

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

Dr. Arunabh Meshram

Department of Materials Science and Engineering

Indian Institute of Technology Kanpur

Week-2

Lecture-8

Greetings, I welcome you to the seventh lecture of this course. So far, we have been discussing on pre-treatment of raw materials. We have discussed various types of raw materials in both the metallurgical wastes and electronic wastes and now we are going into various recycling processes which are mostly extractive metallurgical in nature. In the previous lectures we have seen pretreatment and pyrometallurgical processes in this class.

We will be focusing on electrometallurgical processes and we will see how these processes are useful in materials recycling. When we think of electrometallurgical processes, just like pyrometallurgical processes, these are routes which can be utilized for our specific requirements. Normally, when we think of electrometallurgical processes, our resultant product is metal. We can start with some other raw material that we have produced and then using such raw materials, we can employ our electrometallurgical concepts to extract metallic values. Let us just look at the processes.

What are the key requirements for any electrometallurgical process? The first thing that normally comes to mind is the source of energy. So when we think of source of energy, the constant supply of energy, electrical energy of course, is very important. One has to think of constant supply. Constant and of course stable supply of energy.

That is very important. And the next most important thing is the electrolyte. When we think of electrolytes, we can normally have two different categories. Aqueous electrolytes and fused salt electrolytes and of course based on these electrolyte types we can have different types of electro metallurgical processes aqueous electrolytes of course means it will be water based and fused salt electrolytes would require salts like NaCl, KCl, Cryolite and such which can be fused at higher temperatures, which can be brought down to molten state at higher temperatures and then the extraction of our target metal can be achieved. Fused salt would require salts in molten state. This essentially means that the

temperature requirement for various electrometallurgical processes would vary because aqueous electrolysis would not require high temperatures. These can be carried out at near to ambient temperatures and the recovery of metal is also achieved. However, fused salt electrolysis or fused salt electrometallurgical processes would require high temperatures as per the requirement of the process.

For instance, if we look at Hall-Heroult process, the temperature requirement could be higher than let us say 960 degree celsius and it could range to around 960 to 980 or 990 depending upon the optimization in the operational plant. Again it is focusing on the temperature requirement of the electrometallurgical processes. What type of electrodes are we using? So, of course, type of electrodes, anodes and cathodes, chemical composition, these are important when we are thinking of electrometallurgical processes.

And of course, the next most important thing after considering these points is the electrometallurgical cell. The cell is supposed to be free from chemical reactions and interactions with the surrounding. It has to be such that when we are using an electrolyte, maybe at ambient temperatures or at higher temperatures, the cell that is being used for the electrometallurgical process should not itself start reacting with the raw materials that we are using. What would that do?

It's basically going to interfere with the finished product. So, cell design is one of the most important challenges that people are facing while developing electrometallurgical processes. We have seen the key requirements for any electrometallurgical process. One has to think of constant source of energy as per the process requirements. (Ref. 7:00)

The image shows a digital whiteboard with handwritten notes in blue and green ink. The title at the top center is "Electrometallurgy and Materials Recycling" and the top right corner says "Lecture #7".

Key requirements for electrometallurgical process

- source of energy ✓
constant supply
- Electrolyte
- Electrode
Type of electrodes
chemical composition

Type of electrometallurgical cell
depends on the process

free from chemical reactions

Electrolytes

- Aqueous : Water-based
- Fused-salt : salts in molten state

The whiteboard interface includes a standard toolbar at the top with icons for file operations, editing, and drawing. A status bar at the bottom right indicates "1/28".

The type of electrolyte that we are using either it is fused salt electrolysis or aqueous electrolysis and of course the type of electrodes that are being used the chemical composition, anodes and cathodes and based on all of this and supporting the most important, the electrometallurgical cell that encompasses the electrometallurgical process. We now move towards the classification. This is basically classification of electrometallurgical processes.

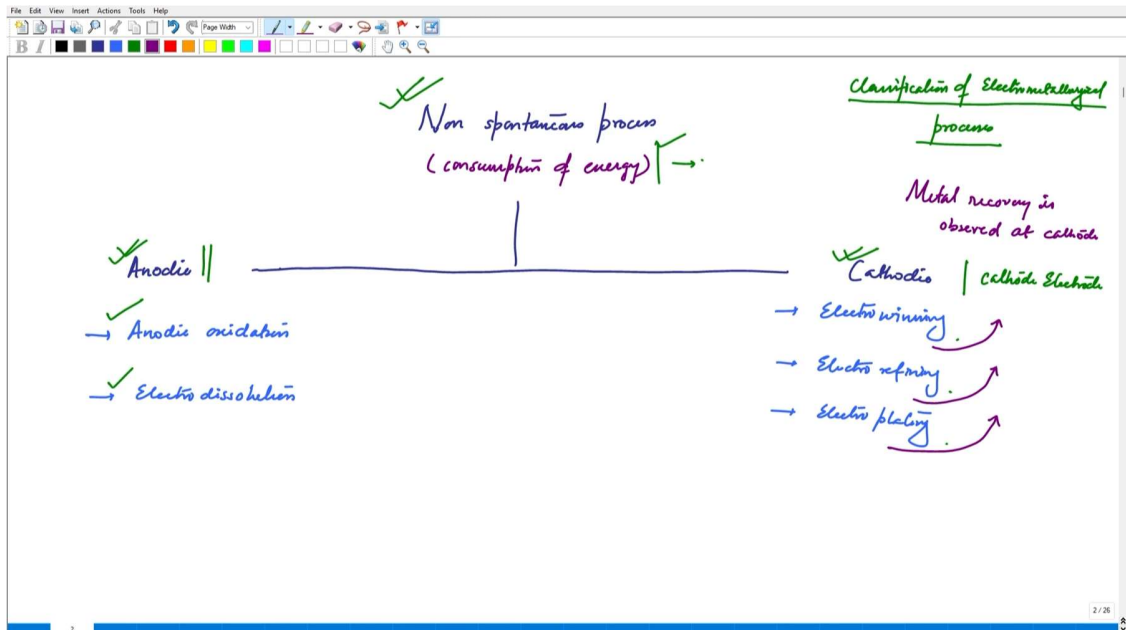
We are looking at non-spontaneous processes. What does that mean? It means that we are supplying energy. The energy is input and consumption of energy is observed. Consumption of energy.

This was of course the requirement that we had, one of the key requirements of electrometallurgical processes. Now when we think of categorizing it, these can be categorized as anodic or cathodic processes. When we think of anodic processes, these would be more dominant on the anode of the whole electrometallurgical cell, most of the processes would involve the anode. When we think of examples of anodic processes, we will have anodic oxidation.

Suppose that we have the two electrodes and the anode is getting oxidized. Such a process would be anodic oxidation and the another example could be electrode dissolution wherein the anode itself is getting dissolved into the electrolyte. Such processes are basically anodic processes because the key operation is observed. The key step is observed in the anodic electrode.

When we think of cathodic electrodes, we have multiple processes that are focusing on the cathode electrode. Normally, we see processes like electro winning, electro refining and electro plating, which means metal is getting, as we have already mentioned in the beginning of this lecture, metal recovery is at cathode. When we say that the metal recovery is observed at the cathode, what we are seeing here is the electrowinning, electrorefining and electroplating. Depending on the type of process that we are following, we can have these types of categorization. Electrowinning would mean that the electrolyte is the source of the metal and of course the electrolyte is made such that it is conducting and using the electrolyte we are able to recover metal onto the cathode.

(Ref. 10:50)



Electrorefining would mean we have an impure anode which is getting converted to pure cathode and the dissolution is taking place at the anodic side, it's going into the electrolyte, the metal is going into the electrolyte and then getting deposited and so on and so forth for various cathodic processes. The main idea of this bifurcation of non-spontaneous electrometallurgical processes is on the basis of the electrodes that are being used. And of course, in the previous, just now we have seen that based on electrolytes as well, there is the division.

Fused salt electrolysis as well as aqueous electrolysis. Let us go there as well and before that, we should also be focusing on the properties of electrolyte. High ionic conductivity. Ionic conductivity should be high and it should be dependent only on ions and not the supply of electricity. The conductivity should be due to the ions present in the electrolyte.

And at times people have arranged the addition of ions to make it conducting. So, apart from the metal that is present in the electrolyte, we can have addition of ions separately to make the electrolyte more conducting. And the next thing should be, it should be inert towards the electrodes. The electrolyte should itself not start reacting with the electrode.

And similarly, the electrode should be chosen in such a way that the electrodes do not react with the electrolyte itself. Such conditions are essential. The electrodes and electrolytes should be such that they are chemically inert. The next most important thing,

property of electrolyte is stable at operation temperature of process. Stable at temperature of process.

Operation temperature is very important. And we have already seen that the temperature of a process governs whether a process is feasible or not. Suppose that if we are applying high temperatures, extremely high temperatures for aqueous electrolysis, it can assist in speeding up the process, but it would start gradually decomposing the electrolyte itself. Aqueous electrolysis need not be carried out at very high temperatures.

Similarly, a very low temperature for fused salt electrolysis is not going to melt the salt mixture itself. So, the process would not begin. Appropriate temperatures are of immense importance when we think of electrolytes because electrolytes themselves are categorized as aqueous electrolytes and fused salt electrolytes so they have their own different regions of thermal stability. Solution containing the metal should be more stable than solute.

Of course this is talking about the electrolyte itself. And the solute is the target metal, target metal and its feed that we are using in the solution. The solute would comprise of the metal ions and these are present in the solution and it means that the solution should be more stable. If that is not the case, then the electrolyte itself would start to decompose under the supply of electrical energy. The stability of electrolyte is of immense importance, both temperature wise as well as composition wise.

Now, we look at the categorization of electrolysis, the processes by which we can extract metals into the metallic form. Fused salt electrolysis is now what we are trying to see. We have water-free salt mixtures. Water-free salt mixtures and salt mixtures would require, say for instance if we have cryolite and some other addition, NaCl, KCl, KBr. These types of salt mixtures could be used for the extraction of metals.

High temperature operation, just now we have seen the stability of temperature and again we are seeing high temperature operations. And we know that the prime example of fused salt electrolysis is basically aluminium extraction. The conventional Hall-Heroult process, which utilizes the raw material from the Bayer process. We have Bayer process and then we have the Hall-Heroult process and this is one of the most important examples of fused salt electrolysis. It uses cryolite as the electrolyte and here we are able to dissolve nearly 4 to 8 % of alumina and then we are able to extract aluminium from this molten bath. **(Ref. 18:17)**

Properties of Electrolyte

- High ionic conductivity *✓* dependent only on ions
- Chemically inert towards electrodes
- stable at temperature of process operation temperature addition of ions → conducting
- Solution containing metal should be more stable than solute Target metal

Fused Salt Electrolysis

- Water-free salt mixtures used for extraction of metals. Bayer Process → Hall
- High temperature operation Example: Aluminium extraction. Hall Hemmett Process

There are some key disadvantages of fused salt electrolysis. Of course, it is one of the most important methods by which we can extract metals so, if we have a molten bath that contains our metallic ions, we should be able to extract the metal under the required temperature, composition and electrical energy. The constraints that we supply, we should be able to extract the metal, but there are some disadvantages.

The mechanical losses at the electrodes. This is talking about the handling losses. The product that is produced may be lost at the electrodes if not handled properly. One has to think of material removal because now if the product is produced it has to be removed from the vicinity, from the system. The next important disadvantage that people have observed is the chemical side reactions.

Mostly, the desired reactions can have side reactions due to the presence of multiple ions and of course, these are taking place at high temperatures. So, if some reactions are not happening at high rates at lower temperatures. These can happen at higher temperatures with a very high rate. The tendency of having side reactions is very large. It is pretty common.

So, how can we avoid that? Choice of electrolyte and operation temperatures. Choice of the electrolyte, the composition of electrolyte, what are the key salt mixtures, what are the key salt mixture components that we are using and what is the temperature range in

which the salt mixture is being used. These are very important parameters that can help in reducing the side reactions.

Of course, it is very difficult to completely avoid side reactions, but we can control to some extent by using these important methods. Choice of electrolytes and the optimization of temperature. And of course the third most important challenge that has been described is the recombination of products. It is fairly possible that the products that are produced in the electrochemical cells, electrometallurgical cells, these can be brought back into the electrolyte. If this type of recombination of product is happening, the overall efficiency of product gets reduced.

It is essential to think of processes in such a way that the recombination of product is avoided. This can be done by designing the cell to ensure the recovery of finished product. The isolation of the electrolysis product by special provisions. What do we mean by special provisions is that basically we are designing the cell itself in such a way that the electrolysis products are easily removed again it looks like these disadvantages, these challenges are more or less interconnected.

(Ref. 23:55)

Disadvantages of Fused Salt Electrolysis

- ✓ Mechanical losses at electrodes (handling losses) | Material removal from the system
- Chemical side reactions Presence of multiple ions, High temperatures
- ✓ Recombination of products

Designing the cell to ensure the recovery of finished product

Isolation of electrolysis product by special provisions.

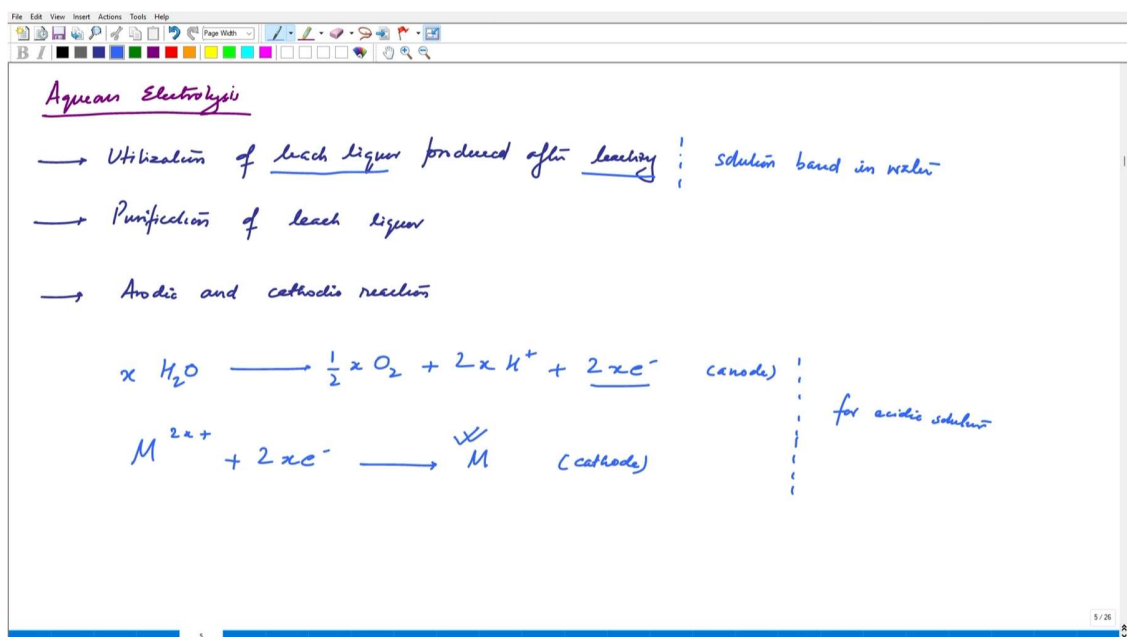
One has to think of the cell. That is the reason why we have begun with the discussion on the type of cell itself. The cell depends on the type of the electrometallurgical process.

We will quickly look at the aqueous electrolysis as well. The utilization of leach liquor produced after leaching.

Of course, we will be looking at the leach liquor that is produced by leaching and this will be covered in the next class. But you use the leach liquor which is solution based in water. And you purify the solution, of course the leach liquor, and you have the anodic and the cathodic reactions. The anodic and the cathodic reactions are described here. We are able to extract electrons which are used at the cathodic side to get the metal.

When we think of electrochemical and electrometallurgical processes it is very important to think of these as tools for metal extraction while we know that our processes have some advantages and disadvantages and these can lead to the generation of various waste like spent pot lining is a waste that is produced when the pot lining itself gets damaged. We can have the electrode stub wastes, we can have spent electrolytes.

(Ref. 25:48)



The image shows a screenshot of a presentation slide with handwritten notes in blue ink. The title is "Aqueous Electrolysis". Below the title, there are three bullet points: "Utilization of leach liquor produced after leaching", "Purification of leach liquor", and "Anodic and cathodic reaction". Below these, there are two chemical equations. The first equation is $x H_2O \longrightarrow \frac{1}{2} x O_2 + 2x H^+ + 2x e^-$ (anode). The second equation is $M^{2+} + 2x e^- \longrightarrow M$ (cathode). A vertical dashed line separates the two equations, and to the right of the dashed line, it says "for acidic solution".

Aqueous Electrolysis

- Utilization of leach liquor produced after leaching : solution based in water
- Purification of leach liquor
- Anodic and cathodic reaction

$$x H_2O \longrightarrow \frac{1}{2} x O_2 + 2x H^+ + 2x e^- \quad (\text{anode})$$
$$M^{2+} + 2x e^- \longrightarrow M \quad (\text{cathode})$$

for acidic solution

These type of wastes are basically generated when we are looking at electrometallurgical processes. But at the same time, we have advantage of extracting the metal in its nascent metallic form using these electrometallurgical processes. We will continue in the next lecture. Thank you. .