

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-4

Lecture-16

Greetings, I welcome you all to the 15th lecture of this course, wherein now we will be discussing about copper smelter slag. In the previous lectures we have had the discussion on materials recycling, wherein we have been focusing on metallurgical wastes and now we are going to focus on copper industrial wastes. Copper smelting slag is one of the most important wastes that is generated in copper industries and before we actually go ahead and discuss the characteristics of how it is generated, the chemical composition, and what exactly is the reason behind recycling it?

We would first discuss a couple of things about copper. Copper is one of the most important metals that is used worldwide. One of the most important metals used worldwide. Why do we use it? Because of course, because of the salient features, high electrical and thermal conductivities.

We know that copper is one of the most go-to metals, go-to materials that can be used for electrical and thermal conductivity applications. High resistance to corrosion, and high scrap value. We already know that the recycling of copper is going to give us good returns. It is also from recycling point of view it has high scrap value.

That tells us a good material, from economic point of view that is why we are saying it's a good material and of course we already know that so many good properties are there that make copper a useful material and of course the mechanical properties, the properties that help in its utilization in various forms such as sheets, wires, ductility etc. these properties are basically going to advocate it's used in various applications.

It's a good material for various fields. What are the key areas of application? Why exactly are we discussing about the applications, the areas of applications? The reason is that these applications dictate, these applications dictate what are the areas from which the waste scrap or end-of-life copper will originate from. So, when we know the area of

application we can expect what type of scrap we are about to receive after the application is over, after the service period is completed what is going to happen. When we understand the area of application, we can understand the type of scrap that is generated. We see that electrical applications, telecommunication, transmission lines, automobile industries and similarly some other automotive industries, the transportation industries like railways and other areas also utilize copper and its alloys. We can also have construction and miscellaneous areas.

These applications basically help us identify the areas where we are supplying copper for applications and after the projected use, after the intended use, we can expect the return of copper back into the original cycle. We are understanding how copper is going into the material application front and how it will return back to the recycling channel.

(Ref. 4:50)

Copper Smelter Slag Lecture #15

One of the most important metals used world wide.

✓ Salient features: high electrical and thermal conductivities, high resistance to corrosion, high scrap value etc. → Good material for various fields.

→ good material

Key areas of applications:

✓
Electrical

✓
Telecommunication

✓
Transmission Lines

✓
Automobile Industry

Construction

Miscellaneous

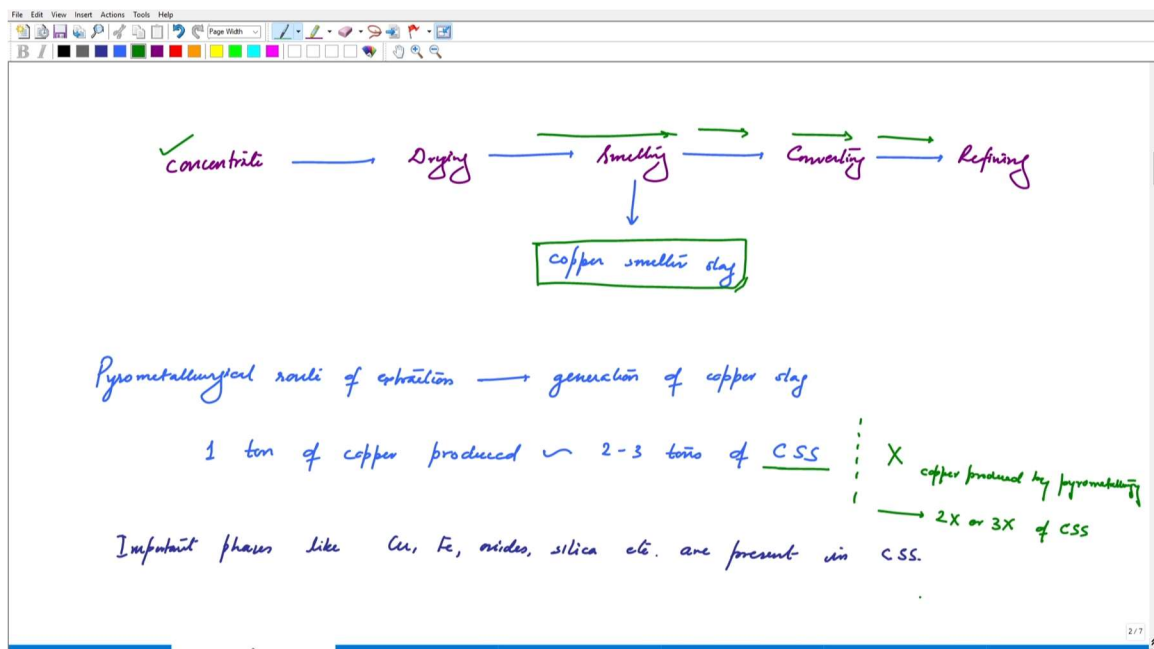
Apart from that, when we think about copper extraction, so we already know that one has to process the ore, normally we use CuFeS_2 ore and we go for various pretreatments. The flotation process is done and we get the copper concentrates. When we do the pretreatment, we get the concentrate of the ore. And using this we can go ahead for the pyrometallurgical route or hydrometallurgical route depending on what is the grade of copper ore that we have or what is the technology that is available in the industry. If we

look at the pyrometallurgical route of copper extraction we know that we will be going for drying and then smelting followed by conversion and refining. After refining which the different types of refining have already been described electro refining, fire refining and so on so forth. These type of refining are performed on various metals and we get the finished product. For the case of copper, we are going for smelting, converting and refining. These are the process routes that are followed one after the other.

In the smelting stage, we get copper smelter slag. We have just discussed concentrate is basically dried and then subjected to smelting. The finished product is actually going forth for conversion and smelting and refining and finally, we get the pure copper that was the expected product. But in this case, we are actually getting copper smelter slag, during the smelting stage itself. We have the product chain and the product cycle, but we also have the sidestep of copper smelter slag generation. Pyrometallurgical route of extraction is basically going to generate copper slag. How much does it normally generate? One ton of copper produced usually leads to two to three tons of CSS. CSS is copper smelter slag.

We can easily say that if X is the amount of copper generated, copper produced by pyrometallurgical process, we can expect nearly $2X$ or $3X$ depending on process parameters and the other inputs that are added here and various parameters of the process, we can have $2x$ or $3x$ quantity of CSS.

(Ref. 8:18)



Important phases like some phases of copper, of iron, other oxides, silica, alumina, and MgO, various phases can be present in CSS depending upon the starting raw material and it is important to note that these phases make it really very difficult to recycle CSS. We see that for every ton of copper produced nearly two times or at least three times or it could be somewhere in between that is the quantity of CSS produced, nearly double. That makes the process a bit challenging, the recycling process, because it is similar to dross generation or aluminium slag generation. We see that some amount of slag is always produced when we are producing metals.

Same is the case with copper. Complexity of ore is dependent upon what type of elements and phases are present in CSS. When we see these tables, we see and of course these tables are again prepared from data that is collected from literature. Some of the references are pointed out here. We see that we have iron and iron here is mentioned as iron total, and this iron total is basically encompassing all of the iron oxides that are present in this melted slag. We see that 53.21 and of course all of these are in different percentages and we see that major contribution comes from iron and silica. If we know what are the important phases that are present in our waste, it is easier to discuss various recycling strategies that are available for efficient material recovery while it is nice to identify the phases present, it is also important to judiciously develop the recycling strategy that can help in efficient material recovery.

If we have 40 to 53% of iron and we have relatively very less quantity of copper. One might say it is a copper slag, but still the amount of copper is very less. It is basically an iron dominated slag, even though it is generated in a copper industry, it is an iron dominating slag. And the next important phase in terms of quantities is silica. The other elements that can be present could be let us say Al_2O_3 or zinc in some phases or MgO or CaO, but the two dominant phases are iron in the form of various iron oxides and silica. Based on these phases, one can help in one can think of developing process. Let us see what type of phases of iron are present in CSS. Basically what we are trying to do is we are trying to see fractions of iron in various iron rich phases in CSS. If we have ferric sulfate, we have magnetite, we have iron sulfide, we've hematite, and fayalite these types of phases are basically present in CSS.

And we see that fayalite and magnetite are two important phases, iron rich phases that are present in CSS and due to fayalite and magnetite and other iron oxide it becomes very difficult to go for conventional comminution.

(Ref. 13:00)

Composition

Phases present	Cu	Pb	Zn	CaO	MgO	Al ₂ O ₃	SiO ₂	S	P
Fe (total)									
53.21	0.75	—	—	3.84	1.04	3.87	32.76	—	—
40.35	0.63	0.79	1.11	1.10	1.96	5.09	32.33	1.4	0.04

(Li et al. 2019, Zhang et al. 2013)

Distribution of Fe in phases

Ferric sulfide	Magnetite	Iron sulfide	Komatiite	Fayalite
0.37	13.79	2.33	10.59	72.89

(Li et al., 2019)

One of the methods that people initially thought of and sometimes it is still applied in some cases, they would go ahead for basic mineral ore beneficiation type of pretreatment for CSS and extract as much as metallic content as is possible. It is due to these phases that are the these phases basically make the processing, the mineral ore beneficiation processing lot more complex.

Multiple stages of beneficiation become necessary for efficient metal recovery. If we have crushing and grinding so one has to sieve it and we have let's say multiple fractions of metallic contents. One could be coarser fraction and then could be have a finer fraction. One can think of characterizing these fractions and identify what type of phases are present in it, what type of concentration step can be done further. What happens is a simple commutation step may not be sufficient because of the complexity of these phases that are present in CSS.

Due to variety of phases, of course we have just discussed this, due to variety of phases and inherent complexity, numerous beneficiation processes are used. Not just a single step numerous beneficiation processes one after the other one has to employ different beneficiation process, screening followed by flotation followed by let's say hydrocyclone or magnetic separation, these are the steps that become necessary for efficient

concentration of iron and copper and they get separated out and of course one might wonder why do we even think of copper because this is an iron rich slag. It happens that some amount of copper is still remaining.

We have always noted that the data that is presented in the literature some outliers may always be present. It is fairly possible to understand that the copper concentration in some CSS, in some slags can be relatively very high. Under such circumstances it becomes necessary to extract copper as well not just iron. What we are trying to impress here is numerous beneficiation processes become necessary because of the complexities and this helps us in recovering metallic values.

We have screening, drying, dry magnetic separation, hydrocyclones, flotations and of course other separation processes for the concentration of iron and copper in various size fragments, size fractions and then the separate utilization strategies can be devised. One has to characterize all of these feed fractions as well as product fractions and then decide what next recycling strategy can be applied. It is very important to decide on the pretreatment of CSS. Because that can help in directing whether we would be interested in pyrometallurgical recycling or hydrometallurgical recycling of CSS.

When you think of recovery of valuables from CSS, we have already seen multi-stage recovery by beneficiation. This part we have just discussed. Followed by pyrometallurgy or hydrometallurgy. Hydrometallurgy we already know, that one has to utilize relatively finer fractions for extraction of valuable materials into leach liquor.

Normally we can go for acidic solutions for general leaching purposes and using that we can have the extraction of copper and iron and if there is zinc or any other metal that is present in the CSS, those type of recovery, metal recovery can be done using the leach liquor. And the pyrometallurgical strategy of using CSS involves various reducing strategies, direct reduction, deep reduction or smelting separation and these strategies help us in identifying what type of product we are interested in making. Many a time we can end up with iron concentrates, we can end up with iron-copper alloy depending if we have some amount of copper, some significant amount of copper we can have iron-copper alloy or we can have copper concentrate or we can have the recovery of iron and copper. It is basically dependent upon what type of raw feed we are using in various pyrometallurgical processes. In hydrometallurgical processes, it is again the utilization of leach liquor and that helps us in recovering most of the metallic values into the solution and then from the solution we can decide what type of purification strategy we can use.

We are using basically solvent extraction or ion exchange or cementation or any other process or precipitation followed by again if we are if we are still left with some solution left we can think of recovering copper by electrowinning also the other way round could be for pyrometallurgical strategies basically taking the raw material all in as whole and trying to recover as much metallic values as is possible. Direct reduction of CSS.

Direct reduction of CSS is basically done by using Na_2CO_3 and CaO followed by magnetic separation. Just in the previous slide we had discussed, we had discussed the use of magnetic separators. We have screening, dry magnetic separation, hydrocyclones, flotations and separations with different types of roots are already present.

(Ref. 20:50)

→ Due to variety of phases and inherent complexity, numerous beneficiation processes are used are used to recover metallic values.

→ | Screening, | dry magnetic separation, | hydrocyclones, | flotation, | separation are done to produce copper concentrates and iron concentrates.

Recovery of valuables from CSS

→ Multi-stage metal recovery by beneficiation, pyrometallurgy and hydrometallurgy

These help in isolation of various valuable phases. This exactly is being discussed here. Direct reduction of CSS by Na_2CO_3 and CaO addition. This is Na_2CO_3 and CaO addition actually. And this addition is done during the reduction process. During the process. Followed by magnetic separation. And reduction separation, this is basically direct reduction separation process, which helps in producing iron and copper and it has really good nearly 80 to 90 percent of recovery of iron and copper and of course we know that the copper amount initially could be relatively very less but the overall recovery can be good. At the same time we also have smelting separation process.

The smelting separation process is somewhat similar to the direct reduction, wherein we are now trying to melt the slag, melt the slag and add various things. For instance if we are adding Al_2O_3 , so people have thought about adding Al_2O_3 or CaO and then they realize that maybe Al_2O_3 addition really does not affect the recovery of copper or iron. But at the same time CaO addition can help in the recovery of iron because it helps in reduction of iron. Slag melting is necessary so the prerequisite would be that CSS is in molten state and this helps in iron separation and CaO addition during this process improves the iron reduction.

(Ref. 23:24)

The image shows a digital whiteboard with handwritten notes in blue and green ink. The notes are organized into two main sections, each starting with a blue arrow pointing to the right.

Top Section:

- Starts with "Direct reduction of CSS by Na_2CO_3 and CaO followed by magnetic separation".
- A green arrow points from "Direct reduction" to "recovery of copper and iron".
- A green arrow points from "magnetic separation" to "recovery of copper and iron".
- Green annotations: "during this process" above "of CSS" and "addition" below " CaO ".

Bottom Section:

- Starts with "Smelting-separation process: slag melting is necessary for iron separation".
- A green arrow points from "slag melting" to "iron separation".
- A green arrow points from "slag melting" to "CaO addition improves iron reduction".
- Green annotations: "CSS is in molten state" above "slag melting" and "iron separation" is enclosed in a green box.

The whiteboard interface includes a toolbar at the top with various drawing tools and a status bar at the bottom right showing "9/7".

What do we mean by iron reduction because we already know that iron is actually present in the form of some iron phase. We have already seen magnetite, fayalite and different types of phases. We would wish that the iron that we get after the processing should remain in the metallic form. Iron reduction is facilitated by CaO addition. We will continue about the discussion of CSS recycling in the next class. Thank you.