

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-2

Lecture-7

Greetings, I welcome you all to the sixth lecture of this course where we will now be discussing the key recycling processes one after the other. We will have pyrometallurgy, we will have hydrometallurgy and electrometallurgy following one after the other and as we all know we have been discussing a lot on pretreatment initially and now we would like to go into the pyrometallurgical method of recycling. It so happens that one has to understand what type of recycling process we are involving for a given material and what would be the finished product.

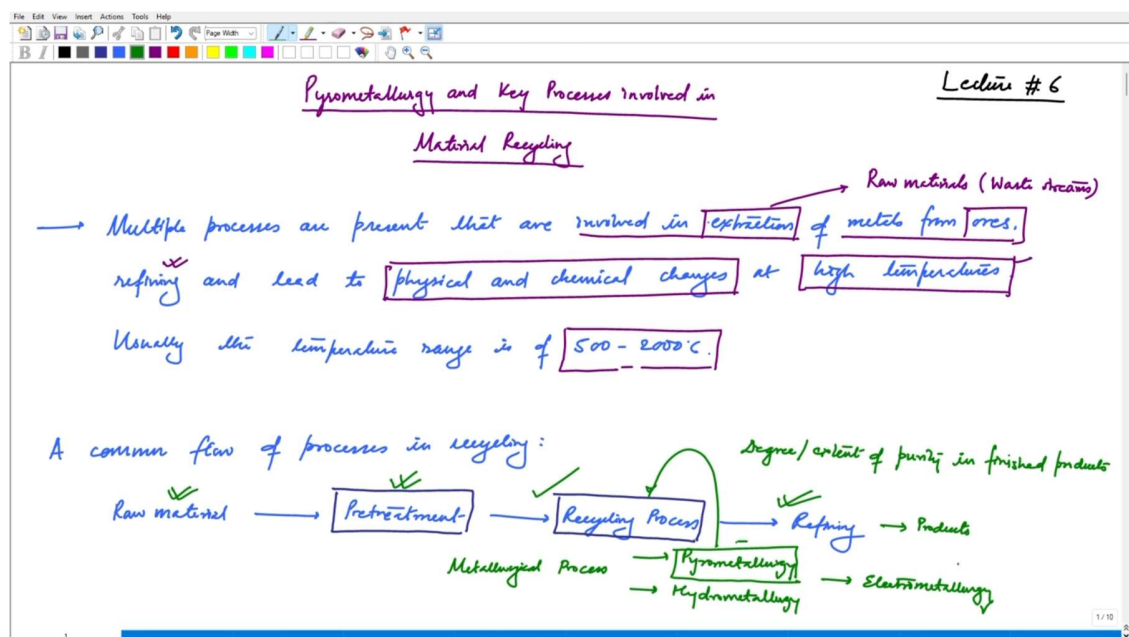
So, again it is directed by what type of raw feed we get, what type of pretreatment was followed and what type of finished product we wish to prepare. So, if we are interested in making metals, pyrometallurgy, hydrometallurgy and electrometallurgy, all of them have their own advantages and disadvantages. For a really large-scale production, usually pyrometallurgy is chosen. Now, what exactly do we mean by pyrometallurgical processes? There are lot many processes, multiple processes that are present that are usually involved in extraction of metals from ores and since we are now interested in recycling we will write raw materials basically waste streams. We are in interested in extracting metals from raw materials. Extraction of metals from raw materials of course, it will also involve refining. And these processes usually lead to physical and chemical changes that basically are going to result in the finished product that we are interested in. And of course, we are interested in carrying out these processes at high temperatures.

What do we normally mean by high temperatures? It can range from 500 to 2000 and again it depends upon the type of metal that we are interested in extracting. So, may be 500 is really lower temperature for a given metal and we could go for a higher temperature. It again depends upon the type of raw feed that we have. What is a usual, usual flow of process in recycling.

Normally we begin as we have been discussing. We have raw materials. We have done pre-treatment. As discussed previously we can have pre-treatment 1, pre-treatment 2, pre-treatment n. Depending upon what type of initial phase we are interested in to begin our recycling process which could have additional step of refining and then we will be ending up with the product phase.

So, we have a raw material, pretreatment, recycling process, refining process and then the products based upon the degree or extent of purity in finished products. Now, recycling processes themselves have three categories and these are broadly categorized on the basis of metallurgical processes, And of course, these are extractive metallurgy processes which could be pyrometallurgy, hydrometallurgy and electrometallurgy. Right now, we are using pyrometallurgy as our starting point. We are trying to fit it here in the recycling process.

(Ref. 5:48)



Pyrometallurgy is one of the possible routes of recycling used for metal recovery, refining and thermal treatment. Not just for extracting metals or refining, we can just simply think of thermal treatment which could lead to changes in phases, changes in properties this could be physical properties or chemical properties and based on these we can think of developing further processes. Now, let us begin by thinking of calcination.

We have already, people have some idea about calcination. Normally, it is basically a thermal treatment to decompose and remove. So, it is a thermal decomposition process. Thermal decomposition that helps in removing volatile matter. Volatile matter could be present in let us say if we say fuels.

Let us say coal. If we have some volatile matter we can try and remove that. But again that may not be termed as calcination. What we are trying to focus here is we are trying to provide some high temperature using furnaces and we are trying to remove the volatile matter from a given raw feed. Now our raw material could be let us say for this case we have calcium carbonate which is the one of the most common examples when we are thinking of calcination.

Calcium carbonate given a temperature of 700 to 900 °C we can have calcium oxide and CO₂ as gas. This gas is basically generated only after the thermal decomposition of calcium carbonate. And this is the volatile matter content that is being released after the thermal treatment that has been provided. So, we have the evolution of CO₂ gas. The second one, the second pyrometallurgical process that we can think of is roasting.

(Ref. 8:30)

Pyrometallurgy is one of the possible routes of recycling and for metal recovery/refining.

Thermal treatment → changes in properties $\left\{ \begin{array}{l} \text{Physical} \\ \text{Chemical} \end{array} \right\}$ developing further processes

✓ Calcination Thermal decomposition fuels → coal

Thermal treatment to decompose and remove volatile matter in a given raw material

✓ $\text{CaCO}_3 \rightarrow \text{CaO} + \overset{\text{gas}}{\boxed{\text{CO}_2}}$ [700 - 900°C]

Evolution of CO₂ gas is observed. —

In roasting the conversion of mineral or raw material. As we are basically trying to see pyrometallurgical processes, we have to use some concepts from conventional extractive metallurgy area of metallurgical engineering. So, that is the reason why we have minerals written in alignment to the raw materials. Conversion of mineral or raw material to a desired chemical phase. If we may be interested in a particular phase, let us say chloride or oxide, because these are easier to process in the

upcoming stages, easier to process in the upcoming stages. We can have chlorides and oxides under required operational environment. So, the apart from temperature itself one has to think of plus environment. Specific environment is required for roasting. The operational environment.

For instance, if we are having a sulphide metal plus S, metal sulphide MS, we are supplying oxygen, this could be oxygen supplying in the furnace itself. We can have the charging of oxygen in such a way that the environment inside the furnace is oxidizing. So, we will have metal oxide. This is our required phase.

And of course, this would be solid and we will have SO_2 gas. In both the cases that we have seen, calcination as well as roasting, we see that there is the evolution of gas. We have CO_2 evolution when we thought of calcination. We have SO_2 generation when we think of roasting. The environment is the key difference that we see in both of these processes and both of these processes are basically using high temperature conditions.

So, based on the thermodynamical guidelines that are available, we can device what is the temperature range, what is the partial pressure that is required basically essential to govern the direction of reactions. Let us say for roasting we suppose we want to oxidize. What is the partial pressure of oxygen that we need to supply in the furnace? What is the partial pressure that is needed that is required to be maintained in the furnace that the resultant product could be an oxide let us say.

These are again governed by thermodynamic principles. Achieving environment for roasting is crucial to produce the desired phase as we have just maintained understanding the metallurgical thermodynamics would help in determining the prerequisites for these thermal operations. The next most important step that needs to be discussed is smelting. We begin with mineral with gangue and of course gangue is a type of mineral that is associated to a mineral of our choice that we are interested in.

One has to think of removing these additional minerals, the gangue mineral from the raw feed such that the resultant product is rich in the metal phase. We can directly get metal or we may get matte which could be further processed. Smelting process is essentially categorized in reduction smelting and matte smelting. We begin again. Mineral with gangue, it may have reducing agent, usually it is carbon and it must have flux so that whatever

impurities we have in the beginning. So, of course gangue will have impurities will end up in the with flux into the slag phase. Now we look at what exactly we are getting out of the smelting process. We will get a metal or matte phase, we will have the slag phase and the gases. Now smelting processes if considered at very small stage, if at very small laboratory scales, they may have small amount of gas evolution but when done in an industrial scale the products that we get metal,

slag and the gases, these are all a very large in quantities. These are not trivial numbers. These are normally very large in quantity. It is essential to pay attention to each and every product and byproduct. We may be interested in metal or matte because we consider it as a product and we may consider slag and gases as byproducts which may be considered as waste.

One has to think of considering the recovery of metal and considering the recovery of materials from slag and gaseous products as well that would help in developing a complete process that takes care of all of the products and byproducts that are generated from a given process. Now we begun, we had started with mineral with gangue. In our recycling process, we begin with raw materials.

And again, here we have already considered that initial pretreatment has been done. Essential pretreatment that is required for pyrometallurgical process is done. And then we may go by either reduction smelting or matte smelting and we may end up with metal or matte. And of course, this again would lead to generation of slags and gaseous phases. So, we have seen the categorization of smelting.

(Ref. 17:40)

Roasting

The process of conversion of mineral / raw material to a desired chemical phase, like chloride or oxide etc. under required operational environment. temperature + environment

Required phase

$$(MS) + \frac{3}{2} O_2 \longrightarrow (MO) + (SO_2) (g)$$

$CO_2 \longrightarrow$ calcination
 $SO_2 \longrightarrow$ roasting

Achieving the environment for roasting is crucial to produce the desired phases

Smelting

Raw material $\xrightarrow{\text{Pretreatment has been done}}$ Impurities $\xrightarrow{\text{Ironmaking slag steel making slag}}$ Product and by product waste

Mineral (with gangue) + reducing agent + flux \longrightarrow metal / matte + slag + gas

This could be reduction smelting and matte smelting and we have already seen that the common reducing agent could be carbon. Suppose that we begin with metal oxide, reacts with carbon, CO is formed and we get metal. Similarly,

$2MO + C \rightarrow 2M + CO_2$. So, basically it is taking up oxygen and producing CO_2 . Now, $MO...$

(Ref. 26:50)

Categorized as reduction smelting and matte smelting

Reduction Smelting

Reducing agents are used [usually carbon]

$$MO + C \longrightarrow CO + M$$

$$2MO + C \longrightarrow 2M + CO_2$$

$$MO + CO \longrightarrow M + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

Environmental burden $\xrightarrow{\text{discourage}}$

Landfilling of waste can lead to inclusion of heavy metals / hazardous metal into Land resources

Introduction

The pyrometallurgical processes have products and by-products and each 'by-product' can become a raw material for recycling.

Matte Smelting

floatation concentrate \longrightarrow Drying \longrightarrow flash smelting \longrightarrow Matte \longrightarrow blister copper

Waste generation is possible at every step of process

Optimizing every step is necessary to achieve maximum metallic values

copper smelting

Again, we begin with this raw material and we have CO. We have this and this. This could also lead to the formation of metal, but this time we are getting CO₂ and the CO₂ in a given system could be used by carbon itself to give us 2CO and this 2CO could be used for the previous reaction.

This type of reaction is common in reduction smelting processes. A common reduction smelting process is observed in the case of iron in the iron making industry. When we look at matte smelting, normally in matte smelting, the use of reducing agent is not required. So, there is no reducing agent, we just begin with the raw material and we do the smelting.

Suppose that we are looking at copper smelting we can have the flotation concentrate which is dried which could be flash smelting again which leads to matte formation and which could be further processed to blister copper. When we think of matte smelting one must pay attention that at every stage of process we can generate different types of wastes. Waste generation is possible at every step of process, as we had seen here as well. Suppose that we were looking at a single step of smelting.

We are interested in metal, but that really does not mean that we can discard slags and flue gases, the gases that are evolved after the process. Metal and matte will be the key interest, but at the same time it is also important to pay attention to the slag and the gases, which is what we are trying to focus here as well. The pyrometallurgical processes have products and byproducts and each, now we are thinking of byproducts only, each byproduct can become or can be treated as a raw material for recycling.

This is important because if we look at slags and gases, we can have let us say iron making slag. You can have steel making slag all of these slags whether they are generated in a given furnace or any different furnace of iron making or steel making industry or let's say copper making industry we must pay attention to these slags decomposition and then develop dedicated recycling routes for these wastes as well. It is fairly possible that we are beginning with a raw material which could be e-waste. And then we may end up in a master alloy here and we may have to refine it further.

But at every stage we are generating slags. We may be generating flue dust. Keeping a given route let's say pyrometallurgy or hydrometallurgy or electrometallurgy and

focusing just on that particular route may not be the best possible route of recycling because any given step that we begin with will lead to generation of product and byproduct and one has to pay attention on what we are trying to efficiently recover, and at the same time, is the byproduct hazardous?

Supposing that if we look at the slags, we can't really dump slags in the landfills. Landfilling of wastes and by waste, we mean pyrometallurgical wastes. Landfilling of wastes can lead to inclusion which basically means penetration or we can say introduction of heavy metals or hazardous metals into land resources which is the primary target which is what people are trying to do when they think of recycling slags or refractories, when we think of recycling metallurgical wastes.

What we are normally planning to do is we think of focusing the recycling process on these wastes so that landfilling is discouraged. All of this we are trying to do because discourage. Because of course it has environmental implications and one has to think of optimizing every step so for instance if we begin with raw material, we think of pretreatment, we think of recycling process, refining process and achieving the products we know that optimizing every step is necessary to achieve maximum possible metallic values from a given let's say pyrometallurgical route and we have been emphasizing that a single route of recycling may not be sufficient for recovering everything that we are interested in and not just recovering metals we want to avoid the penetration, the inclusion, the introduction of hazardous metals into the environment, into the land resources, into the water resources, the water table and the soil. The soil pH can change because of these hazardous materials.

We will now continue in the next lecture.

Thank you.