METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-3

Lecture-12

Greetings, I welcome you all to the eleventh lecture of this course where we will now be discussing on the metallurgical industry wastes. Right now, we have begun the discussion on aluminium industries and in the previous class we had discussed aluminium dross. We are going to focus on spent pot lining what exactly is spent pot lining When we look at the aluminium production process flow sheet, we see that the alumina is used as a raw material for production of aluminum and this whole process is done under the name of Hall–Héroult process.

Basically, it is the electrometallurgical route of producing aluminum. And we know that such a process requires the cell that is dedicated for the production of aluminium. These cells are called pots. When we look at the Hall–Héroult cells, we see that these are used for production of aluminium and these cells itself, these Hall–Héroult cells generate the pot lining waste.

It is basically during the Hall–Héroult process that these pot linings are used and when the service of these pot linings come to an end, these are discarded as wastes. The lining is normally exposed to wear and high temperature during service. We already know that the electrolytes, molten salts, are used and we know that the cryolite is one of the most important electrolyte component that is used for aluminium. Molten salt is used and which means we will have to have high temperatures operation and we had discussed that nearly about 960 to 980 or even higher or lower around that range the temperature of Hall–Héroult process has to be maintained and of course the optimization is done unit by unit and plant by plant. Under such circumstances the wear and high temperature exposure is common for the lining and why we are because it is the molten salt and molten aluminium that is always coming in contact with the lining. What happens?

The chemical composition of lining changes. Initially, if we have refractory bricks and carbon lining, the chemical composition of the lining changes during service. This is happening during service. When it is exposed to wear and high temperature, the chemical composition of the lining changes. What happens at the end of life?

At the end of life, when we observe that the pot lining is degrading, the cell is relined and SPL is removed. SPL is basically the spent pot lining. That is removed and it is discarded. Now comes the challenge of recycling the discarded SPL.

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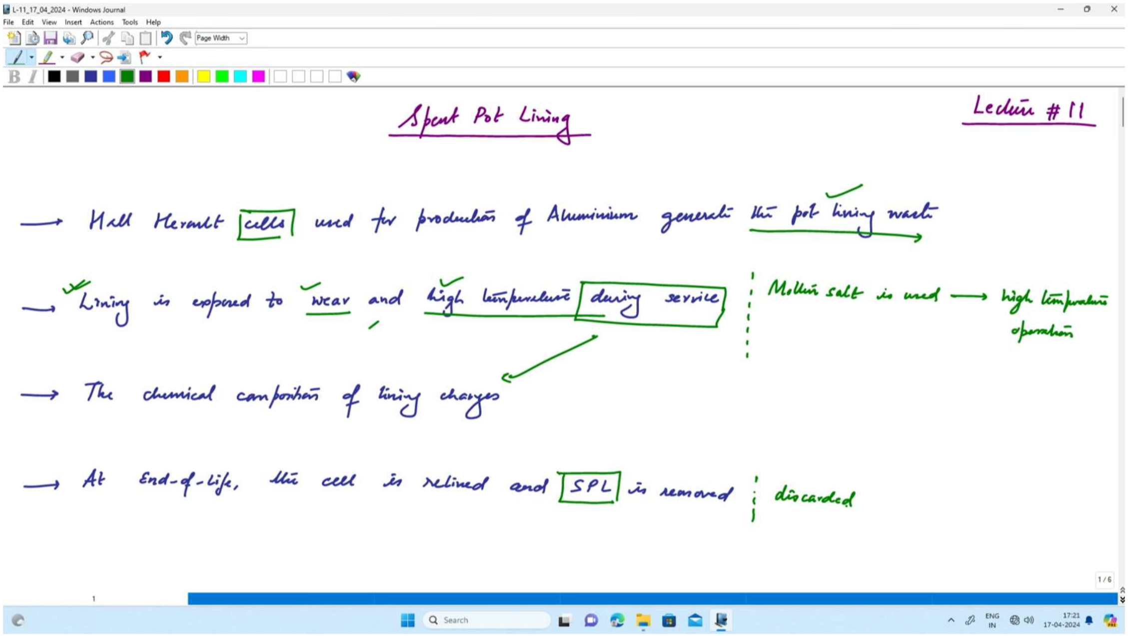

Spent Pot Lining

Lecture # 11

→ Hall Heroult cells used for production of Aluminium generate the pot lining waste

→ Lining is exposed to wear and high temperature during service ⁞ Molten salt is used → high temperature operation

→ The chemical composition of lining changes

→ At End-of-life, the cell is relined and SPL is removed ⁞ discarded

We will first begin by understanding the chemical composition of the spent pot lining. We have just seen that for a lining we must have some refractory bricks and it has to be covered with the carbon lining that was the initial composition but after service we get a very different set of phases attached to the spent pot lining. Normally, we get two cuts, two cuts of SPL.

It could be refractory dominating and the other could be carbon block dominating, carbonaceous. Refractory linings can be recycled by a different route, but the carbonaceous lining that is coming in contact with the molten electrolyte, the molten metal and the wear and tear and high temperature of the service conditions, it is that cut, it is that part of the SPL that is taking up all the hazardous components, all the hazardous phases and it needs to be recycled. Let us just now look at the general composition.

And we have just discussed the carbon block cut and the refractory cut. If we look at the carbon block cut, the elemental composition are shown here and of course these are collected from the references, and such compositions can vary from sample to sample and these are just shown to explain that such can be the composition of the SPL. And these compositions are shown as the generalized compositions.

There could be outliers also. We see that carbon is of course supposed to be the most important element in the SPL. We have 46%, nearly 50%, nearly 30%, 33% of carbon in various samples of SPL. The next most important element we can see is fluorine, sodium, aluminium. Aluminium of course because the whole system is basically the extraction of aluminium from alumina so we expect some amount of aluminium to be present and since we have added cryolite as the raw material during the Hall–Héroult process for the molten salt electrolysis, we expect fluorine and sodium to be present as well. The other impurities that could be present are oxygen, iron, silicon and calcium which are also being described. Some amount of cyanide are also generated which has been presented in milligrams per kg and this describes the general composition of spent pot lining. What are the major phases that present in SPL? When we think of the SPL, we must note that the lining is exposed to the molten aluminium as well as the electrolyte. Sodium, Na3AlF6 is an important phase, NaF, CaF2, Al2O3, Fe2O3 and other phases, These are most commonly present in SPL. These can be present in various quantities. These could have larger dominance in some samples whereas these could be present in lower quantities but it is common to find these phases in the SPL sample. And of course, there could be some metallic aluminium entrapped as well.

The quantity of such aluminium entrapped in SPL surfaces The possibility is relatively lower, but a possibility still exists. What exactly is the driving force when we think of recycling SPL? One has to think of understanding the fact that the SPL has hazardous substances, hazardous phases present in it.

The hazardous nature of spent pot lining. In the previous slide, we have just seen that cyanide and fluorine present as of course fluorides. These are already present as major phases.

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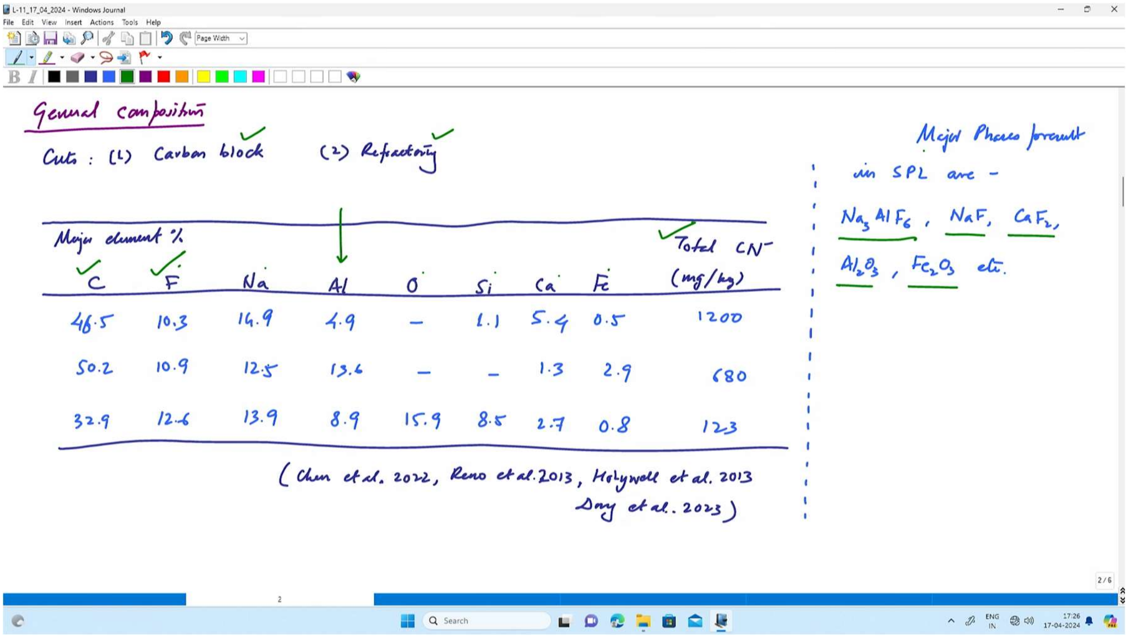

General composition

Cuts : (1) Carbon block (2) Refractory

Major element % C	F	Na	Al	O	Si	Ca	Fe	Total CN^- (mg/kg)
46.5	10.3	14.9	4.9	–	1.1	5.4	0.5	1200
50.2	10.9	12.5	13.6	–	–	1.3	2.9	680
32.9	12.6	13.9	8.9	15.9	8.5	2.7	0.8	123

(Chen et al. 2022, Reno et al. 2013, Holywell et al. 2013 Dong et al. 2023)

Major Phases present in SPL are -

Na_3AlF_6, NaF, CaF_2, Al_2O_3, Fe_2O_3 etc.

So, major phases have fluorine and cyanides. So, we have different metals and their metal oxides. This itself is a marker that the environmental pollution is possible when SPL comes in contact with water. Indiscriminate, improper disposal of SPL leads to pollution. Because we already know that cyanide and fluorides and of course some amount of metal oxides are also present which could be easily leached.

This is what here we are mentioning. Environmental pollution is possible when SPL comes in contact with water. And this actually means leaching of heavy metals and hazardous materials into groundwater, which again makes impact, it creates impact. It makes the surrounding environment basically flora and fauna surrounding environment is affected. When it comes in contact with water, we can see that cyanide phases, fluoride phases, the metallic content that may be present in SPL will be the most important phases that percolate into the environment and these will cause hazardous impacts into the surrounding environment. How do we look at it from a different perspective? When we think of recycling wastes, one way of evaluating a waste is what type of economic worth we are able to extract from a given waste. What type of value are we getting when we recycle a waste?

The other important aspect that one must keep in mind is if the waste itself is very hazardous, it becomes a responsibility, it becomes essential to recycle the waste because at times, the landfilling, controlled landfilling, even controlled land filling becomes very difficult. Storage becomes very difficult. Because such facilities would require extensive investment on their own.

Land resources, if we look at the land resources used for SPL itself, then of course we would be investing large amount of land resources and the complementary facilities for storing the SPL. One must think of devising recycling routes that can look at wastes from both perspectives. From environmental beneficiation to basically environmental uplifting or burden reducing perspective or the economic perspective. How much worth of valuable materials are we able to make from the process by recycling the waste.

These are two aspects that should be taken care of while recycling any waste. The same goes on with the spent pot lining as well. On separation of hazardous phases, SPL can be used as a source of carbon. If we somehow remove cyanides, fluorides, metals and metal oxides and other hazardous materials from SPL, all we are left with will be basically carbon. Because that was the initial composition of the raw material that was basically used in the hauler or process.

We initially had the refractory plus carbon lining. When we know that the refractory and carbon lining were used, we know that if we are able to remove the impurities, we will end up with carbon only. People have tried to investigate how can we remove these hazardous phases?

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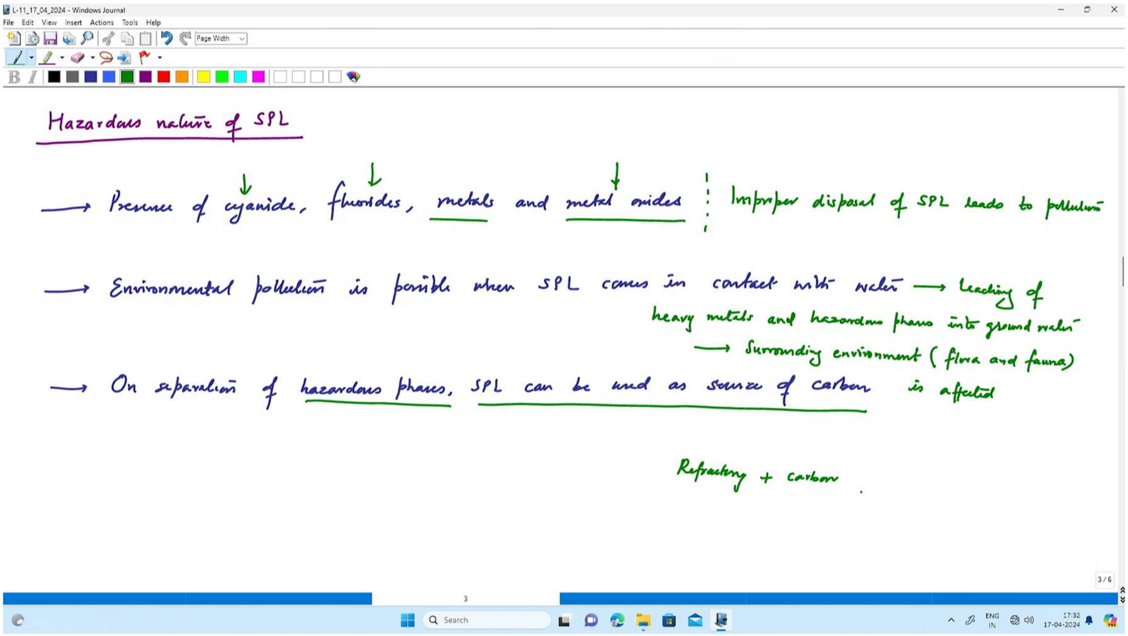

Hazardous nature of SPL

→ Presence of cyanide, fluorides, metals and metal oxides | Improper disposal of SPL leads to pollution

→ Environmental pollution is possible when SPL comes in contact with water → Leaching of heavy metals and hazardous phases into ground water
→ Surrounding environment (flora and fauna) is affected

→ On separation of hazardous phases, SPL can be used as source of carbon

Refractory + carbon

Methods of recycling SPL. Let us just begin with a hydrometallurgical scheme of recycling SPL. This is the hydrometallurgical route of recycling SPL. If we take SPL, and of course here we are assuming that it is, we make the common assumption that it is sorted, characterized, sorted and pre-treated. And the pre-treatment would depend upon what type of process we are following.

The most common pre-treatment that can be expected is the comminution and reduction of particle size. So that the leaching itself becomes easier. We have SPL that is pre-treated. We go ahead with the aqueous leaching, which is basically leaching with water.

And we get fluorides and cyanides right at the beginning itself. And when we have these phases separated out, we can now go ahead and With either of these two routes. The solid residue. This time we are just using the solid residue. Because our end result Is basically making the hazardous phases disappear from carbon lining. Spent pot lining was essentially carbon lining. As we have just discussed in the previous. It's just carbon. We want to target carbon.

The recovery of carbon is supposed to be aimed at. So, we are trying to remove the hazardous phases here. Fluorides and cyanides can be removed by water washing and we will again use the residual solid for acidic as well as alkaline leaching. When we look at acidic leaching directly, we can use let us say HF or fluorosilicic acid and we can get alumino silicates and cryolite and CaF2 as the products and we are subtracting these phases one after the other, and finally we would go for water treatment to get our desired composition of SPL, which is basically just removing all the hazardous phases by acidic leaching. The other route would be combination of alkalis and acids, so we have we begin with alkaline. After aqueous leaching we have the alkaline leaching.

In this case, we had the acidic leaching. We are beginning with alkaline leaching. We can use NaOH or KOH and of course, NaOH is a better reagent here. We get cryolite and alumina phases out of the feed and then we can follow the leaching with let us say H2SO4 and perchloric acid. And here we will get cryolite, alumina and CaF2 as the phases and we are recovering important phases, salt phases from the SPL as well. One could not just see it as a recovery of the SPL, but it also could be seen as the recovery of various phases like Cryolite, alumina, CaF2, and alumino silicates.

This means that using the SPL as a raw material, we can get a wide variety of products, phases and carbon.

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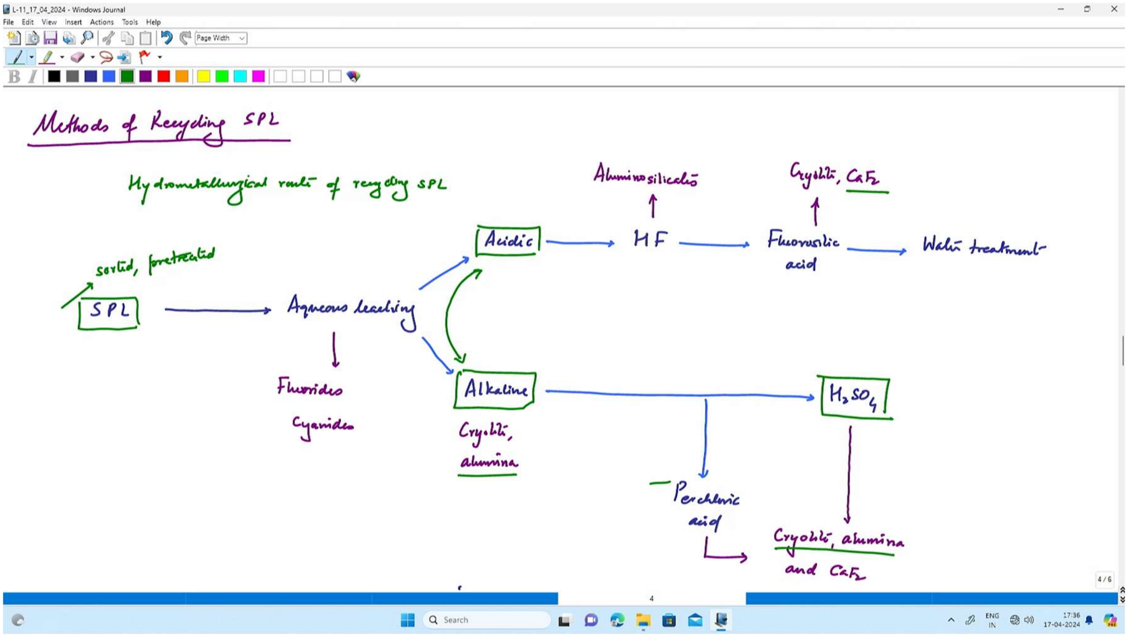

That was hydrometallurgical route of treating the SPL. When we think of using SPL as a raw material for pyrometallurgical routes, we can see that the decomposition of cyanide at high temperatures is possible through combustion. We are just using SPL for combustion. SPL combustion is being done and decomposition of cyanides is taking place. It also means, it also could be seen in a different way. For instance, if we are using SPL as the raw material for combustion, large amount of heat is also generated.

Because the major component of SPL, still 50% or more at times, could be just carbon. Large amount of heat is generated when SPL is subjected to combustion process. And this could be used in various industries. Heat can be used industries like iron making, steel making etc. or cement making. What exactly we are trying to do is we can target the heat energy that is evolving while combustion of SPL. Let us just now look at a general scheme of SPL recycling. If SPL that is generated in Hall–Héroult process or let us say aluminium industries. The SPL is generated in the aluminium industries.

We can think of either disposal or recycling. When we think of disposal and the disposal could be controlled landfilling or it could also mean that we have temporary storage after treatment. Both routes are possible. We have landfilling and storage after treatment.

The treatment would be maybe let us say removal of some amount of fluorides and cyanides by washing. This could be some treatment that could be done for SPL making it less hazardous and relatively more safe for storage. The other way could be when we start to recycle it and we can just think of it as a raw material for steel and iron making industry or cement industry where it could be used for generating heat when we just directly use it as a raw material for combustion.

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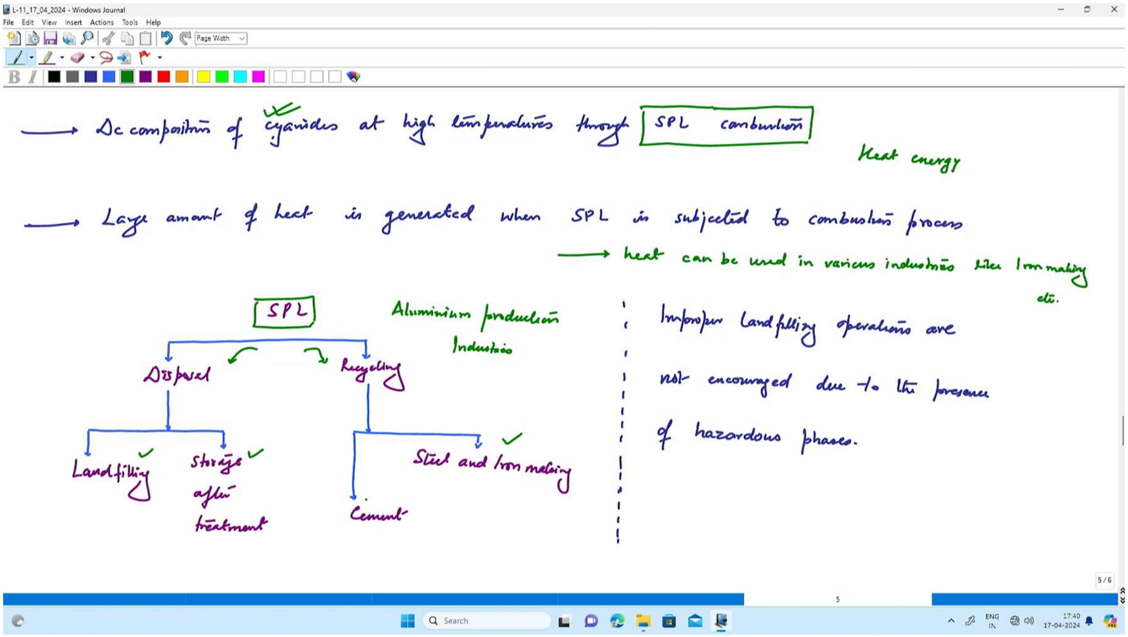

→ Decomposition of cyanides at high temperatures through SPL combustion

Heat energy

→ Large amount of heat is generated when SPL is subjected to combustion process

→ heat can be used in various industries like Iron making etc.

Improper Landfilling operations are not encouraged due to the presence of hazardous phases.

We should note that improper land filling operations are not encouraged due to present of hazardous phase. We have been discussing this in the previous slides as well that it is very important to note the phases that are present in the SPL and given the difficult complex nature of the raw material, it is very much important to devise methods that can help in recycling the SPL. We have seen the production of SPL, we have seen the general composition, we have seen that the SPL consists of two cuts. The refractory cut can be recycled separately and the carbon cut can be recycled by hydrometallurgical route or pyrometallurgical route. And we have also seen various types of leaching operations that can be done to recover various phases as well as carbon. And we have seen that the direct application of SPL could be done for generation of heat energy.

In the upcoming lectures, we will be discussing some more wastes that are generated in aluminium industries. Thank you.