

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week-3

Lecture-11

Greetings, I welcome you all to the 10th lecture of this course where now we are going to concentrate on the metallurgical based recycling. In the previous lectures, in the previous set of lectures we have seen the various strategies that we have developed for sorting, pretreatment and the metallurgical based recycling followed by refining. We are going to employ all of these strategies for recycling the metallurgical wastes that are generated in metallurgical industries. We will begin with the aluminium industry and the first waste that we are going to discuss is aluminium dross. This lecture will be focusing on aluminium dross and we will be going to discuss how it is generated, what are the general composition and of course, we will see why it is so important to recycle this waste and finally, we will be seeing what are the methods of recycling dross. To conclude this lecture, we will be just encompassing all of these in the brief outlook and let us now begin with the discussion on what exactly is aluminium dross. Aluminium dross is formed when molten aluminium comes in contact with atmospheric oxygen. The most important requirement of the dross formation is that it forms when there is the contact of molten aluminium which means it will either be formed in a smelter unit or in a melting unit where melting of aluminum is carried out and casting is carried out.

Molten aluminum will be coming in contact with atmospheric oxygen which we can easily say that it is such a system is open to air, open to atmosphere. When it is open to atmosphere, molten aluminum comes in contact with atmospheric oxygen and it forms aluminum oxide. The formation of oxide takes place on the surface so what happens is, if we have a molten bath of aluminium and atmospheric oxygen is coming in contact with it, we will have the formation of dross, aluminium oxide is forming at the surface. When this is happening it and so when the oxide layer is removed of course, when we think that we have sufficient molten metal or whatever process that we are involved in with the molten aluminium when it is done, we would like to cast it or take it to the further processing.

When such a step is about to be done we normally remove the aluminium oxide layer. When this is done, some metallic content of aluminum gets entrapped in the oxide matrix. This oxide that is generated will entrap some molten aluminum, the metallic content and be removed along with the oxide itself.

The oxide matrix is picking up the molten aluminium, molten aluminium metal with it and it is getting removed from the system. In this sense, we are actually losing molten aluminium. We are losing aluminum on two fronts. First is the aluminum oxide that is forming at the surface and the second when we are trying to remove this aluminum oxide layer, we are also experiencing the loss of molten aluminum which is entrapped in it.

This heterogeneous product of oxide metal entrapped in the matrix and salt fluxes, where are salt fluxes coming from? The salt fluxes are present in the system to bring down the operation temperature, the smelting or melting or whatever process pyrometallurgical process that we are involved in, it brings down the temperature and it also acts as the protective layer so the salt fluxes are essential.

(Ref. 5:20)

The image shows a screenshot of a digital note-taking application with the title 'Metallurgical Waste Recycling' and 'Lecture #10'. The notes are written in purple ink and describe the process of aluminium dross formation. It starts with 'Aluminium dross' and explains it is 'formed when molten aluminium comes in contact with atmospheric oxygen'. A green arrow labeled 'open to atmosphere' points from 'molten aluminium' to 'atmospheric oxygen'. To the right, it notes the 'formation of oxide on surface of molten aluminium'. Below, it states that 'when oxide layer is removed, some metallic content gets entrapped in oxide matrix'. At the bottom, a summary sentence reads: 'The heterogeneous product of oxide, metal entrapped and salt fluxes forms the dross'. The application interface includes a toolbar with drawing tools and a Windows taskbar at the bottom.

It is basically a heterogeneous mixture of product of oxide, aluminum interact with the oxide and salt fluxes which gradually when allowed to cool it becomes hard lumpy mass called dross. Now that we understand what dross is, we will now look at the general

composition of dross. And we are saying general composition because it is a fairly possible that we may come across some dross samples that may not fall in the compositions that are being described in this table and of course this table is collected from by observing some of the data in the literature and we see that the dross can be categorized in three different categories. White dross, black dross and salt cakes which has various compositions of percentage aluminum, aluminum oxide and salt fluxes and we see that white dross has highest amount of metallic aluminum concentration. What it means is, it means that in this dross, large amount of aluminium get entrapped in the oxide matrix. And similarly, the oxide concentration is relatively lower and salt fluxes are very less. From a primary smelter, if we see that aluminium is being lost as dross, we will have large percentage of metallic aluminium in it. Along with the aluminum oxide that is entrapped it and very less concentration of salt flux.

Black dross however has lower concentration of aluminum and higher concentration of aluminum oxide. And similarly, it will have a larger concentration of salt fluxes. This could be coming from a secondary smelter unit or secondary remelting unit. The salt cakes or salt slags will have the least amount of aluminium and very large amount of aluminium of salt fluxes that have been used.

It could have nearly 20 to 80 percent salt flux wherein these salt cakes are formed only after recycling aluminium dross or aluminum scraps. It happens that the molten aluminum, the metallic aluminum in the salt cakes is very less, some amount of aluminum oxide is also observed but the major dominance of the composition is of salt fluxes which is observed. We also observe that multiple aluminum containing phases, aluminium containing phases like carbides and nitrides are also present in the dross. These types of phases are formed due to the presence of various elements.

(Ref. 9:00)

General composition

Dross	% Aluminium	% Aluminium oxide	% Salt flux
✓ White dross	15-80	20-85	< 5
✓ Black dross	7-50	30-50	30-50
✓ Salt cake	3-10	20-60	20-80

(Manfredi et al. 1997, Manikhand, 2012)

Multiple aluminium-containing phases like carbides and nitrides are also present.

→ Trace elements like Mg and Zn are also present as impurities

When the aluminum is in the molten state if there is large amount of oxygen, we will have aluminum oxide forming some amount of nitrogen and carbon are also present, we will have the formation of the carbides and nitrides in the dross as well.

Some amount of trace elements why are we calling them trace elements because these are present in very less quantities so trace elements like magnesium and zinc are also present, and these are present as impurities. Although these are not essentially part of the molten aluminium, these are also included as metallic impurities. But of course, the composition of such trace elements can vary from sample to sample and from unit to unit and batch to batch that is produced at various aluminium industries. Why exactly is it hazardous? When subjected to improper recycling aluminium dross, or we can say improper recycling could be also referred as uncontrolled/ unsupervised landfilling, what would it do? Basically, dumping aluminium dross in various landfills is not going to help. Because, as we have just seen, many phases that are aluminium rich, they can be present and at the same time, there is a possibility that there are heavy metals that are present in dross.

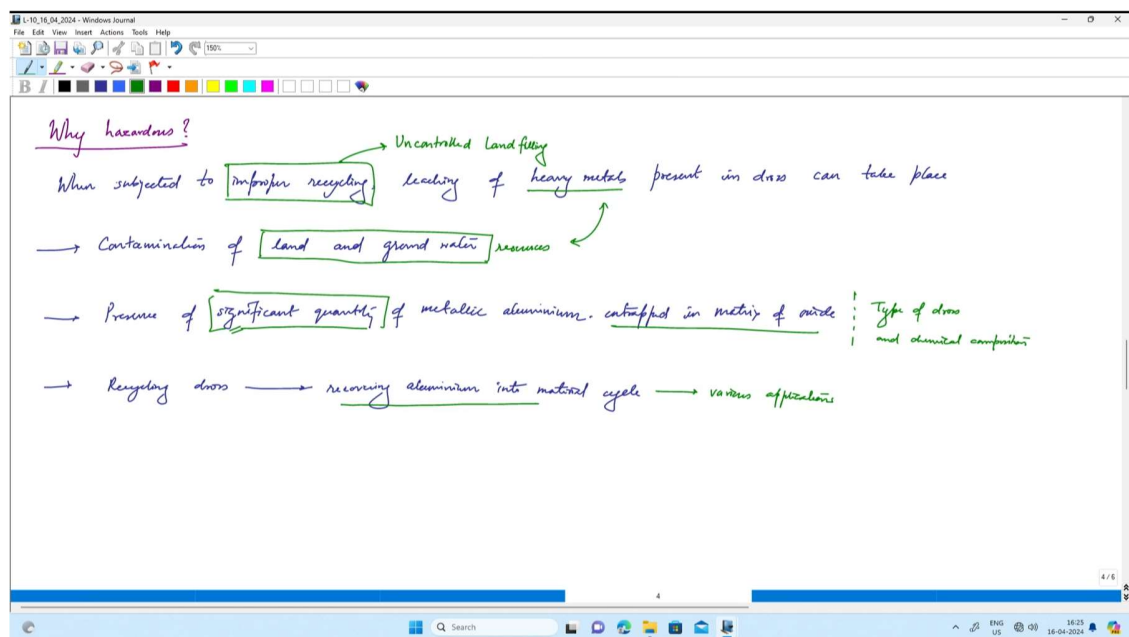
These heavy metals can be leached from dross to the various resources that are present in the landfill, which could eventually lead to contamination of land and groundwater resources. Land resource and groundwater resources are contaminated because of heavy

metal leaching so what it does is basically it can change the pH of the groundwater and this affects the flora and fauna around the land the landfill.

The other way of looking at the importance of aluminium dross could be that of course, the dross is hazardous but at the same time it has significantly large amount of metallic aluminium, again that depends upon the type of dross and chemical composition. The type of dross and the chemical composition basically helps us in identifying the value that can be recovered by recycling the dross. Presence of significant quantity of metallic aluminium. Significant quantity. We have already seen the types of dross. So we know that it can have really large amount of metallic aluminium.

And of course it is entrapped in the matrix of oxide. And of course when we are able to recycle all of the dross. The recovery from aluminium oxide is also, possible, so when we recycle dross it is basically recovering aluminium into material cycle, so bringing back aluminium from the dross into material cycle which could be again used in various applications.

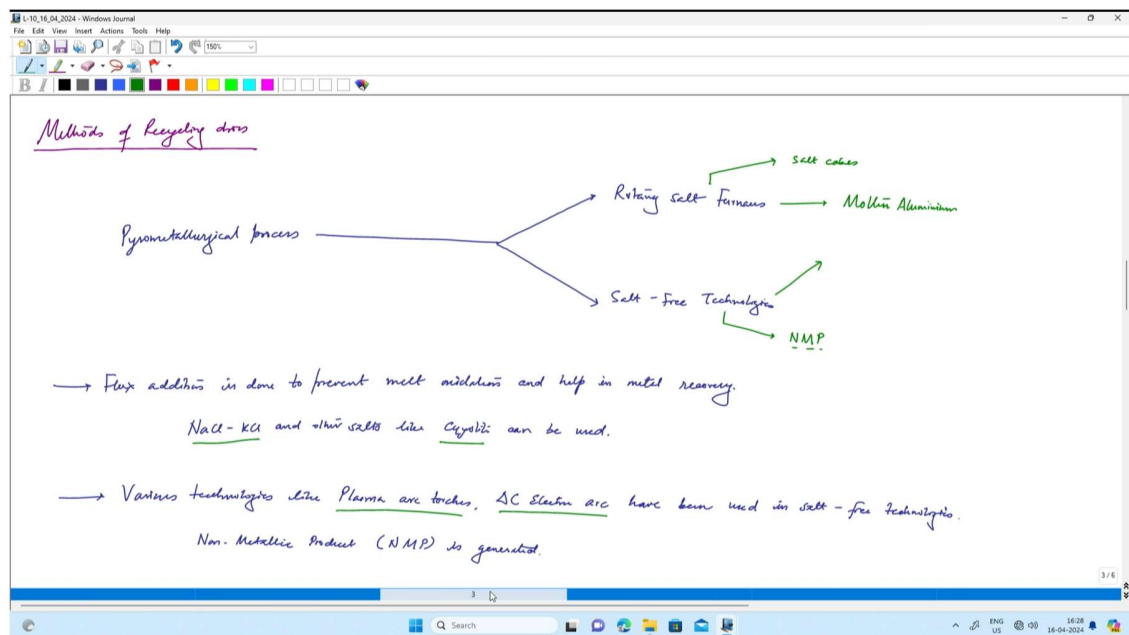
(Ref. 13:26)



And that would be done only after extracting the metal and refining it and achieving the desired composition as we had discussed in the previous class. What are the methods of recycling dross? The conventional method, the most commonly used method is the

pyrometallurgical route of recycling dross and this can be categorized as the conventional rotary salt furnaces and the modern/the new age salt free technologies. What exactly is the difference in these two routes, rotary salt furnaces as the name suggests, is using furnace that can rotate and has the provision of salt addition as fluxes. Fluxes will generate different salt cakes, as we have already discussed previously in the lecture today. Addition of dross is done, temperature is maintained to about 800 to 900 to 950 degree Celsius and the rotation of the furnace is carried out at various rpm and the salt flux addition is also done. It helps in removal of metallic aluminium in the molten state and so in both the cases what we are actually getting is molten aluminium in both the cases. But in rotary salt furnaces we are getting salt cakes whereas salt-free technologies are giving us NMP, non-metallic product which is free from metallic aluminium but it mainly contains the non-metallic products like impurity oxides or aluminium oxides.

(Ref. 15:39)



Rotary salt furnace is basically a furnace that can rotate. It consumes salts. And what are the salts that are normally used? NaCl, KCl and other salts like cryolite and other salts can be used for the mixing of the salt fluxes and this mixture is again used here. So, NaCl KCl with cryolite is one example or KBr could be another example and this is used in the RSF. When we look at salt-free technologies, it basically employs newer strategies. Newer strategies like plasma arc torches and DC electric arcs which are being used for

melting dross and then recovering the molten aluminium without using the salt fluxes. A significant change that has been observed in the modern recycling strategies is the use of salt-free technologies which can employ extremely high temperature arcs, plasma arc torches and DC electric arc furnaces for the recovery of aluminium by these processes. What we normally get after the SFT is molten aluminium and NMP.

When we get molten aluminium again we can bring back the molten aluminium into the material cycle and reuse it after composition adjustment. NMP could have various different applications based on its chemical composition. Hydrometallurgical process, so the process that we have seen can be categorized into at least two routes the pyrometallurgical route which basically produces metal and of course, after refining it could be directly used in applications. But the hydrometallurgical route basically takes aluminium dross and again we are assuming that this dross is sorted which means again classified and characterized and pre-treated. Sorted and pre-treated. So, when we have dross like this, we subject it to leaching operation which is the first step we have already studied this the first step of hydrometallurgical process we after pre-treatment we leach it and we can choose our reagent acidic or alkaline and we can see that we get leach liquor and of course the residual solid. Normally we would expect aluminium to go into the leach liquor. But of course, there is a possibility that some amount of aluminium may be left behind in the residual solid as well. Based on, again one has to think of characterizing.

Characterization of liquor and residual solid. We can then decide upon what type of further processing we can apply for both of these products. For leach liquor we can have, we can go for precipitation or crystallization based on the desired aluminium-rich product. Again, this is aluminium-rich product. And from the residual solid we can think of developing composites.

If the chemical compositions of the residual solid are in alignment with the composition that is required in the composite making process. What are the key products that can be made using aluminium dross? We have seen various processes that are utilizing aluminum dross as raw feed. We've already seen that normally when we devise a recycling process, you must have raw material. We do the pretreatment, we follow the recycling strategy, recycling process one and two and so on and so forth and then we are into refining if metal is produced, if not then we can refine the product itself and then we can use it, use/application. So what are the key products that have been described in

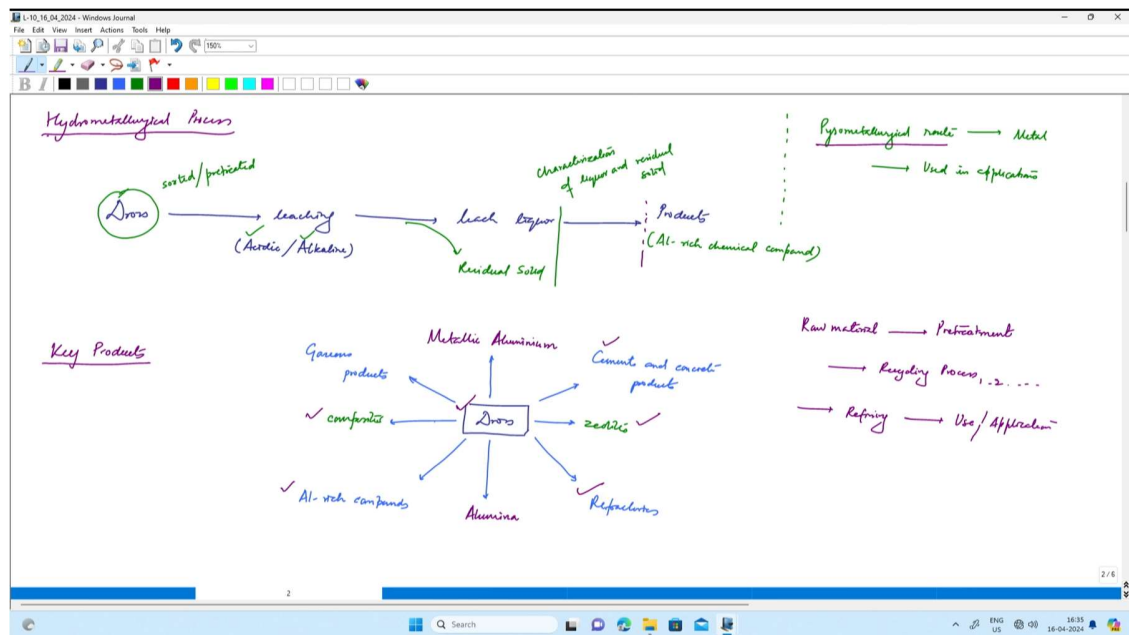
literature. From dross, the first and the most important product that has been described is of course the metallic aluminum and it is produced by the pyrometallurgical route.

We just take the raw material, the dross and we just melted either in the RSF or in the SFT or using the SFT and we will be achieving our goal of producing molten or metallic aluminum. Also, we can produce alumina, which can be produced by the hydrometallurgical route and purifying the leach liquor and precipitating alumina from the leach liquor. Aluminum as well as various phases of alumina can be produced by the hydrometallurgical and pyrometallurgical route.

The other products that can be produced include zeolites, which can be produced by the hydrothermal processes. Composites taking raw materials directly, taking raw materials including aluminium dross directly for making composites. Similarly, we can use aluminium dross for making cement and concrete products. Various aluminium-rich products, again this can be produced by employing the hydrometallurgical route, taking leach liquor and trying to direct the composition in such a way that the chemical composition is achieved. Refractories that for instance high alumina refractories or such refractories can be produced and the applications of such refractories can be shown that of course the recycled alumina, the recycled refractories works on par with the conventional refractories as well and one of the most important aspects that can be produced including all of these products is the gaseous products.

Recently, it has been seen that important gases like ammonia, hydrogen can be produced using aluminium dross using various solutions like alkaline and acidic solutions. Again, all of these routes are being investigated. Pyrometallurgical route has been used extensively in the industry and it's a common method to just take dross and melt it in a furnace and extract the molten aluminum.

(Ref. 24:00)



But the hydrometallurgical process and the hydrothermal process are relatively newer and these are being explored extensively in the present day research. What we would like to conclude by just summarizing what we have learned in the context of aluminum dross. Aluminum dross is basically a waste that is generated when molten aluminum comes in contact with atmospheric oxygen and the layer of alumina is formed on top of the molten aluminum. When such a layer is removed, metallic aluminum is entrapped in it and then there are multiple phases of aluminum-rich compound that are aluminum rich which can be present in it. And based on the composition of aluminum, metallic aluminum that is entrapped in dross, we can have various categories of dross. The recycling of dross can be done by pyrometallurgical as well as hydrometallurgical processes.

We can get metallic aluminium from pyrometallurgical process and aluminium-rich products from hydrometallurgical processes and we have a wide variety of products like metallic aluminium, alumina, zeolites, composites and so on and so forth based on the composition that is that is required we can develop or add and subtract the processes and attain the desired aluminum-rich product. This is how we can think of recycling aluminum dross.

In the upcoming classes, we will be discussing other aluminum wastes and we will see how these can be recycled. Thank you. Bye.