

METALLURGICAL AND ELECTRONIC WASTE RECYCLING

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Week- 6

Lecture-30

Greetings. In the previous class we had discussed the recycling of iron and steel making scraps and before that we had discussed the iron and steel making slags and now, we are at the end of this discussion on iron and steel making industry wastes where we will be discussing waste water recycling. Why exactly is water being described in steel making waste club? The idea is that in this collection of wastes that we look at from iron and steel making industries, water waste is very much prominent. It does not appear to be prominent unless we look at the total quantity of water that is used. In today's class we will be discussing about how wastewater is generated, in what fronts and what are the variations in chemical compositions and what we can do to recycle this wastewater to make it fit enough to either reuse in the industry itself or if at all it has to be discharged into the water stream what is the chemical composition treatment that one needs to do before it is released into the environment.

Because we know that the different types of metallurgical wastes that we have seen from aluminium industries, copper industries, zinc industries and in iron industries we know that the direct discharge of these wastes is hazardous but most of these wastes were solid and zinc dust is also actually a solid but it can be released in the atmosphere also. But most of these wastes are solid. What happens if a liquid is discharged and if this liquid is discharged directly into the water source? We are talking of wastewater that is generated in iron and steel making industry in various units and the composition of wastewater can change depending on where it was generated and one has to think very judiciously as to what is the process that one has to follow to recycle these wastewater streams. We will just begin. Wide range of processes generate wastewater streams. This is not just one single stream. These are wastewater streams. Let us just broadly see. One might not consider but mining wastewater is also; one might call it mining drains. So, mining waste water, there is coking plant waste water that is happening in the metallurgical coke generating unit.

Then we have sintering unit. We have sintering waste water. And these are just pre-treatment units. Finally, we are reaching the iron making. Iron making waste water. After iron making, we will have steel making waste water. Then we have steel rolling because rolling process consumes lots of water. It generates wastewater and then we have the cold rolling process itself consumes water and that water can contain large amount of metal ions which can be brought back into the material cycle. We see that these are the broad categories of wastewater that is basically generated in different processes.

We know that such is the consumption. What exactly is the overall consumption per ton of steel? Let us look at that. It has been found that nearly 28.6-meter cube water is used for 1 ton of steel production which means this is the estimate of waste water generation per ton just multiplying it to let us say the world production of steel in a given year would give us the water that is used directly in steel making industries taking into account the totality of the steel making industries of the world.

This is what we are really looking at and this itself is a very large quantity of course, this number is not big when we are just considering one ton. But consider the complete steel production throughout the world then this number becomes very much significant and which is itself a big motivation why really it is a big problem and why really discharging this waste water into let us say nearby river or any other water source is definitely not a good option. Quantity of steel versus quantity of water used is basically what we know and we know that nearly 90% of the water that is used is basically it can get reused by after pre-treatment and removal of ions because at times we also have to consider some evaporation loss.

Even if we consider a given quantity of water is used and we have some losses in evaporation still the water can be recycled so releasing of water in environment is definitely not an option, at least untreated water. One has to think of treatment so that we can reuse it or else it can be safely discharged. Only if we are not intending to reuse it. That is how we can proceed.

(Ref. 9:10)

Wastewater Recycling

Lecture # 29

Wide range of processes generate wastewater streams | broad categories of wastewater

→ Mining wastewater → coking wastewater → sintering wastewater

→ Ironmaking wastewater → steelmaking wastewater → steel rolling wastewater

Nearly 28.6 m³ water is used for 1 ton of steel production

Treatment → Reuse
→ Safely discharged

We must note that what are really the variations in chemical compositions. We have seen the categories of wastewaters and such a classification of wastewater and the chemical compositions that we are now about to study, the variations are enormous because these are generated in different sources. So, one really cannot club these wastewaters together. These wastewaters should be ideally separately treated. We know that it may not be possible, but the chemical compositions vary a lot. We will now discuss the chemical composition. And here we have table 1, table 2 and table 3, collected from different sources. These are from different-different categories of steel making of steel making wastewater. We have steel making unit, we have cold rolling and again we have steel making and with this we can take an estimate that really the chemical composition fluctuates a lot from sample to sample, from unit to unit and of course, from plant to plant. If in a steel making waste water sample if we have iron 4.8 milligrams per liter. We can also have different other elements. These are heavy metals. We have As, Cd, Cu, Cr, Hg, Ni, Pb and Zn.

These are present in relatively very less quantities. Mercury is also in micrograms per liter. That is the scale for mercury in this specific data. Similarly, if we look at cold rolling wastewater, we see that this data is milligrams per liter and these are the concentration of ions. We see that here we have sulfates and chloride described here and we have the metal ions on the side. We have sodium, calcium, magnesium, iron and we see that sodium is present in very large quantities in cold rolling wastewater. Cold rolling

wastewater is having sodium, sulfate, chlorine, calcium, magnesium and iron and we see that iron is very less. Again, from a different steel making wastewater stream, we see that the concentration of iron, Fe^{2+} , Pb^{2+} , Zn^{2+} and Cr^{6+} , hexavalent of chromium, these are present in such quantities. The concentration is given in milligrams per liter and we see that such 309 milligrams per liter is the concentration of iron. We see that the concentration of various metal ions can fluctuate by a large margin.

(Ref. 12:55)

Chemical composition of wastewater

#1	Wastewater	As	Co	Cu	Cr	Fe	Mg	Ni	Pb	Zn	(mg/L)
Steelmaking		<0.01		0.005	<0.004	4.8	<0.1	0.02	<0.005	0.007	

(Blanco-Vicente et al., 2022)

#2	Wastewater	Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	SO_4^{2-}	Cl^-	(mg/L)
Color rolling		1855.2	254	364.8	0.03	5988.5	87.2	

(Jiang et al., 2014)

#3	Wastewater	Fe^{2+}	Pb^{2+}	Zn^{2+}	Cr^{6+}	(mg/L)
Steelmaking		309	20.5	40.4	10.9	

(Ravash et al., 2023)
(Lawal et al., 2020)

At times we can have single digit concentration and at times it can go to hundreds. This depends on what is the source of waste water. Identifying that okay we will recycle this type of waste water is not going to help. One has to precisely monitor what is the concentration of metal ions in water, what source if water sources vary or let us imagine a situation where different water streams are merged then keeping a track of concentration becomes very difficult because then the homogenization of ions may or may not take place and then one has to build a special reaction mechanism where most of the metals can be isolated. That may also become fruitful if we have such technologies developed, but if we have separated sorted streams of wastewater and dedicated units then we can recycle these waste water appropriately. Application of technology, the recycling technology for waste water and the technologies that we are about to discuss, like reverse osmosis or ion exchange resin beds or nanofiltration units. If these technologies are

available, then these can be clubbed one after the other and waste water in general can be processed.

But such facilities have to be developed so that efficient removal of these heavy metals from the waste streams is achieved. From this table what we see is that in most of the waste water samples we have iron and we have other heavy metals like chromium, zinc and in some cases copper, lead, magnesium, and sodium these are present. One can devise a strategy of precipitating or removing these metal ions and then if at all these salts can be separated out further pH balance can be done so that these can be reused in the plant itself. One has to think of wide range of chemical composition available for, chemical composition dictates the recycling process. If we know that wide range is available, we just directly focus on the available chemical composition and then directly just work around the given wastewater samples.

What are the recycling strategies, recycling processes? We know that the chemical composition has to be the key because we have a wide range of waste waters and why do we really need to recycle? Why recycle waste water? We know that the quantity is enormous, just need to multiply the numbers here so X meter cube, in this case it is 28 meters cube into the total steel. That is how we could say that it acts it is actually not and then we know that chemical composition has heavy metals and it's not safe to discharge so environmental concern. If that was an engineering concern this is an environmental concern and it is very hazardous waste. How do we really go about the recycling process itself. The conventional processes, are the precipitation, chemical precipitation. If we are using sodium carbonate or calcium carbonate that is the chemical precipitation so that we are able to precipitate some salts. What we might get is some salts or we can have chemical reactions. If we are targeting some specific product from waste waters then we can have chemical reactions. This can also be aiming removal of these heavy metal ions that so why we are recycling because we want to bring it out, so removal of heavy metals as compounds products.

(Ref. 20:30)

Wide range of chemical composition ^{available} for this recycling : Chemical composition ^{disables} this recycling process

Recycling process

Why recycle wastewater?

- Quantity of wastewater generated is enormous
- Chemical composition has heavy metals ^{hazardous waste} [Environmental concern]

Conventional processes

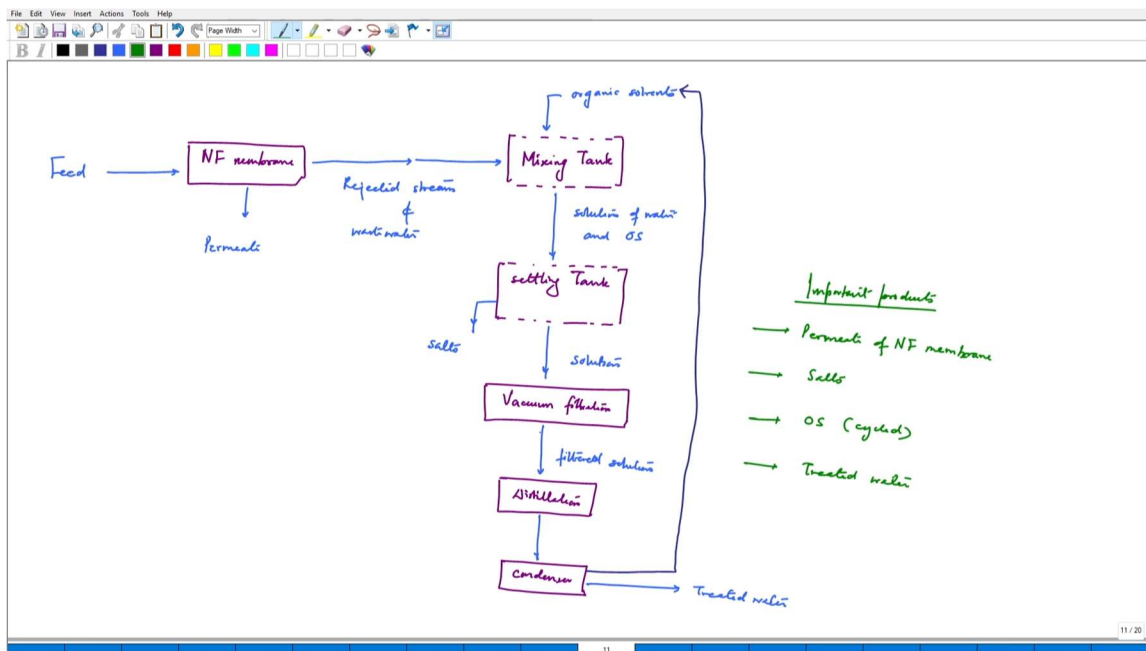
- Chemical precipitation (Salt)
- Chemical reactions
 - removal of heavy metal and compounds

This can be done. Conventional processes involve the precipitation or we can also have some sort of oxidation or reduction reaction that can help us in removal of these these products. At times, these might work but now the chemical variation itself in wastewater is enormous one has to think of devising other strategies also on top of them. We will now look at those strategies which are beyond the regular precipitation strategy. One can think of use of ion exchange or reverse osmosis but we will have this different strategy wherein we have feed, we have membrane, nano filtration membrane, this gives us permeate rejected stream of wastewater.

Nano filtration membrane is generating two types of feeds. After filtration the reject of the nano filtration membrane unit is basically released that is being processed with organic solvents. Mixing tank is present and this mixing tank is picking up reject of waste water stream coming from NF membrane and this is organic solvents. Organic solvents that can be miscible with water this leads to generation of solution of water and organic solvents and we have a settling tank. So, we had a mixing tank, now we had settling tank and after that we have the removal of salts. After the mixing of organic solvents, we let it move to the settling tank where there is the ejection of salts and we also have the movement of solution to a vacuum filtration followed by a distillation unit and condenser unit. This is the filtered solution and after condenser what we get is treated water and one stream is actually going up to the organic solvents.

This is the organic solvent stream that is recycled here in the condenser. What we see here is that we have a wide variety of products actually. What are important products here? First step is permeate of NF membrane, nanofiltration membrane, the second one is the salts that is generated in the settling tank, the third one is the organic solvents. These are cycled and the treated water which is what we really wanted.

(Ref. 26:00)



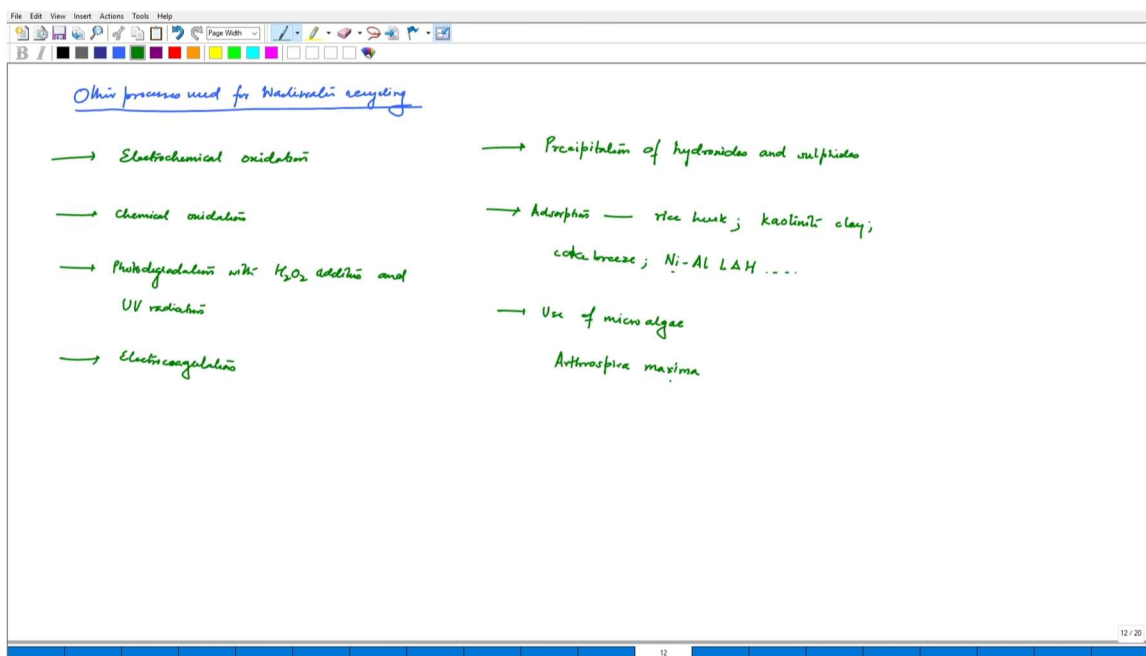
This is just one method by which we can club different types of operations one after the other and remove salts. But it is lot of investment to you know even think of such recycling strategy. One has to be very sure about what we really wish to remove and to what extent. Because we know that most of these processes have their own advantages and disadvantages and their limitations as to what is the limit of metal extraction.

If we are able to achieve the desired chemical composition after these processes then it is acceptable else one really is in a dilemma what type of processes should be used to achieve the chemical composition. What are the other other processes used for waste water recycling? We are just going to jot down some of the processes that people have explored in wastewater recycling and what are the key points that they wish to put up for addressing the wastewater issue. Some of the processes are electrochemical reactions.

Electrochemical reaction that is oxidation. We can have chemical oxidation. We have photodegradation with H_2O_2 addition. and this is H_2O_2 addition and UV-radiation.

We have electrocoagulation. Similarly, we have precipitation. We know that precipitation is a conventional route, but still people have tried different methods. Precipitation of specific products hydrates, hydroxides and sulfides. Adsorption of various products of and various heavy metal ions has been explored using lot many different materials. We will just write adsorptions using rice husk or kaolinite clay or coke breeze or Ni-Al, LDH, layer double hydride, layer double hydroxide actually, LDH, Ni-Al LDH and so on so forth. Many adsorption reagents have been used for the adsorption reactions wherein people have tried to use materials as adsorbents and the heavy metal ions or the material of that of their choice are absorbed in turn leading to the wastewater recycling and there is the use of microalgae. One of the microalgae could be *Arthrospira maxima*, *A. maxima* and such microalgae have been used for the remediation of wastewater.

(Ref. 31:00)



The degree of success for various types of processes are varied and this again depends upon sample to sample, processing conditions, from one type of process to the other and what exactly was the chemical composition, such data is available and one can really

devise an ideal strategy for wastewater recycling if we are able to club these strategies one after the other.

But again, it depends upon the economic and technological constraints that are present in the industry. Now, we are at the end of this metallurgical waste unit of iron and steel making and now in the upcoming classes we will be focusing on electronic wastes, where we will be discussing different types of electronic wastes and the general methods of recycling such wastes. Thank you.