Basic Environmental Engineering
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Lecture 47
Industrial Pollution Control in GPI 3
(Pollution Control in Tannery)

Hello everyone. Now we will discuss on the topic industrial pollution control in grossly polluting industries part 3, and in this class we will focus on pollution control in tannery.

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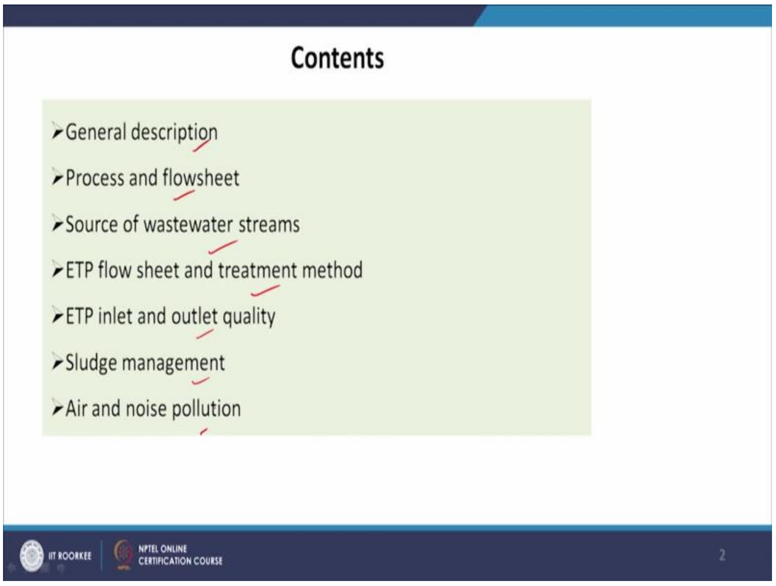

The contents of discussion are general description, then process and flow sheet of tannery and then source of wastewater streams, ETP flow sheet and treatment method, ETP inlet and outlet quality, sludge management, air and noise pollution.

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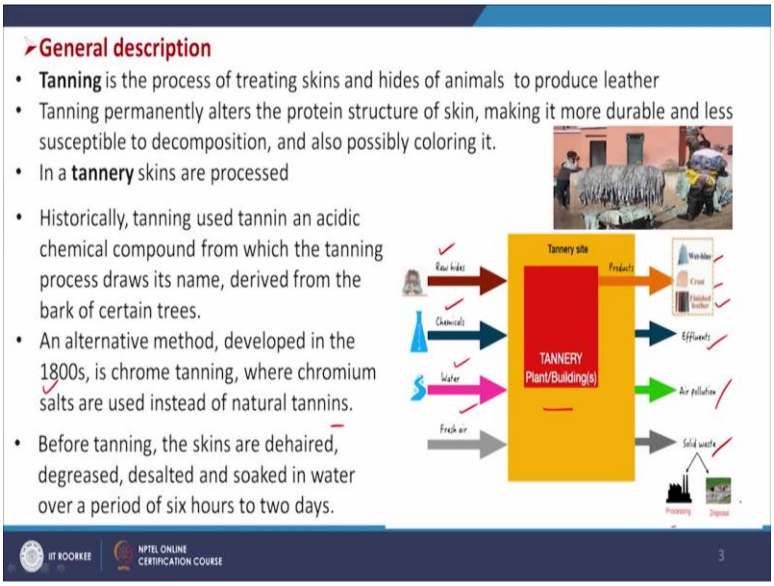

So the tannery is the process through which the animal skin is converted to leather. The protein available in the skin is basically converted so that it gets more resistance and more durable and less susceptible to decomposition and also possibly coloring it, so this is the tanning process. And in a tannery skins are processed and the term tannery are tanning has been taken off on the name of a chemical compound that is available in the bark of some type of trees and that is the natural resource or natural material that was used for the tanning purpose.

But in 1800s the chrome tanning was used and the natural tanning process was replaced, where the chromium salts are used instead of natural tannings. And if we see the whole process in this tannery we need raw hides, then some chemicals, water, fresh air and it gives the products. The products you see here there are 3 products are shown, one is finished leather and other crust, and wet blue.

So wet blue is the first intermediate product which is generated from the hides through some chemical processes and then more processes are applied on the hides and then crust is formed another intermediate product and further polishing or finishing steps if we follow then ultimately finished leather we can get. And along with this product, there will be some influence, emissions, that air pollution and solid waste will also be generated and that solid waste needs to be processing and disposed off. And this figure shows us the how the schemes are converted to final or intermediate products.

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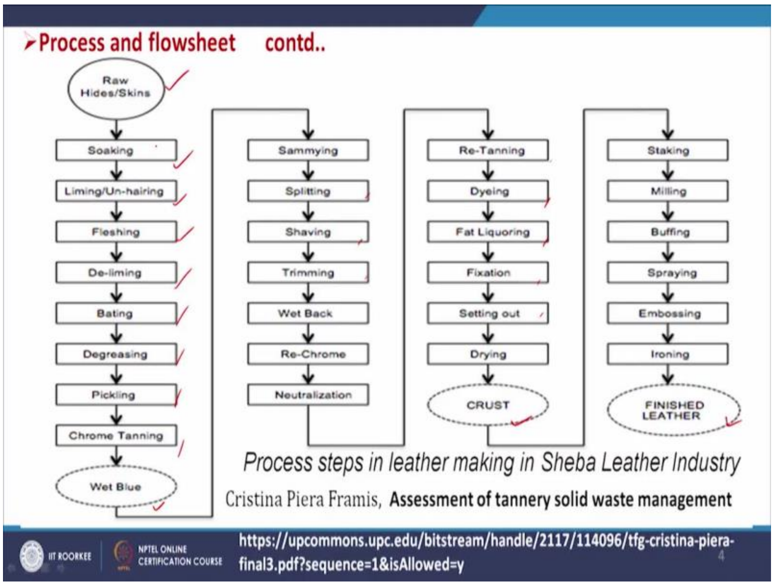

Now we will see that process flowsheet. As you know the raw material is the animal skin or hides and as I mentioned the finished leather is our ultimate product and intermediate products are wet blue and crust. So there are different types of tannery units a complete processes may be available in a complex plant or somewhere for a small unit only wet blue can be produced and somewhere up to crust can be produced. So whatever may be the size of the plant, there are a number of steps are there and the steps will be varying to some extent from the size of the unit.

Like say for wet blue will be having this type of operations up to crust will have all those operation and up to finished all those operations mentioned in these 4 columns. So our raw material is hides and skins and then it is going through different steps like soaking, then liming, un-haring, and fleshing, de-liming, bating, degreasing, pickling, and chrome tanning. After chrome tanning we get the wet blue and then further sammying, splitting, saving, trimming, wet back and re-chrome and then neutralization.

Again re-tanning, dying, fat liquoring, fixation, settling out, drying and then crust. And then further staking, milling, buffing, spraying, embossing, ironing and finally we get the finished leather. So these are the different steps, but our focus is on environmental control aspect, so detail of this process we will not discuss, we will be discussing only the few fundamentals or important processes, and we will see where from the wastewater is generated and emissions are generated and how we can control those.

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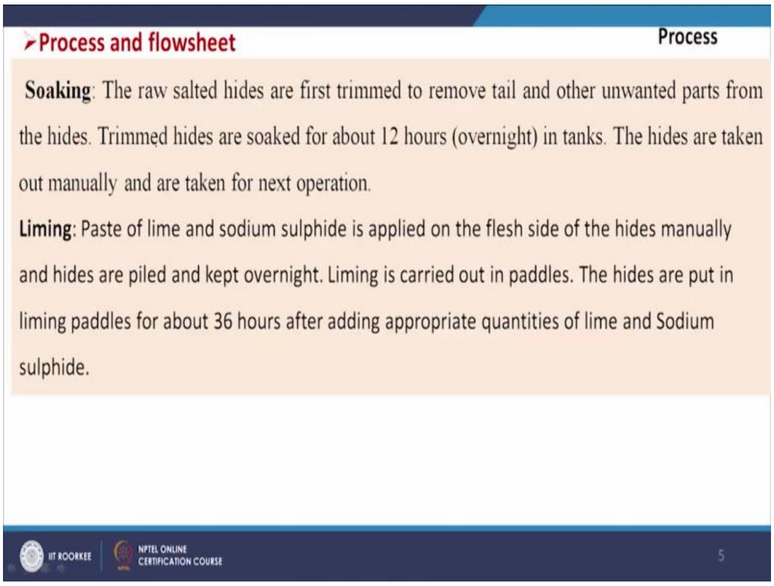

So the first step is soaking. So raw hides which we are taking that is put in a soaker. So here water and some salt are added and then the raw salted hides are first trimmed to remove tail and other unwanted parts from the hides. Trimmed hides are soaked for about 12 hours in tanks, the hides are taken out manually and are taken for next operation. Next operation is liming, so liming means the hides one side that will be flesh, so addition of lime is necessary to remove the flesh. So before removing the flesh without damaging the hides, the liming step is necessary.

So paste of lime and sodium sulphide is applied on the flesh side of the hides manually and hides are piled and kept overnight. Liming is carried out in paddles, the hides are put in liming peddles for about 36 hours after adding appropriate quantities of lime and sodium sulphide.

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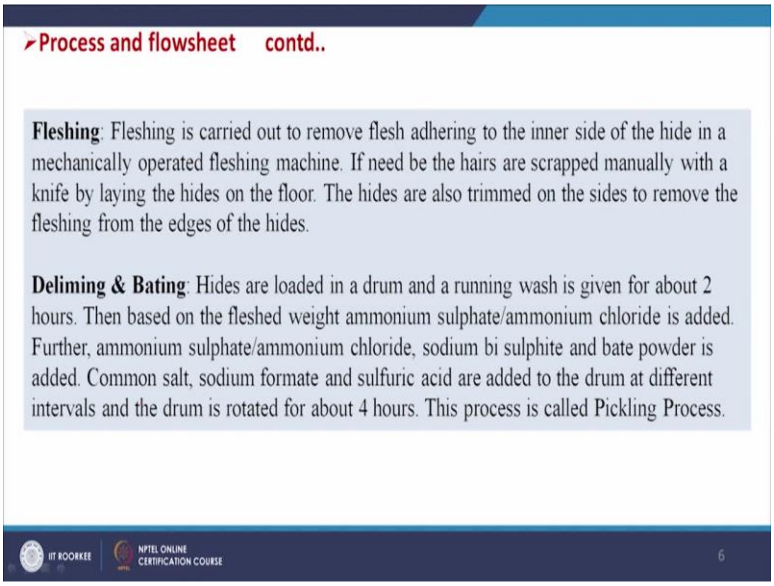

Our next step is fleshing. So here we have to remove the flesh from the hides and fleshing is carried out to remove flesh adhering to the inner side of the hide in a mechanically operated fleshing machine. If need be the hairs are scrapped manually with a knife by laying the hides on the floor, the hides are also trimmed on the sides to remove the fleshing from the edges of the hides. And after fleshing we need to follow the de-liming and bating steps. So the hides are loaded in a drum and running wash is given for about 2 hours. Then based on the fleshed weight ammonium sulphate or ammonium chloride is added.

Further, the ammonium sulphate or ammonium chloride, sodium bisulfite and bate powder is added. Common salt, sodium formate and sulfuric acid are added to the drum at different intervals and the drum is rotated for about 4 hours, this process is called pickling process. So the pickling process is necessary to make the acidic environment and so that chromium will further be impregnated into the hide.

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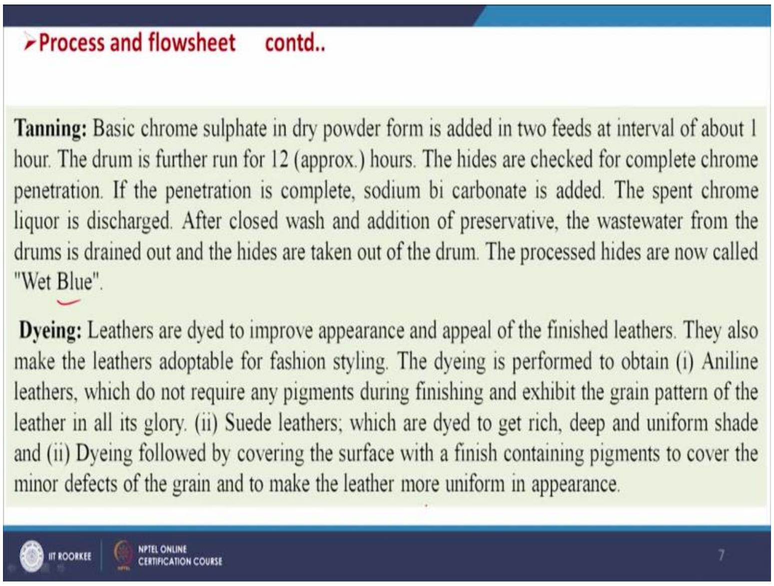

And the next step is tanning. So basic chrome sulphate in dry powder form is added in two feeds at interval of about 1 hour, the drum is further run for 12 hours approximately, the hides are checked for complete chrome penetration, if the penetration is complete, sodium bicarbonate is added the spent chrome liquor is discharged. After closed wash an additional preservative the wastewater from the drums is drained out and the hides are taken out of the drum. The processed hides are now called wet blue. Now we are getting wet blue.

So after wet blue, this is one intermediate product. So small scale units can stop after this and then it is sent to another bigger unit. And dying this is necessary to make some color to the leather. So leathers are dyed to improve appearance and appeal of the finished leathers. They also make the leathers adaptable for fashion styling.

The dyeing is performed to obtain aniline leathers which do not require any pigments during finishing and exhibit the grain pattern of the leather in all its glory. And suede leathers, which are dyed to get rich deep and uniform shade and dyeing followed by covering the surface with a finish containing pigments to cover the minor defects of the grain and to make the leather more uniform in appearance.

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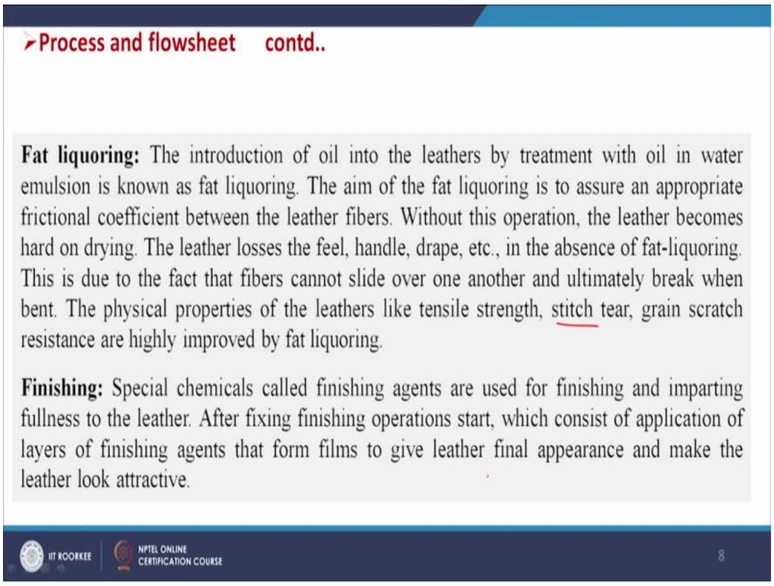

Next step is fat liquoring. So the objective is that the some oil will be allowed to go through the pores of these hides and the introduction of oil into the leather by treatment with oil in water emulsion is known as the fat liquoring. The aim of the fat liquoring is to assure an appropriate frictional coefficient between the leather fibers. Without this operation, the leather becomes hard on drying, the leather losses the field handle drift etc. in the absence of fat liquoring. And this is due to the fact that fibers cannot slide over one another and ultimately break when bent.

The physical properties of the leathers like tensile strength, stitch tear, grain stretch, resistance are highly improved by fat liquoring. And then finishing the special chemicals for finishing agents are used for finishing and imparting fullness to the leather. After fixing finishing operation start which consists of application of layers of finishing agents that form films to give leather final appearance and make the leather look attractive.

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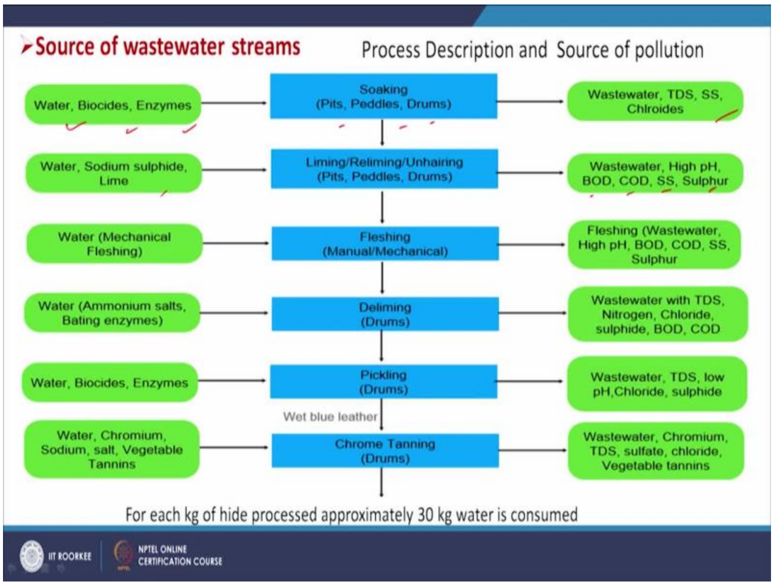

Now, we will see what are the different types of waste which are generated through different steps of the tanning process and what are the composition of those wastewater streams. So the soaking we use water, biocides, and enzymes and this operation can take place in pits, peddles and drums and ultimately wastewater is generated that is full of TDS, SS, and chlorides. In the liming, re-liming, and un-hairing process water sodium sulphide and lime is added and also pits, peddles and drums are used for this operation and wastewater contains high pH, BOD, COD, SS and sulphur.

Similarly, in fleshing step, the water is used mechanical fleshing, so then it can be done manual and mechanical as well. So here wastewater high pH, BOD, COD, SS and sulphur. And de-liming step again, water, ammonium salts, bating enzymes are used and it is done in drums and the wastewater contains TDS, nitrogen, chloride, sulphide, BOD, COD, etc.

Then pickling step, so water, biocides, enzymes are used and again the drums are used again it contains TDS, low pH, chloride, and sulphide because the main objective of the pickling step to reduce the pH. And then chrome tanning here we use water, chromium, chromium sulphate and then sodium salt, vegetable tannins maybe in some operation and then the wastewater which is generated that contains chromium, TDS, sulphate, chloride, vegetable tannins, etc. and the operation is done in drums.

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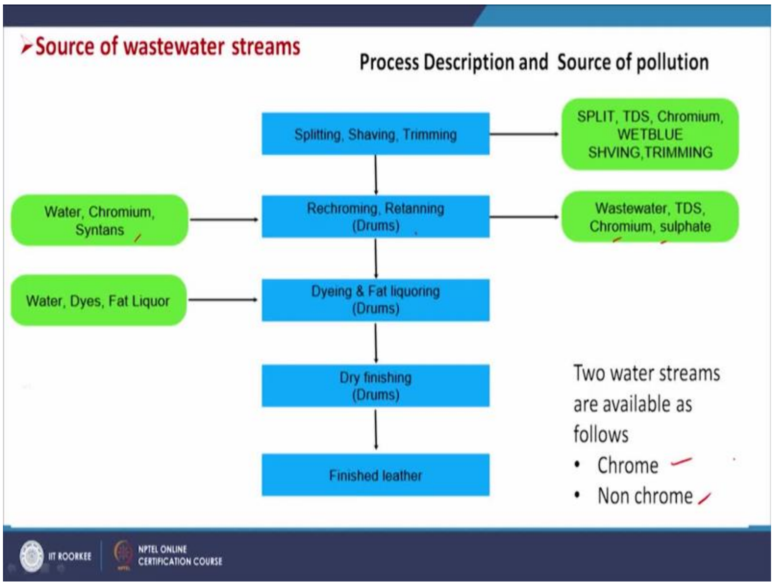

After that splitting, shaving and trimming operation takes place where we get different compositions in the water like chromium, TDS, splits, etc. And then next step is re-chroming, retanning and which takes place in drums when water, chromium and syntans are used and wastewater contains TDS, chromium, sulphate, etc.

And drying and fat liquoring step that water, dyes, fat liquor is used again the wastewater will contain this oil, COD etc. And then dry finishing and then finished leather ultimately we get. So these are the different steps and through different steps wastewater is generated which contains different components or different pollutants. And if we see the whole wastewater can be classified into two stream, one is chromium rich, another is your non-chrome wastewater.

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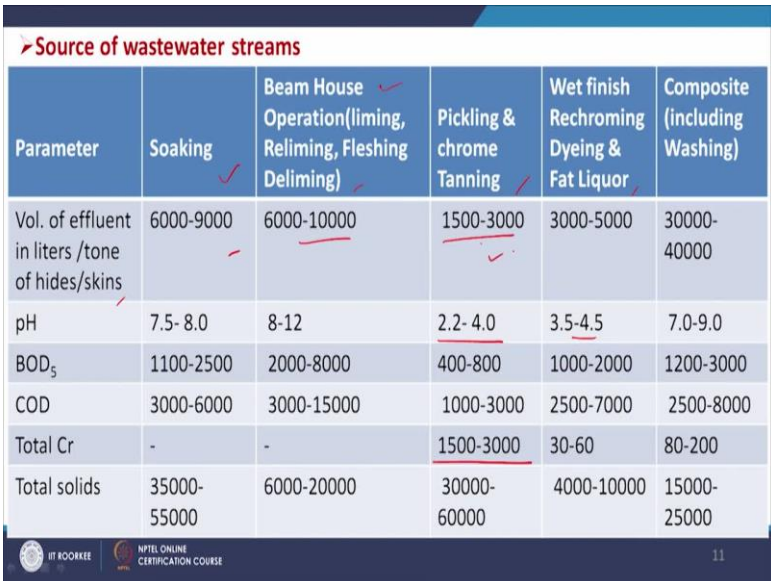

Source of wastewater streams

Parameter	Soaking	Beam House Operation(liming, Reliming, Fleshing Deliming)	Pickling & chrome Tanning	Wet finish Rechroming Dyeing & Fat Liquor	Composite (including Washing)
Vol. of effluent in liters /tone of hides/skins	6000-9000	6000-10000	1500-3000	3000-5000	30000-40000
pH	7.5- 8.0	8-12	2.2- 4.0	3.5-4.5	7.0-9.0
BOD_5	1100-2500	2000-8000	400-800	1000-2000	1200-3000
COD	3000-6000	3000-15000	1000-3000	2500-7000	2500-8000
Total Cr	-	-	1500-3000	30-60	80-200
Total solids	35000-55000	6000-20000	30000-60000	4000-10000	15000-25000

And here we will see different important sources of wastewater like say soaking and beam house operations that is liming, re-liming, fleshing, de-liming and pickling, and chrome tanning. Then wet finished re-chroming, dyeing, and fat liquoring and composite. So these are the different ends a volume of effluent in liters/ton of hides or skins. So here see this here we see that beam house creates maximum wastewater along with the soaking. Although the pickling and chrome tanning produces less volume of water with respect to others, but the concentration of chromium here is the main concern and that makes a major problem for the treatment of this type of wastewater, so separately it is treated and that part we will discuss.

And then pH is also given here, so that pickling here you see the pH is very less and wet finish that also pH is less with respect to the process. BOD_5 also varies widely from process to process and certainly it is more in beam house and soaking. And then COD it also varying from process to process, and chromium we see maximum chromium is present in case of pickling and chrome tanning wastewater and it is not much in other cases in this soaking and beam house we do not have any chromium because chromium is not added up to this, chromium is added here, so the downstream processes will also have some chromium.

And total solids are also mentioned here. So these are the major pollutants present in different wastewater streams generated in a tannery. Now it is the choice of the industry to treat these separately or as a mixer after mixing that is composite including washing. So this is the composite concentration of pollutants in the composite wastewater.

Mostly it is advisable at least to treat this chromium containing stream separately then recover chromium because it will give some value addition and improve the economy of the process as well and it will also help to treat the wastewater more easily and the performance of the ETP will be much more.

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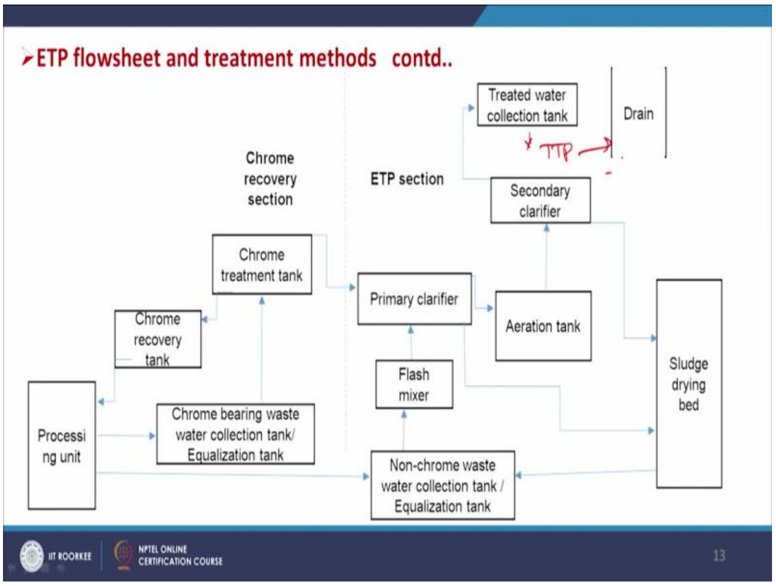

Now if this philosophy is applied, then what will happen? The wastewater which is generated that will be considered into 2 part. So processing unit if we consider this is, so it has 2 types of wastewater one chrome bearing wastewater and this wastewater is going to chrome bearing wastewater collection tank and another process water where chromium is not present, so non-chrome wastewater collection tank and equalization tank.

So these two separate streams we can consider for treatment in separate ways. So this stream chrome bearing wastewater that can be passed to the chrome treatment tank, so that in treatment tank some magnesium oxide will be added and then the chromium will be precipitated.

So the supernatant liquid that can go to now the primary clarifier of this ETP. And the chromium sludge which is generating here as a chromium hydroxide that will be transferred to chromium recovery tank and in chromium recovery tank on the basis of need sulfuric acid addition can take place and then that will be be sent to the processing purpose in the chrome tanning step. So this is one way of chromium recovery and then waste water treatment will be non-chrome wastewater and this wastewater after chromium recovery is entering into the primary clarifier and it is going to flash mixer.

And here we will be adding some chemicals, and then we will be getting some sufficient time for the settling and then the primary sludge will get from it and then the supernatant liquid will go to the aerobic tank, so there will be some microbial reaction. So BOD, COD containing wastewater, so microbial reaction will be taking place.

And again it will go to secondary clarifier and then we will get one sludge that sludge will go to sludge drying bed, here also the primary sludge will also go to sludge drying bed and in the sludge drying bed the water part will be recycled to the non-chrome wastewater collection tank and again it will be go through flash mixer and primary clarifier.

And supernatant liquid which we are getting from the secondary clarifier that will go to the treated water collection tank and this treated water collection tank will further be treated through tertiary treatment and then it will go to drain. So then we have to monitor the quality of the water continuously. And the sludge which is generated here that is very typical one in nature because of the presence of chromium.

So the handling of the sludge is not so very easy in terms of its application in agricultural field is not recommended, so it has to be vanished through landfilling, neither these can be incinerated because of the presence of high concentration of chromium. And this aeration tank which is used here, so that is a secondary treatment. So if we can use efficient microorganisms which have good capacity to capture chromium, so the effectiveness of the chromium separation will be very high and the quality of these treated water will also be very high.

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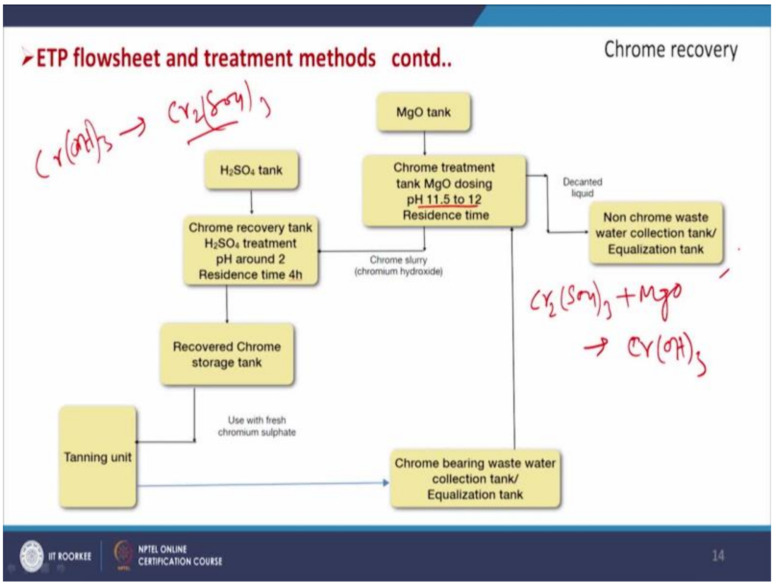

Now, we will discuss in chrome recovery part. So as you mentioned, that from the tanning unit, the chrome bearing wastewater is coming to the collection tank, then it is sent to the chrome treatment tank, where MgO magnesium oxide dosing is taking place at pH 11.5 to 12. So here we have chromium $Cr_2(SO_4)_3$ in the solution, because chromium is here in +3 step chromium sulfate is used and which is added with magnesium oxide, so it will give us chromium hydroxide here as a precipitate.

So this chromium hydroxide is coming here as a chrome recovery tank and where sulfuric acid is added. So then in these reactions, chromium hydroxide $Cr(OH)_3$ is converted to again this $Cr_2(SO_4)_3$. So then that will be used for recovered chrome storage tank and for the tanning purpose that this can be used. And the supernatant is going for non-chrome wastewater collection tank or equalization tank, and then it will be going to the primary clarifier.

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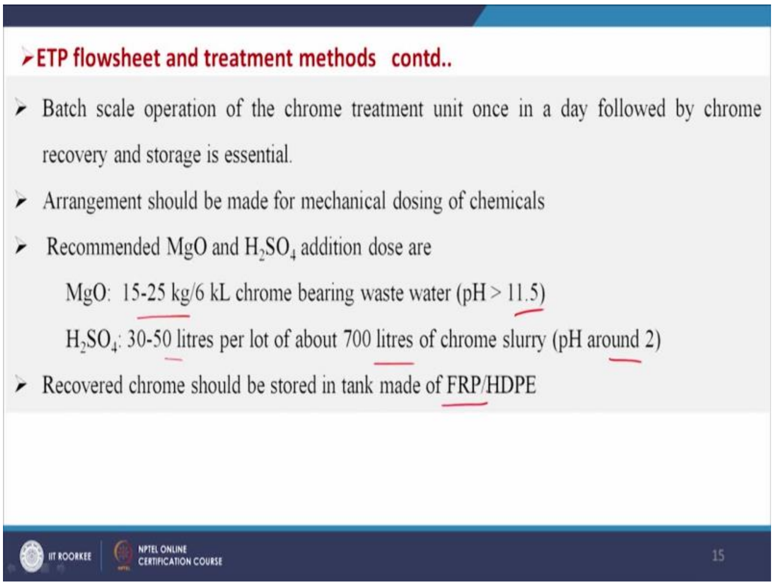

So in this case, the batch scale operation of the chrome treatment unit once in a day, followed by chrome recovery and storage is essential. Arrangement should be made for mechanical dosing of chemicals. Now recommended MgO and H_2SO_4 addition dose are 15 to 25 kg/6 KL chrome bearing wastewater, and 30 to 50 liters per a lot of about 700 liters of chrome slurry, pH around 2. And in this case, pH is around 11.5. And recovered chrome should be stored in a tank made of FRP, HDPE, etc.

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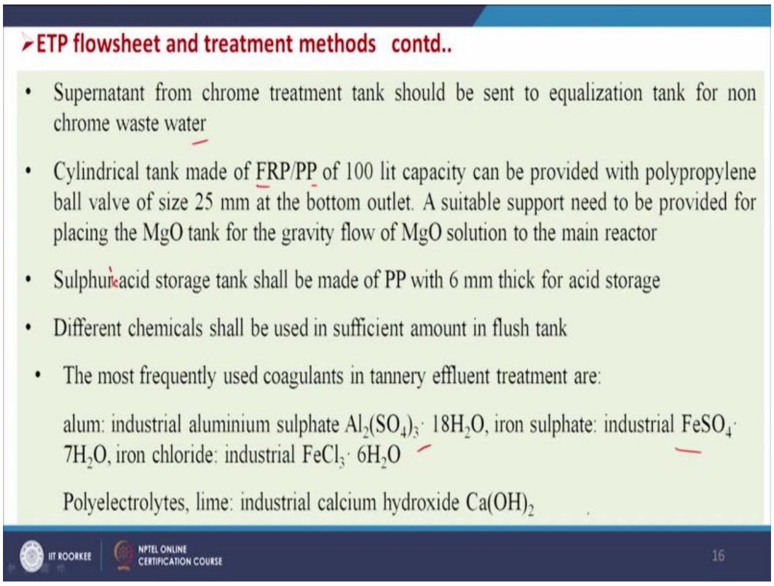

And then supernatant from the chrome treatment tanks should be sent to equalization tank for non-chrome wastewater and cylindrical tank made of FRP and PP of 100 liter capacity can be provided with polypropylene ball valve of size 25 mm at the bottom outlet. The suitable support need to be provided for fleshing the MgO tank for the gravity flow of MgO solution to the main reactor.

Sulfuric acid storage tanks shall be made of PP with 6 mm thick for acid storage and different chemicals shall be used in sufficient amount in flush tank and most frequently used coagulants in tannery effluent treatment are industrial aluminium sulphate $Al_2(SO)_418H_2O$, iron sulphate, industrial $FeSO_47H_2O$, iron chloride industrial $FeCl_36H_2O$ and polyelectrolytes, lime, industrial calcium hydroxide $Ca(OH)_2$.

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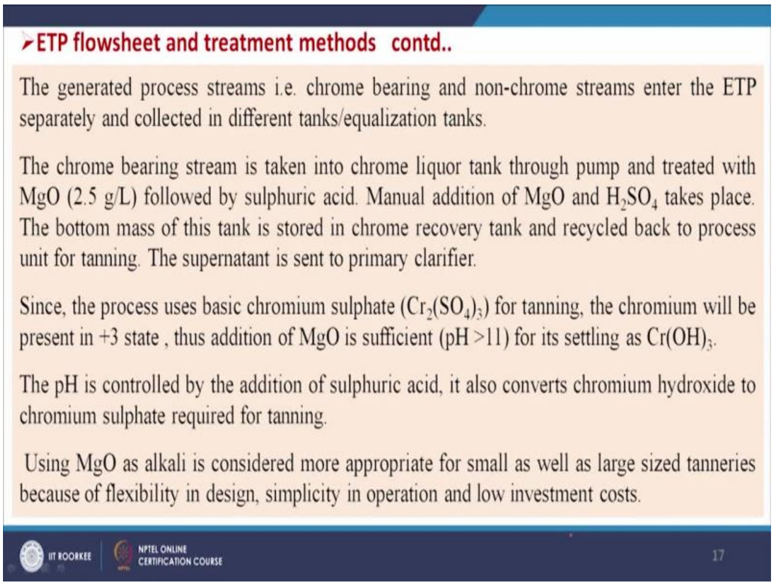

The generated process stream that is chrome bearing and non-chrome streams enter the ETP separately and collected in different tanks, equalization tanks that we have discussed. And the chrome bearing stream is taken into chrome liquor tank through pump and treated with MgO followed by sulfuric acid, manual addition of MgO and H_2SO_4 takes place. The bottom mass of this tank is stored in chrome recovery tank and recycled back to the process unit for tanning. The supernatant is sent to primary clarifier.

Since the process uses basic chromium sulphate for tanning, the chromium will be present in +3 state, thus addition of MgO is sufficient pH 11 for its settling as $Cr(OH)_3$. The pH is controlled by the addition of sulfuric acid it also converts chromium hydroxide to chromium sulphate required for tanning. Using MgO as alkali is considered more appropriate for small as well as large size tanneries because of flexibility in design, simplicity in operation and low investment costs.

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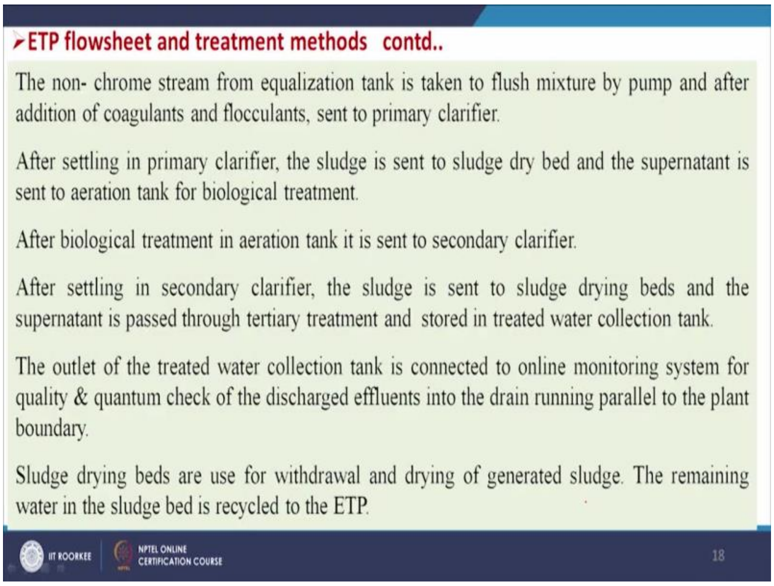

And then non-chrome stream from equalization tank is taken to flush mixture by pump and after addition of coagulants and flocculants sent to primary clarifier. So after settling in primary clarifier the sludge is send to sludge dry bed and supernatant is sent to aeration tank for biological treatment. After biological treatment in aeration tank it is sent to secondary clarifier. After settling in secondary clarifier the sludge is sent to sludge drying bed and the supernatant is passed through tertiary treatment and stored in treated water collection tank.

The outlet of the treated water collection tank is connected to the online monitoring system for quality and quantum check of the discharge effluents into the drain running parallel to the plant boundary. Sludge drying beds are used for withdrawal and drying of genetic sludge. The remaining water in the sludge bed is recycled to the ETP.

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ETP flowsheet and treatment methods contd..

REFERENCE	ORGANISM	COD %	BOD %	CROMIUM
Lata et.al. (2004)		98		
Mondal et.al. (2010)	*Thiobacillus ferooxidans*	69	72	5%
Mazumder et. Al. (2008)		70.9		
Onyancha et.al. (2008)	*S. condensata* *R. hieroglyphicum*			>75%
Vankar and Bajpai (2008)	*Trichoderma sp.*			97.39%
Rajasimman et.al. (2007)	Mixed	46.85	65-93	

ETP flowsheet and treatment methods contd..

REFERENCE	ORGANISMS	COD%	BOD%	CROMIUM
Ramteke et. al. (2010)	*Escherichia coli* *Vibrio sp.* *Pseudomonas sp.*	98.46 87.5 96.15	90	
Ryu et.al. (2007)		75		
Sekaran et.al. (1996)		81	85	
Shakoori et.al. (2000)	*Bacterial strain*			87
Sivaprakasam et.al. (2008)	*P. aeruginosa* *B. Flexus* *S. aures*	80		
Song et.al (2003)		60.75		
Song et.al. (2004)		32		77

ETP flowsheet and treatment methods contd..

REFERENCE	ORGANISMS	COD%	BOD%	CROMIUM
Srivastava et.al. (2007)	*Acinetobacter sp.*			90
Srisvastava and Thakur (2006)	*Aspergillus sp.* *Hirsutella sp.,*			70
Sumathi et.al. (2005)	Biological waste (coir pitch)			94
Thanigaval (2004)	mixed	89.5		
Vidal et. al. (2004)		80	99	
Wang et.al. (2007)	*A. thiooxidans*			99.7

And different microorganisms, which have been investigated for the removal of chromium are mentioned here, these are the different references, these are the different organisms microorganisms and COD, BOD and chromium removal are provided here. And these are some other examples. So various types of microorganisms with different COD, BOD and chromium removal capacity have been investigated. This slide also provides a similar information.

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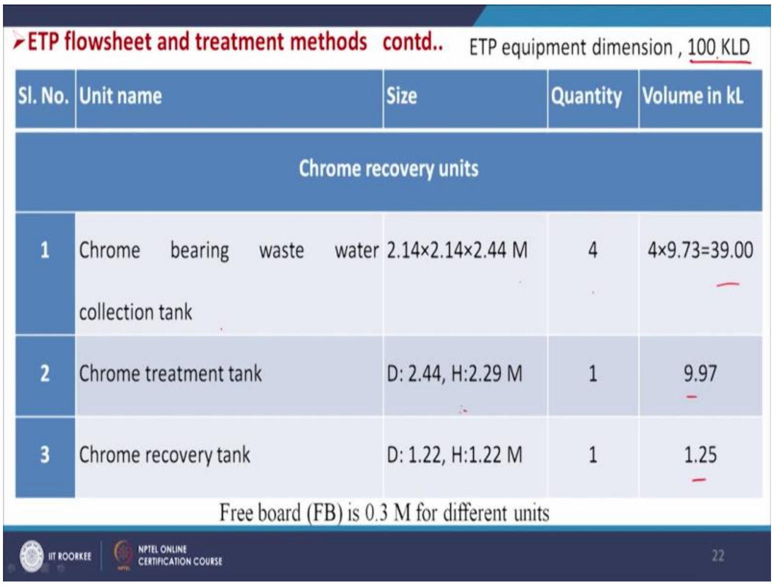

Now, this slide gives us some idea about the requirement of ETP equipment and their size for 100 KLD ETP plant. So chrome bearing wastewater collection tank is this one. So 4 number quantity, so total volume is this one and chrome treatment tank is given here. So this is the treatment tank is 9.97 and chrome recovery tank is this one. So these are typical dimension for 100 KLD ETP for chrome recovery units.

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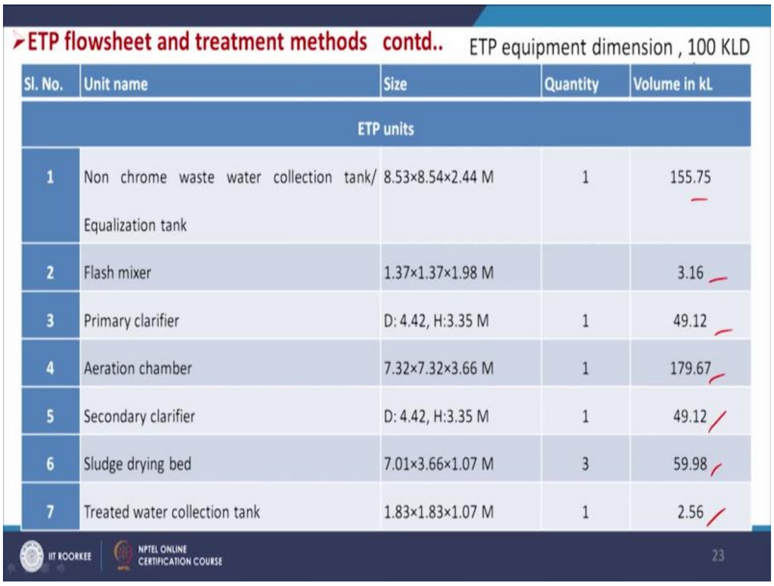

Sl. No.	Unit name	Size	Quantity	Volume in kL
ETP units				
1	Non chrome waste water collection tank/ Equalization tank	8.53×8.54×2.44 M	1	155.75
2	Flash mixer	1.37×1.37×1.98 M		3.16
3	Primary clarifier	D: 4.42, H:3.35 M	1	49.12
4	Aeration chamber	7.32×7.32×3.66 M	1	179.67
5	Secondary clarifier	D: 4.42, H:3.35 M	1	49.12
6	Sludge drying bed	7.01×3.66×1.07 M	3	59.98
7	Treated water collection tank	1.83×1.83×1.07 M	1	2.56

And for ETP units non-chrome and the supernatant of the chrome containing wastewater stream. So that non-chrome wastewater collection tank is 155.75 KL volume, flash mixer, this one and primary clarifier this one, aeration chamber this is, secondary clarifier mentioned here, sludge drying bed this is, and treated water collection tank this one. So these are the different size required for 100 KLD ETP plant.

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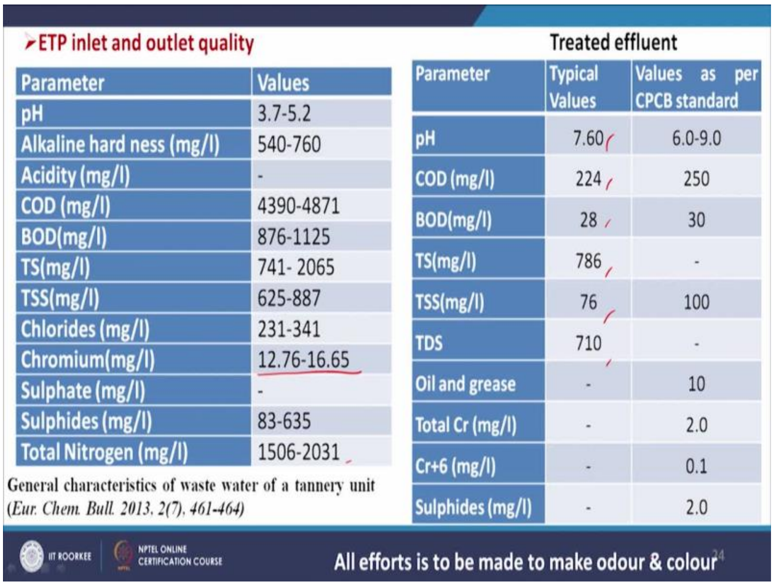

Parameter	Values
pH	3.7-5.2
Alkaline hard ness (mg/l)	540-760
Acidity (mg/l)	-
COD (mg/l)	4390-4871
BOD(mg/l)	876-1125
TS(mg/l)	741- 2065
TSS(mg/l)	625-887
Chlorides (mg/l)	231-341
Chromium(mg/l)	12.76-16.65
Sulphate (mg/l)	-
Sulphides (mg/l)	83-635
Total Nitrogen (mg/l)	1506-2031

General characteristics of waste water of a tannery unit (*Eur. Chem. Bull. 2013, 2(7), 461-464*)

Parameter	Typical Values	Values as per CPCB standard
pH	7.60	6.0-9.0
COD (mg/l)	224	250
BOD(mg/l)	28	30
TS(mg/l)	786	-
TSS(mg/l)	76	100
TDS	710	-
Oil and grease	-	10
Total Cr (mg/l)	-	2.0
Cr+6 (mg/l)	-	0.1
Sulphides (mg/l)	-	2.0

Here we will see treated effluent quality and influent quality. So this is inlet and outlet, so these are the parameters and these are the inlet values. So before treatment so this gives the composite characteristics. And then pH 3.7 to 5.2, alkaline hardness 540 to 760, COD 4390 to

4871, BOD 876 to 1125, TS 741 to 2065, TSS 625 to 887, chlorides 231 to 341, chromium 12.76 to 16.65, and sulphides 83 to 635 and total nitrogen 1506 to 2031.

So these are the different pollutants which are available and this is our recommended values and these are the typical values which is obtained and this is our values as per CPCB. And color and odor as we have discussed earlier that all efforts to be made to make the effluent free from odor and color.

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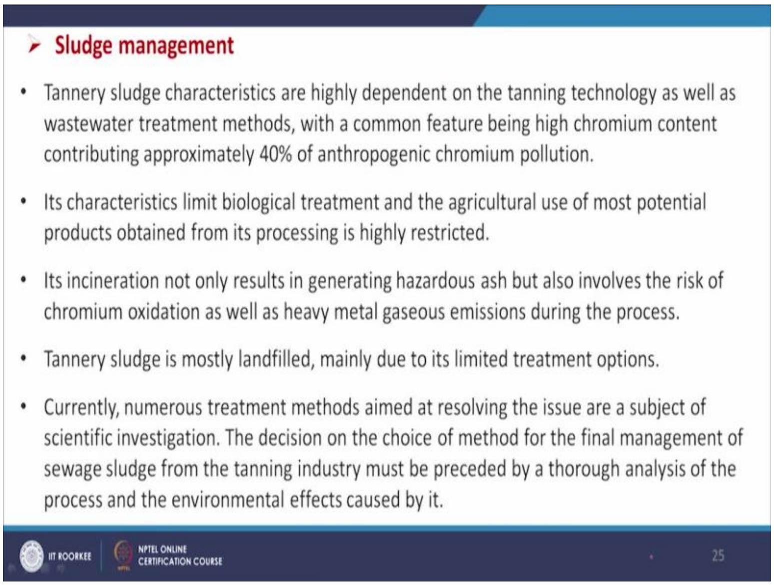

Now sludge management. The tannery sludge characteristics are highly dependent on the tanning technology as well as wastewater treatment methods with a common feature being high chromium content contributing approximately 40 % of anthropogenic chromium pollution. And its characteristics limit, biological treatment, and the agricultural use of most potential products obtained from its processing is highly restricted because of high chromium concentration.

Its incineration not only results in generating hazardous ash but also involves the risk of chromium oxidation as well as heavy metal gaseous emissions during the process. And tannery sludge is mostly landfilled, mainly due to its limited treatment options. And currently, numerous treatment methods aimed at resolving the issue are a subject of scientific investigation. The decision on the choice of method for the final management of sewage sludge from the tanning industry must be preceded by a thorough analysis of the process and the environmental effects caused by it.

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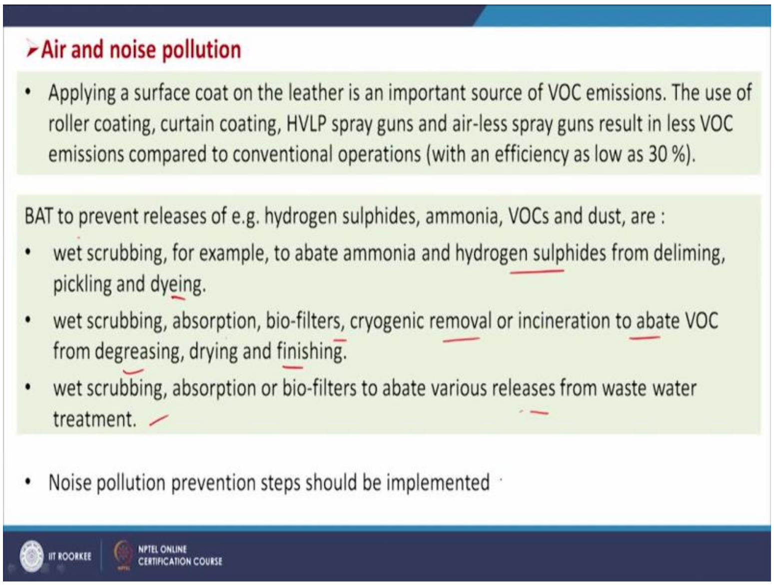

And air and noise pollution. So applying a surface coat on a leather is an important source of VOC emissions and the use of roller coating, curtain coating, HVLP spray guns and airless spray guns result in less VOC emissions compared to conventional operations. So these are some advancements in the process to reduce the VOC emission.

And best available techniques to prevent releases of hydrogen sulphides, ammonia VOC's and dust are wet scrubbing, for example to abate ammonia and hydrogen sulphides from de-liming, pickling and dyeing. And then wet scrubbing, absorptions, bio-filters, cryogenic removal or incineration to abate VOC from degreasing, drying, and finishing.

And wet scrubbing absorptions or bio-filters to abate various releases from wastewater treatment. These are the some recommended or best available techniques for air pollution control under VOC reduction. And noise pollution prevention steps should also be implemented. So we have discussed different aspects of pollution control in a tannery unit. So up to this in this class, thank you very much for your patience.