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Lecture – 12 Metal Recovery Process

So, welcome back. So, we will continue our discussion on recovery of metals from electronic waste that we have been talking about in this particular week so far. So, this is the second module of the third week. So, you have seen this, this was the last discussion we had in the previous video, we were trying to go over the different processes that goes in terms of a recycling and recovery of electronic different components from electronic waste.

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So, we will continue that discussion. Now let us look at that was the previous one we are looking at for this particular company Huei Chia Dien companies are basically essentially from a Chinese form, but today we will look at the other company and I will go through an you will see that there are several similarities and some of them are unique as well.

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So, again this has been collected by looking at their website, looking at their literature and other stuff of these different companies which is out there doing E-Waste recycling.

So, in terms of this particular company which is a Union Miniere companies copper smelting flow sheet where they are again a scrap IC board they are using. So, they have the scrap IC board to start with and then that is you, then it says copper smelter is there which is the slag, you have the copper smelter using the sulfuric acid plant, then you have you have the slag which is further treated in the blast furnace.

So, what in terms of in like you copper pellatization is done the recovered copper is paralyzed, then whatever is the precious metal is goes through a precious metal refinery where a copper like a gold silver and other are recovered then there are some other special metals are also recovered using say different process. So, it is just showing your flow sheet of how the different process is run as part of this particular company and welcome back to each one of these detail in very shortly.

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So, if you look at the other option into this is our nearby it is only like 2 hours from here like Jamshedpur. So, CSIR lab the animal national metallurgical lab they also have a process for pulverization of printed circuit boards. So, the shredding and pulverization of printed circuit board again they have will have if you look at the process some of the process will be similar magnetic separation gravity concentration froth flotation you use the electrostatic separate separation metallic powder non metallic powder, then you try to do gold and silver recovery, then you have generate gold and silver powder you do the acid leaching and then with the leach solution you have the thiourea leaching you get the solution from where you recover gold and silver you have the recovery of tin, lead powder, copper powder, iron and aluminum. So, this is a kind of combination of the physical as well as the chemical leaching. So, that the combination of both is used.

So, of course, some of these some of these process would be proprietary process some of them will have the IP intellectual property rights. So, of course, there are certain things, but as if you are a as if you are thinking of setting up in a US recycling facility where you want to recover this precious metal these are the, this is in broad picture these are the different components that you need to go for. It is a combination of physical and chemical processes.

Some of these chemical processes we will talk about a little bit more in detail. Physical processes are the same as physical processes that is being used here is used for other

things as well. It has been used for many many years for a municipal solid waste recycling. And chemical process also is not new they are also used in the chemical industry for different types of applications refining and other things refineries, chemical refineries, metal refineries, it has been being used for many many years it is just the application of those to those processes in electronic waste a stream which is that is the new part.

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So, in terms of the pyrometallurgical process that we are looking at, let us look at some of the example here.

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What is the pyro metallurgical process? It includes incineration, is melting in a plasma arc furnace. So, plasma arc very high temperature lot of energy required that is why you have cost involved, you have you do the drozing, you do sintering and melting and reaction in the gas phase at high temperature. So, note all those things does happen.

Then there has a traditional methods to recover non ferrous metal as well as the precious metal for an electronic waste it has been it has been in use for last two decades it people are using it for last two decades. So, it is nothing like a brand new. And what is done in the process that crust is scrapped or burned in a furnace or in a molten bath to remove the plastic first then you have the reflective oxide from a slag phase together with some metal oxide. So, those are used for in terms of recovery of, these are the like as a part of the process.

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Then material and en entering the reactor you put it in 1250 degree centigrade, so you does require a like a pretty strong to like a reaction chamber which is churned by a mixture of supercharged air. So, up to 39 percent oxygen you have. So, up 39 percent oxygen at 1250 degree centigrade you are trying to have an oxidation process then. So, from a register you make a agitated oxidation zone that converts impurities including iron lead and zinc into oxide. So, and that fixed, they get fixed in a silica based slag. So, then we cool the slag and then the slag is milled to recover more metals before disposal.

So, these are different ways again, it is called Noranda process. So, this is a Noranda process which is being used and that is what it is used in other areas to. So, this is how a click a metals could be potentially recovered from electronic waste.

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The copper matte containing precious metals is removed and transferred to the converters.

After an upgrading in the converters, liquid blister copper is refined in anode furnaces and cast into anodes with purity of 99.1%.

The remaining 0.9% contains the precious metals, including gold, silver, platinum and palladium, along with other recoverable metals, such as selenium, tellurium, and nickel

The copper containing the precious metal is removed and transferred to converter. So, after a grade upgrading in converters the liquid blister copper is refined at the anode furnace. So, use like a furnace in the anode furnace and cost into anode set purity of 99.1 percent, the remaining 0.9 percent containing the pieces metal including gold silver platinum and palladium along with other recoverable metals such as selenium and other nickels are present in there. So, other things are, so records such as selenium trillium and nickel. So, those represent in the other 0.9 percent. So, those things are there.



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So, in terms of the process if we can look at that, so this is your Noranda process again. So, you have the recycling recyclables coming in you do some sort of short shorting here. So, you have the recycling these cycle about coming in then you do some sorting shredding they can make it is small you have the copper concentrate 24 percent copper sulfuric acid plan Noranda converter this is their IP thing and then you have the reactors. So, basically your converter, you use different process and get the copper out. So, this is a in this particular process in which how copper is recovered.

So, and this is a very copper since, if you remember from the percentages of different heavy metal copper was the number 1. So, copper recovery and copper is a costly likes it is costly it is not I probably as costly as gold or silver, but it is also a precious like a it is a precious metal and copper used in many applications in wires and other places. So, copper has a value and copper is one of the highly recyclable metal as well.

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So, then the other this is another process Ronnskar Smelter this is another application of pyrometallurgical process here E-Waste, it is done in Sweden this is used in Sweden in Boliden Limited in Sweden. This is known as the Ronns. So, if I hope I am pronouncing it correctly also known as the Ronnskar Smelter.

In this process the scouts are fed into the process in different steps depending on their purity and high copper containing is scrap is fed into converting process directly. Low grade E-Waste is fed into the Kaldo furnace. So, there is a different. So, along the process chain depending on the purity of your metal present you put it in different you input into the process at different level. So, that is what in kaldo reactor.

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Blended feed material with E-Waste and let concentrate concentrate is charged by a skip hoist plus you have a oxygen lance supply. So, you basically see what you whenever you do a combustion combustion is an oxidation process. So, for oxidation you need to supply oxygen, we know many many times we do not really supply oxygen we supply air. So, we are sometimes we do supply oxygen if we do not want nitrogen and other gases to be present. So, oxygen lance supplies needed oxygen for combustion with an oil oxygen burner. So, this off gas subjected to additional combustion a twelve hundred degree centigrade, very high temperature.

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So, mixed copper alloys sent to the copper converting. So, we have copper gold all these are present in that. So, remaining dusts containing leads as we cadmium are sent to other operations for metal recovery.

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So, this is a diagram for how the schematic Ronnskar Smelter. So, you have kaldo furnace electronic scrap and lead concentrate coming in here and that it will go into the converting part this is refining that will get lead, then you have a part of it going into the copper production copper here you have the roasting, drying, is melting, some conversion gas cleaning, sulfuric acid plant, then you have the precious metal plant, nickel sulfate plant, crude nickel sulphate is selenium gold is come out from there. What is happening exactly inside this of course, that is the part of the IP so that you will not get those detail you have to if you are trying to planning to setup a plan you have to get in touch with those companies to get those units like basically you need to buy those units and then you can use them.

So, this is again another example of how things are done. So, if you look at all these example all these sketches that we have seen so far there is a there is some sort of commonality that essentially it goes through some sort of physical process and chemical process. The nature of process might be different different process works at different temperature they have different operating conditions and based on the operating conditions on the process the purity and the recovery percentage will be differ and of course, the cost will also differ. But overall it is a combination of some sort of some physical process and some chemical process and chemical process mostly it is a smelting or leaching and those kind of user use of acid to recover metals we know that as metals have a tendency metals do this dissolve in liquid, in the acid in high concentration. So, that helps in terms of placate recovery of different types of heavy metals.

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So, then we have the Umicore, Umicore which is a very very common in Belgium it is a Umicore precious metal refining process which is a very common process. It is like a most of the metal most of the batteries around the world actually end up in this particular company. It is a first step in this precious metal operations they appropriate as PMO is say smelting using an IsaSmelt furnace. So, again they have their own names. So, the smelter what is it separates precious metal in a copper bullion from mostly all other metals concentrated in lead slag which is further treated in at the base metal operation. So, they precious metal is it is separated with all other metals. Then copper bullion is then treated by copper leaching and electro whining and precious metal refinery for copper and pieces metal recovery. So, that is happening over there.

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Umicore's Precious Mercil Refining Process (Hoboken, Belgium)

- The main processing steps are lead blast furnace, lead refinery and special metals plant.
- Transforms them into impure lead bullion, nickel species, copper matte and depleted slag
- The impure lead bullion, collecting most of the nonprecious metals, is further treated in the lead refinery (Harris process)



Base metal operation process is the byproduct from the pieces metal like a PMO which was the precious metal operation and the main processing steps are you have the lead blast furnace, lead refinery and a special metals plan, you have the transformer they are a process which transforms the impure lead nickel species, copper mate and depleted slag. So, those, the impure lead bullion, that is collected most of the non precious metal is further treated in the land lead refinery which is known as the Harris process.

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So, again these are the different processes that is being used then it is some of the special metals they are their residues are generated in the lead refining process, pure metals are recovered in a special, air emission control system is there, hygiene gases, hygienic gases and process gases are cool with energy recovery and clean using some techniques such as bag house filter electro filters and scrubbers and all that. So, again if you look at this process as well it is it is essentially combination of different chemical processes that is happening which is very similar to the previous process as well.

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Every process has their certain uniqueness and they walk in a slightly different way, then sulfur because of the oxygen sulfur is converted into SO 2 which is configured to sulfuric acid emissions from the plants are well below the European limits because they have to meet the European limit is standard then. So, those are in terms of the uninore or Umicore process, remember process.

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Recovery of Gold from E-Scrap(Dunn et al.,1991: US Patent, US5004500.

■ The gold scrap reacted with chlorine at a temperature with the range of about 300–700°C to form a mixture containing metallic gold, silver chloride, and other metal chlorides.

The mixture was washed with air-sparged hydrochloric acid to dissolve the impurity metal chlorides other than silver chloride forming a metallic gold/silver chloride mixture.

Then other process like in this particular process in terms of the recovery of gold from a scrap which is it is by done at all in 1991 they put that paper out. So, here that you have the gold scrap you react with chlorine at a temperature with a range of around 300 to 700. So, that can make a mixture of metallic gold then you have silver chloride and other metal chloride there. The mixture is actually washed with a responder chloric acid and then you dissolve metal chloride other than the silver chloride same a metallic gold and silver chloride mixture.

So, you add like again as a course, so I would not like those of you those of the students who are taking this course if you are you might, if you might be getting worried that there are. So, many chemistry here am I going to be tested on my chemistry, am I going to be tested on all these a small small process definition and the description, my answer is no in your quizzes or in your exam and those of you are planning to take the exam as I understand many of these students of many of you who are taking this course actually you are taking it for credit as part of some program in your university or in your colleges.

So, I am not going to we are environmental engineers, we are environmental scientists, we are not a hardcore chemist. So, all the questions will not be hard core chemist oriented question, do not worry.

Why these details then do the next obvious question is then why I have all these details and just to give you an idea say, there are what are what are the different things goes into when we are trying to recover. So, it is not an easy process because the reason I want to highlight that these are not an easy process, lot of things goes in there and then at the same time this is not something rocket science or these are not something which is has something which not been done earlier or it is not being practiced in industry right now, these are all well established with slight modification, these are standard operate or standard things which is done in typical chemical industries and other of metallurgical industries, refining processes, metal refining especially, metal mining. So, these are all being used it is just we have to take that process maybe adapt it for the electronic scrap and use it over there.

So, that is what these companies or these organizations have done and they have come up with these processes, they have patented those processes as well and which is being used in a formal recycling of electronic waste in different places in Western Europe, North America and other places. In India also we have several companies set up now. Most of the Indian recycling companies does not go all the way of recovery of the precious metal they actually go up to dismantling and try to recover some of the easier recoverable material and then the hard one they again send it to Belgium and other places for further recovery.

It would be really nice to get all those gold out in India itself is not it. I think the gold consumption is India is probably the most in the world. So, if I am not I think I am correct and then. So, that is we have a big market for recovered gold here as well. So, this it would be nice to recover all this gold rather than sending it to say Belgium on other countries to recover gold on the E-Waste that we have produced.

Say I have already paid for my phone. So, I have my phone. So, if it has little bit of heavy metals present in there a little bit of gold or little bit of silver that should be stay in my country because I have already paid for it and, but I should not go to any overseas country, but we have to set up those facilities here, we have to set up those plants and we

have to get the waste coming to those plants. So, that is another again. So, I think I was telling in one of the earlier videos the problem in India is not in terms of the rules, not in terms of the technology, not in terms of the; technology if there is a we do if certain areas we may lack in technology, but we can technologies are nowadays available, you can buy those technology, you can have some sort of partnership as well with some foreign technology. But in terms of know how there is the problem is its even if there is a problem it is very minimal problem, the real problem is implementation, implementation.

If somebody asks you what is the three major problem in terms of the Indian environmental system I would say implementation, implementation, implementation. So, if we have to implement those like our rules and regulations make the conditions suitable for an implementation. So, that is where we lack. So, there are lots of processes out there we looked at some let us look at some more. So, in terms of this is this process for recovery of gold from east scrap this was published nearly now it is almost 20 years ago like it was so published. So, it was the ammonium hydroxide nitric acid is used where you try to dissolve gold and silver and you try to get the traces of metallic silver from metallic gold.

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So, it is a in terms of the duns processing what is developed for refining high grade gold material that contains more than 80 percent gold. So, first of all; what we need to do for

that? So, we need to in the electronic waste we need to get rid of the other material. So, what will left with only the per area which has gold and some other metals present so that in that four we can recover the gold from that particular process. So, it may not work all the time. So, it is clear that.

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So, in terms of look if you look at the hydro pyrometallurgical process that we have been looked trying to see in this particular lecture so far it is the real traditional technology, it is in terms of traditional technology the pyrometallurgy is used for recovery of precious metal, from waste electronic is practiced for years. But however, most methods even this give rise to following limits it is the integrated the smelter they cannot recover aluminum and iron as a metal. So, that is one problem we have.

In the presence of halogenated flame retardants the in the smelter feed can lead to formation of dioxin unless a special interim measures are present. So, those are that we have. So, if you somebody wants to do research in here, somebody wants to do some Phd in this particular area these are the topic you need to look at if you are a chemical engineer or a metallurgical engineer the first topic is makes more sense to you in terms of trying to come up with the recovery of aluminum and iron as well within the integrated smelter how to make that possible. And if we are like if you are, if you are an environmental engineer or even a chemical engineer we can try to look at that how to get rid of this halogenated flame retardants. So, in the smelter feed so that we how to how to

how to manage that so that we do not have the formation of dioxins, and if there is a dia formation of dioxins how to manage it how to control it that that my environmental engineering student friends should focus on that aspect.

So, and then we have some other issues like a ceramic components and glass ink in the us that increases the amount of slag from the blast furnace and if you have more slag then you have the loss of precious metals and the base metal from this scrap. We have only a partial separation of metals can be achieved using pyrometallurgical so that is what we need to have some use other process as well. And hydro metallurgical prior technique or other electro chemical processing are subsequently necessary. So, only pyrometallurgical process will not be enough. The precious metals they stay for a long time in pyrometallurgical process are obtained at the very end of the process. So, it is you have a recovery does happen, but it takes it will happens towards the end of the process. So, that is also it is a concern.

So, with that we had a quick overview of the pyrometallurgical process. So, now, we will look at the hydro metallurgical process and we will start this let us say and then let us see how long we can make progress in this particular video and then we will continue in our next video.



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So, in terms of the hydro metallurgical process if you look at kind of an overview of that it is a more exact, more predictable, more easily controlled.

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Introduction

Hydrometallurgical method is more exact, more predictable and more easily controlled.

Consist of a series of acid or caustic leaches of solid material

So, this is a benefit on top of a pyrometallurgical process and the hydro metallurgical process let us say we have a better control and we can predict what will happen and, but as its it is series of acid and caustic leaching. So, essentially it is a sequential leaching lot of leaching happening in this hydro metallurgical process. So, we are doing a lot of leaching and then in the process we end up producing lot of hazardous waste as well. So, we have to manage those hazardous wastes which we will see in a minute as we try to explain that.

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Introduction

Solutions are then subjected to separation and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest

 Final treatment by electro-refining process, chemical reduction or crystallization for metal recovery. So, here we have solutions we are subject to separation and purification procedure. What we try to do, we try to play with solubility, we have tried to play with the solubility product, so we will have precipitation of impurities, solvent extraction, adsorption, ion exchange all those typical stuff that we use for other treatment as well. So, similar things are used to isolate and concentrate the metals of interest. So, we try to do that.

Final treatment electro refining process or chemical reduction or crystallization for metal recovery so that is the final treatment is done as well in terms of electro refining process chemical reduction is done, crystallization is done.

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***************** **Cyanide Leaching** □ It is an electrochemical process utilized in the mining industries for more than one century. □ The overall reactions are $4Au + 8 CN^{-} = 4Au(CN)_{2} + 4e$ $O_2 + 2H_2O + 4e = 4OH^2$ Maximum dissolution of gold, silver, palladium, and platinum in cyanide solution can be obtained at pH 10–10.5. □ The order of activity for noble metals is Au>Ag>Pd>Pt

So, in terms of different types of method that is used the most common which has been until very recently is on cyanide leaching which is not actually the popularity of this method is going down because it produces cyanide, its produces a lot of hazardous waste along with that it is an electrochemical process and it is used in mining industry for more than a century it is being used.

So, its overall reaction what happens is you have gold, it reacts with cyanide and produces gold cyanide complex and then you have like a basic conditions like OH minus is also produced. So, what it does it is the gold present in the solid form in those, electronic waste or in the ore get dissolved into the liquid form. So, maximum dissolution of gold, silver, palladium and platinum it happens at the ph of 10 to 10.5. So, it happens in a caustic environment in alkaline environment around 10 to 10.5. The order

of reactivity like we have more reactive is gold than the silver, then palladium, then platinum. So, those are in that sense in that sequence the reaction takes place.

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So, and they use halide system for gold dissolution predates us as like a cyanides in for. So, halide is also used like fluorine, chlorine, bromine, they were used to use gold dissolution or before the cyanide use. Gold forms both Au I and Au III complex with fluoride bromide and iodide depending on the solution. So, only chlorine and chloride has been applied industrially on a significant scale. So, that is the halide leaching is also done. So, cyanide leaching is done with, but even before cyanide leaching halide leaching has been practiced.

So, these are all practices which has being used in the gold mining. So, we are trying to use the same process which have been used in gold mining where gold mining also gold is not free it is with the certain other material other mineral other complexes are there. So, similarly in for electronic waste the gold is present with other complexes and other things. So, we are trying to use the same concept in terms of the recovery of gold from electronic waste.

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Halide leaching

- Chlorination rates are favored by low pH, high chloride and chlorine levels, increased temperatures, and high surface areas.
- □ The first step is dissolving gold into aqua regia and the reaction involved in these process are:

 $2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2$ $2Au + 11HCl + 3HNO_3 \rightarrow 2HAuCl_4 + 3NOCl + 6H_2O$

So, in terms of the halide leaching where here it is chlorination is, it is a low ph high chloride increase the temperature high surface area. So, first step here is you dissolve gold in aqua regia and the reaction involve this process. So, you make first aqua regia and then you dissolved gold in aqua regia to make that gold solution and then you can recover it from there.

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So, chloride leaching of gold is more difficult to apply than cyanide extraction because for chloride leaching you need a specialist stainless steel and rubber lined equipment to resist the corrosive acid acidic an oxidizing condition. Chlorine gas is highly poisonous and must be avoided at any health risk.

If you think about, if you look go on YouTube and look at the how the E-Waste is managed in the informal sector you will see the people are you aqua regia in highly open atmosphere without any kind of protective air pollution control thing and then they have all these chlorine gas and other things out there which is being exposed. So, they are all these workers in the informal sector is getting exposed. And the gold there is only to recover that little bit of goal and they in the process since the process is not in a; it is not a refined process, it is not as it is done in a very crude manner they also lose lot of gold. So, it is not that they end up losing gold as well, but that is their the way they manage it with, it is just to recover whatever they can recover and since they do not have to follow all these as pcb and cpcb rule. The cost wise it works out for them.

But it is the same thing that is in done in the informal sector in the same process could be used in a formal environment with a better environmental control bit with better personal protective equipment. So, the workers working there does not get exposed to all these chemicals and does not get sick. Most of the informally waste workers does not stay alive for a long they problem or many of them do not see their 40th birthday. So, they die before they reach 40 years of age because of getting all these things exposed day in and day out for several years.

So, there are issues in that. So, with that let us we looked at some of this hydro metallurgical process. So, we will continue the discussion again in the next video. So, I hope that you are enjoying this course so far. Again any questions, any suggestions, any feedback, send it to us through the discussion forum.

Thank you and I will see you again in the next video.