

# **METALLURGICAL AND ELECTRONIC WASTE RECYCLING**

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**Week-4**

**Lecture-17**

Greetings, I welcome you all to the sixteenth lecture of this course. And just in the previous lecture, we had discussed the importance of various recycling steps that are involved in the recycling of copper smelter slag. We will go ahead and continue that discussion and we have already seen that copper smelter slag is an important waste that needs recycling because of the sheer amount of the quantity that is generated.

We already know that if 1 ton of copper is generated it is nearly 2 to 3 times of the amount of copper that is generated. The slag is of that quantity if X is the quantity 2X to 3X is the quantity of copper smelter slag. And we know that the important phases that are present in the copper smelted slag are iron, some amount of copper, some trace elements and silica. The most go to material that people focus on recycling, when we think of copper smelted slag recycling it is basically iron. But if some amount of copper is also extracted, we can go off about developing a process that can help us in separating out iron fraction as well as copper fraction.

And in the previous class, we have already discussed the importance of material beneficiation, the importance of having multiple stages of beneficiation that can assist in recovering the iron fraction and the copper fraction. And of course, one has to devise the next stage recycling strategy when we get such fractions, the iron rich fraction or the copper rich fraction. We will discuss and of course, we after that we had thought of the focusing on pyrometallurgical strategy as to let us say what was the process that is focusing on smelting separation or what was the process that focuses on direct reduction.

And we had various types of raw materials that help in improving the iron reduction. For instance if we had CaO what effect would it do? Now, we are going to focus on the recycling of copper smelter slags and again in the sheet that we are going to see, we see

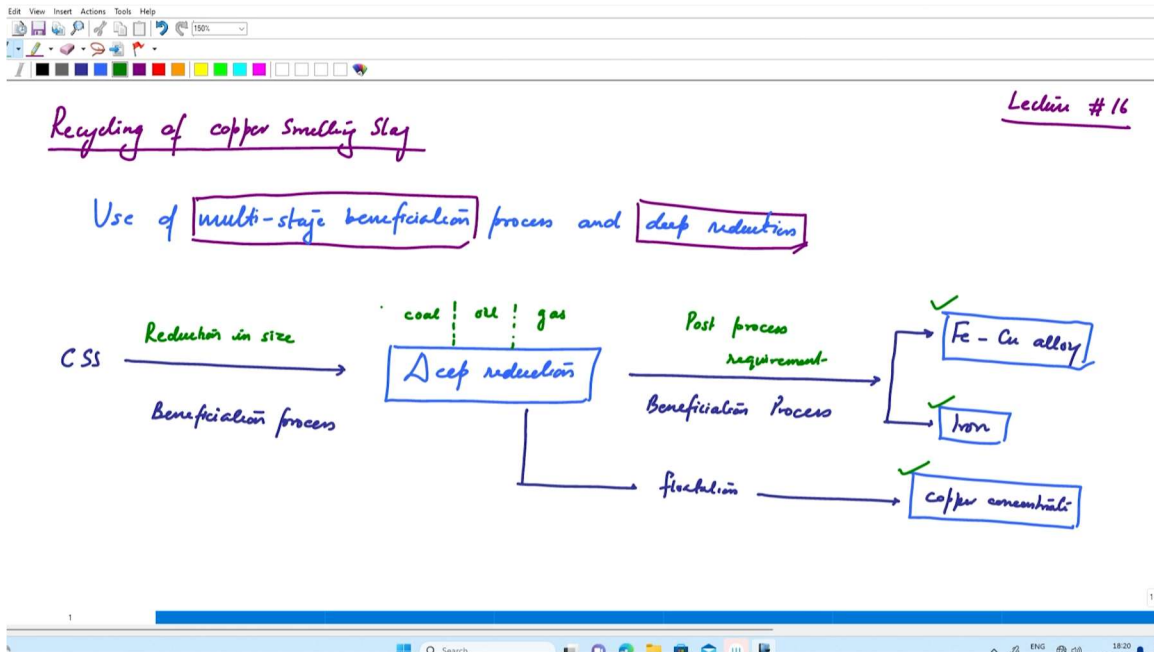
that the use of multistage beneficiation process and deep reduction. We are going to again go into the multistage beneficiation and deep reduction.

Deep reduction is basically the use of various additions that we do during the pyrometallurgical process that help in the reactions that we expect. The main raw material that we would like to react with the input that we give is iron oxide and of course, the iron rich phases. The iron rich phases should react with the additions that we do. If we are going for coal it will react with carbon, if we are adding oil the various hydrocarbons that we have added will react with iron rich phases to give us different versions of other iron rich phases and finally, we expect iron.

Finally, it should get reduced to iron. And similarly if we are adding gas, so normally the gas that is added to the process for deep reduction is basically carbon monoxide. When we are adding carbon monoxide again the same strategy we are looking at iron rich phases that will react with carbon monoxide to give us finally after all of the multiple reactions you should get iron as a finished product. If we have CSS as a starting raw material, the reduction in size, and we already know the crushing, grinding process is already done and then we go for deep reduction. We have three different categories we can have coal based that will be coal based reduction, we can have oil based reduction or we can also have gas based reduction.

Different types of additions that can be done to get to give us different types of products and of course at times we would need further beneficiation processes after the reduction itself so we can have grinding and magnetic separation. We can also have supplementary of course, this one this part of beneficiation was before we went into deep reduction this is post process requirement This really helps us in getting various types of products. If we are going into extraction of specific materials, for instance, if we are interested in iron only, then magnetic separation becomes important. At times, if we are interested in getting copper concentrates, then flotation process can be done. Depending on various type of products that we are getting, we can employ different types of beneficiation processes that are following after the deep reduction stage itself. What type of products, we get iron copper alloy, we get iron, we get copper concentrates and of course the tailings can be brought back of say for instance, if you are doing flotation after deep reduction we can just bring back the tailings, back into the comminution stage and reuse it.

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Basically, reuse the raw material multiple times so that as much as metallic content can be extracted that is achieved so the target of material recovery in all of the processes is done one after the other. As we've already seen, deep reduction can be done using coal, gas... gas of course is CO and oil as I have mentioned CxHy, this is basically denoting the composition of hydrocarbon that will be engaged in the reaction with the iron rich phases to give us finally the reduced iron. Generation of iron rich products or phases finally it will should be giving us metallic iron. Now, this is one of the methods by which we can study or extract or investigate CSS recycling by pyrometallurgical route.

We have discussed previously the general hydrometallurgical route of recycling. If we have CSS we can just go ahead and use it as a raw material for leaching, but before that we need to do the pretreatment again crushing, grinding and sieving so that the particle size is reduced and using that raw material we will be able to extract the metallic iron and copper into the leach liquor. One has to do leaching and the choice of the leach reagent, s/l, temperature, the period of leaching all of this has to be optimized so as to get the of the maximum efficiency of the raw material. Finally, it is important to note that along with these processes it is also possible to look at different types of CSS. If we are looking at a slag that is generated from waste brass. We have in the brass slag we will have zinc as a very important component in the slag. In the conventional CSS we the quantity of

zinc was relatively very less, but when we look at brass slag the quantity of zinc can be very important and in that slag, it becomes important to recover copper as well as zinc.

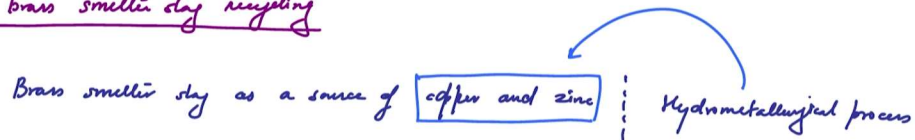
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→ Deep reduction can be done using coal, gas (CO) and oil (C<sub>x</sub>H<sub>y</sub>) as fuel source

→ generation of iron-rich products / phases

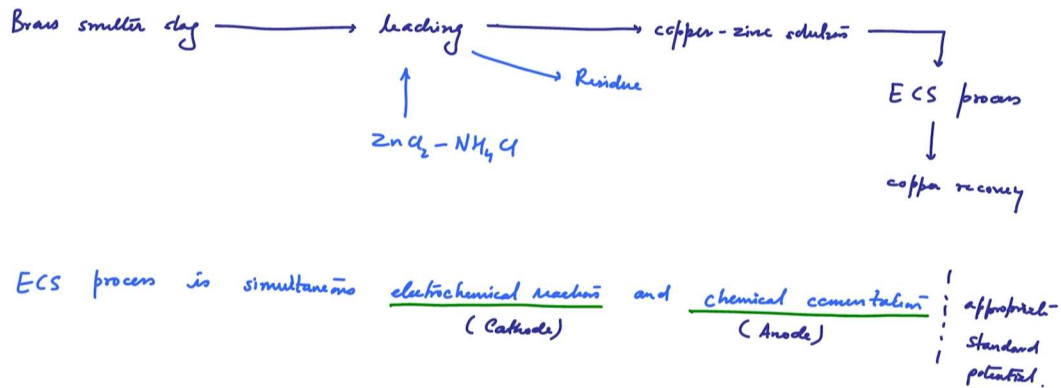
Waste brass smelter slag recycling



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A hydrometallurgical process could be such that we can have the recycling of copper and zinc. Hydrometallurgical process for copper and zinc and the most go to process would be utilizing it as a raw material leaching it and bringing back the values into the leach liquor. Brass smelter slag is leached and we get copper zinc solution, we follow the ECS process, we will be discussing what ECS really means and we get copper as the finished product. What we are actually adding as the leach liquor is basically zinc chloride-ammonium chloride solution and what we get after the leaching and filtration we get basically the leach residue. Leach residue is one part of the CSS, the leach liquor is used for ECS route of recycling and we get copper recovery. What exactly it does is basically we are able to simultaneously have electrochemical reaction and chemical cementation in the same setup.

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We have let us say an electrochemical setup which is utilizing the leach liquor and this leach liquor at the anode side we have the cementation process and at the cathode side we have the electrochemical reaction. On using both of these steps we are able to recover copper and this copper is generated at the same stage. The advantage of this ECS process is that the consumption of energy is relatively lesser and one does not have to invest on the cementation process and electrochemical process at different stages.

One can just directly have both of these two processes combined in one single process. And this is usually performed at an appropriate standard potential. These are some of the good advances that have been described in literature and what we normally get is finally, copper and some amount of leach liquor is still left after let us say ECS process. It can be used for zinc recovery because we started with a brass smelter slag and it had good amount of zinc also. Not just copper recovery we are also thinking of zinc recovery, but zinc recovery comes after the ECS process. One can think of going for a separate electrowinning process that can help in producing zinc and the whole process helps in recovering the metallic values that are present in the slag. What we have discussed till now is basically an overall perspective of the different processes that are available for CSS recycling, where we can think of iron recycling if we are conventionally going into pyrometallurgical route of recycling.

Or if we have different types of raw materials, of course, that are related to CSS, we can think of recovering these metals through hydrometallurgy as well. We will now proceed to the next copper waste, which is basically generated in the copper industry. It is the raffinate recycling.

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Raffinate Recycling

Hydrometallurgical extraction of copper : leaching of raw material → Utilization of leach liquor for metal recovery

→ After metal recovery, raffinate solution is generated.

→ Good raw material for the process

Raffinate utilization : Reintroduction of raffinate into leaching stage : High concentration of acid

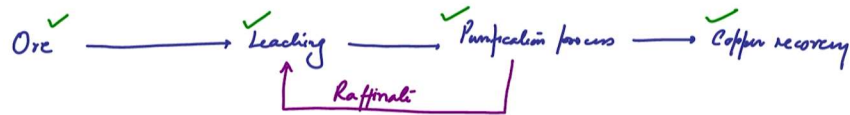
Raffinates are solutions that are produced after the utilization of leach liquor. It is related to the solvent extraction process. Hydrometallurgical extraction of copper is basically the leaching of raw material and after that we have the utilization of leach liquor for metal recovery and since we are discussing copper. We know that the leach liquor is basically rich in copper. After the recovery of copper from the solution in the solvent extraction process we get raffinate solution. The advantage of this raw material is that this raffinate solution is very rich in the acidic ions because it was directly used before it came before it became a raffinate it was the leach liquor.

After copper was extracted it is devoid of copper, but still rich in other metallic ions and let us say sulphate ions if it is a sulphate solution. Such solution can be directly reintroduced into the leaching stage because of the high concentration of acid. The reintroduction is the most common method of basically tapping the potential of raffinate. What is exactly happening here is basically ore going for copper recovery and ore follows

the leaching process after which the leach liquor is going for solvent purification process which ultimately leads to copper recovery but the raffinate is the solution that is devoid of copper.

This can be directly reused for the leaching itself just that one has to think of balancing the ions so before we even think of bringing it back and reintroducing into the leaching stage one has to characterize it. Normally the general characterization is presented, we can see that sulfate ions are having the highest concentration, this of course, mg per l is basically the concentration in milligrams per liter. Sulfate ions, iron, zinc, As, Cu, Cd, Ni, Cr we see that Cu, As, Zn and Fe are present in significant amounts compared to let us say Cd, Ni and Cr. Ni can be present in some some quantities.

(Ref. 17:00)



Compositions

(Lin et al. 2020, Kazanides et al. 2019)

Constituents	(mg/L)	Constituents	(mg/L)
$SO_4^{2-}$	45200, 23200	Cu	135, 219
→ Fe	11800, 11700	• Cd	5.31, 17.76
→ Zn	336, 1737	• Ni	4.26, 117.2
→ As	636, 67.6	• Cr	3.89, 1.92

Again these values are not completely sacrosanct, these values are in ranges as we are able to see the data from different sources and this literature is expanding so we can have values that are outliers as well. We see that these ions are present in really large quantities. When these ions are present in really large quantities we can directly think of reutilizing this solution as a raw material for leach liquor because it is the ions that we will be you losing if we waste this raffinate solution. We will be discussing more on the raffinate solution recycling in the upcoming lectures. Thank you.