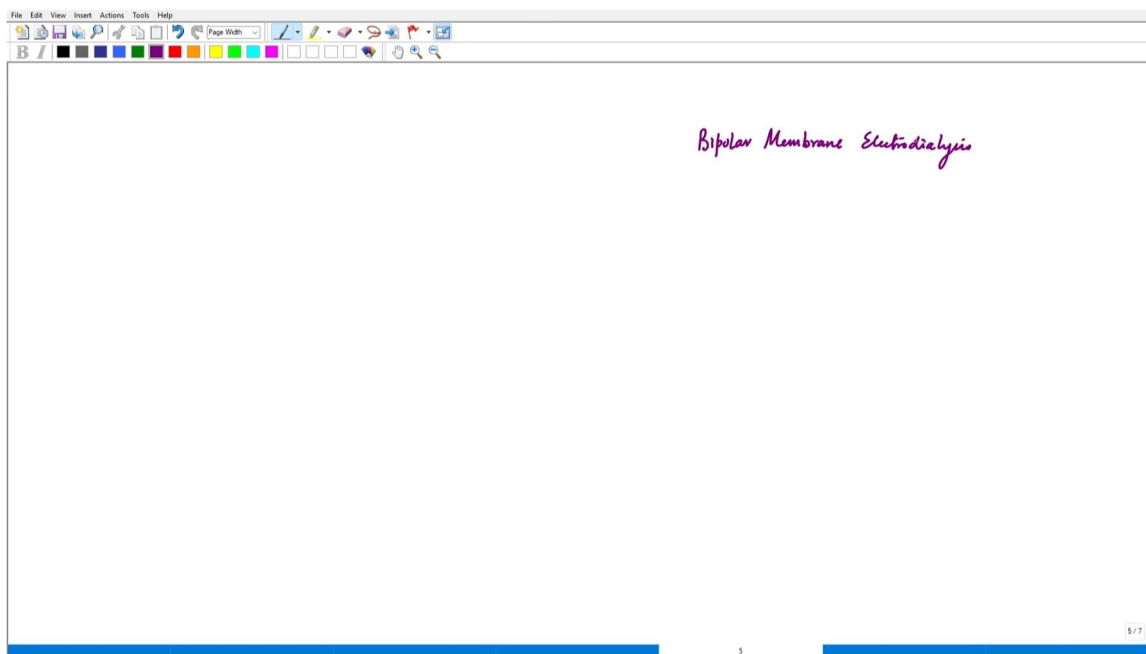
Just by using a waste solution that contains the ions, it is possible to extract a really good amount of metallic content from low grade ores. Low grade ores which are normally used by hydrometallurgical processes. What happens it is just a common way of understanding that the higher concentration of metallic values, the ores that have these types of metallic values are normally subjected to pyrometallurgical route.

If the metallic content is relatively very less then these lean ores can be subjected to hydrometallurgical processes as these processes really do not require high temperature and it is the process economics and process speed. In hydrometallurgical processes the leaching process can be taking up relatively larger time compared to the pyrometallurgical processes. These are the differences that can be seen in hydrometallurgical processes as well as the pyrometallurgical processes. It is seen that lean ores are subjected to hydrometallurgical processes because the extraction of metallic values from lean ores is relatively more easier in hydrometallurgical processes.

One might want to discuss this that it is also possible that you can use lean ores in the pyrometallurgical route as well, but the amount of other phases, the other minerals, the gangue minerals that are associated with the lean ores, these are relatively in very large quantities. One has to invest a lot on the pretreatment of the ores itself so that they are made more fitting for the pyrometallurgical process. It becomes a little bit more easier on the hydrometallurgical process.

Just the same concept is being used in this process as well. Instead of having a fresh acid solution, one could use the raffinate solution and adjust the concentration of the acid as per requirement and then subject the whole process of leaching. And then what it does, it helps in the extraction of metallic values such as 96 percent can be recovered from these low grade ores. There is an important other process that we can think of and which helps in recovering metallic values and the anions and cations that are present. We will just discuss this in brief. It can be referred to as Bipolar Membrane Electrodialysis.

(Ref. 25:07)



Some of these processes that are being discussed in the course are being explored on laboratory scales. One has to be considering the fact that it is a process that can be used on a lab scale and some of these processes can be scaled up. Bipolar membrane electrodialysis is one of those processes that are being investigated.

What we know is that there are membranes and the solutions are inserted in various cells and then these membranes are helping in extracting the ions in different compartments that can be arranged across these membranes. We know that such type of membranes, we had mentioned in the previous lectures also, are polymer inclusion membranes, liquid membranes, ionic membranes, ionic-liquid membranes. These membranes are helping in extracting the required metallic or anionic or cationic whatever types of ions these are targeting. These ions are captured and transferred to the other solution that is on the other part of the membrane. Many a times one has to supply electricity and at times since this process is electrodialysis it is easy to understand that one will be supplying electricity across the solutions. We will have separate electrodes and it will help in the movement of ions, but at times for instance in many other inclusion membranes or other membrane processes, one really does not need the electrodes and one really does not need the current to be flown. It is just the concentration of ions in the solution that helps in removing the ions from the solution and these are selectively picked up and then

transferred to the next solution. These types of processes are also present in the current literature that helps us understand that raffinate solutions can also be recycled by not conventional processes only. We already know that if one has to tap on the metallic content and the anionic content, the cationic content of the raffinate solution may be, and one can follow the conventional processes. Solvent extraction, ion exchange, precipitation but there are other processes also. The direct utilization of raffinate is one of the common routes that are being employed for good metal recovery. In the upcoming classes, we will be looking at some other wastes of copper industries.

Thank you.