Electrochemical Technology in Pollution Control

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Lecture – 35
Zero Liquid Discharge

Greetings students say almost last class in my course. And today I will be doing a little bit about Process waste handling and Zero Liquid Discharge concept and in the last class I had done. In the last class I had discussed about the batteries and fuel cells and after the discussion on electrochemical technology and electro analytical techniques and atomic structure and other related topics.

Now, we come to the end of the course that is on process waste handling and zero liquid discharge concept. I have already completed I have already yeah I have already talked to you about process waste handling. So, I will not talk much about process waste handling except to say that many of the processes process wastes are in large volumes low concentrations and may be toxic and hazardous wastes, because most of the process wastes in electroplating industry and electro chemical industries are acids alkalis and metal ions in the effluent.

And of course, there will be vapours and gaseous pollutants will always be there. And then there will be a solid waste. So, both liquid solid and vapour waste effluent will be there in the in the chemical industries. I think I have completed most of this just for the sake of for the brevity, I am showing you these slides. I am not going to explain much to you during these except until we start our discussion on ZLD.

So, this is for your kind reference let us see how best we can do. And these are the metal finishing industries.

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AFTER METAL FABRICATION THEY ARE FINISHED TO FINAL PRODUCT REQUIREMENTS THIS INVOLVES

- Stripping
- Removal of undesirable oxides
- Cleaning
- Processing – plating, phosphating , anodizing etc.
- Rinsing
- Drying

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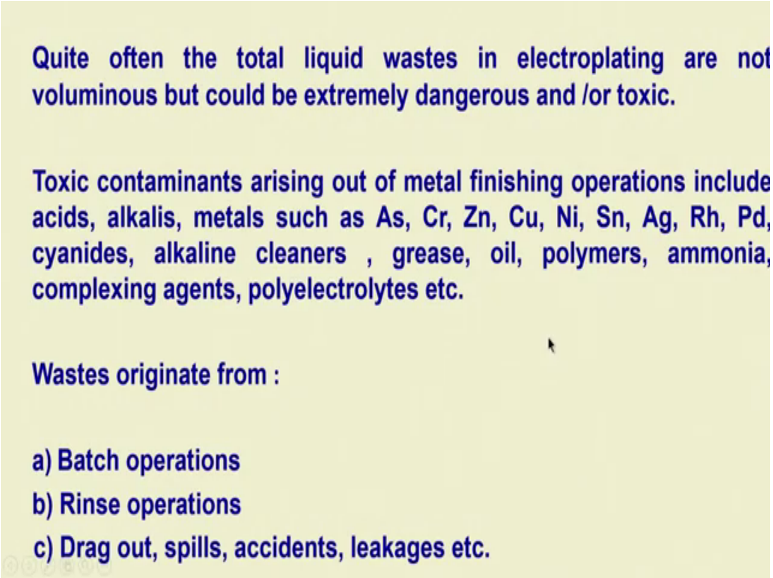

Quite often the total liquid wastes in electroplating are not voluminous but could be extremely dangerous and /or toxic.

Toxic contaminants arising out of metal finishing operations include acids, alkalis, metals such as As, Cr, Zn, Cu, Ni, Sn, Ag, Rh, Pd, cyanides, alkaline cleaners , grease, oil, polymers, ammonia, complexing agents, polyelectrolytes etc.

Wastes originate from :

a) Batch operations
b) Rinse operations
c) Drag out, spills, accidents, leakages etc.

And then they are final product, what are the typical operations? And then waste origination.

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MAJOR TYPES OF WASTES FROM ELECTROPLATING

1. Proprietary solutions – process accelerators ,surface finish
2. Cyanide concentrates – plating solutions and dips
3. Chromates – plating and rinsing
4. Cyanide rinse waters
5. Conc. Acid and pickling – stripping and cleaning of metal
6. Strong acid rinse waters – Acid dips, process solutions
7. Conc. alkalis – spent alkaline cleaning solutions
8. Other wastes – metal compounds, oils, soaps, s.s
9. Cooling water, steam condensates – do not require treatment

This is regarding major types of wastes in electroplating industries, other industry waste also will be almost similar.

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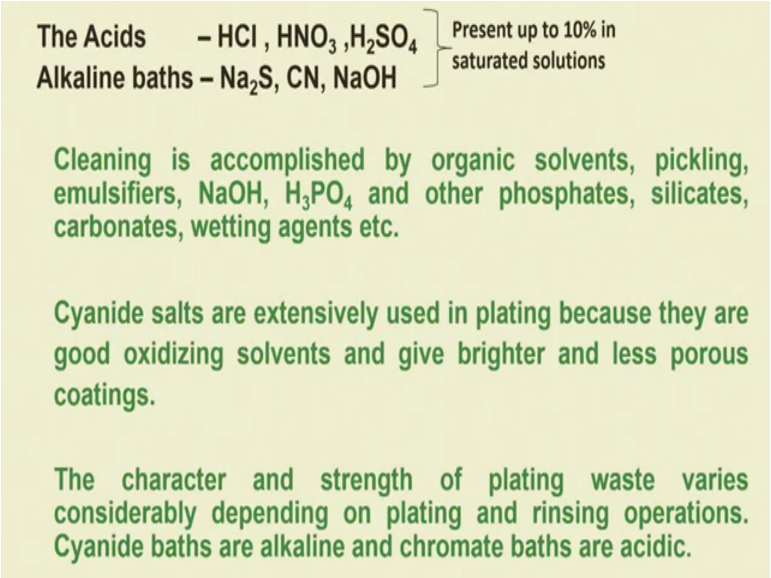

The Acids – HCl , HNO_3 ,H_2SO_4
Alkaline baths – Na_2S, CN, NaOH

Present up to 10% in saturated solutions

Cleaning is accomplished by organic solvents, pickling, emulsifiers, NaOH, H_3PO_4 and other phosphates, silicates, carbonates, wetting agents etc.

Cyanide salts are extensively used in plating because they are good oxidizing solvents and give brighter and less porous coatings.

The character and strength of plating waste varies considerably depending on plating and rinsing operations. Cyanide baths are alkaline and chromate baths are acidic.

Then this is these are salts cyanides etcetera. Then treatment corresponding to different types.

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TREATMENT OF METAL PLATING WASTES

1. MINIMIZATION OR ELIMINATION OF WASTE AND RINSE WASTES
2. PHYSICO-CHEMICAL TREATMENT

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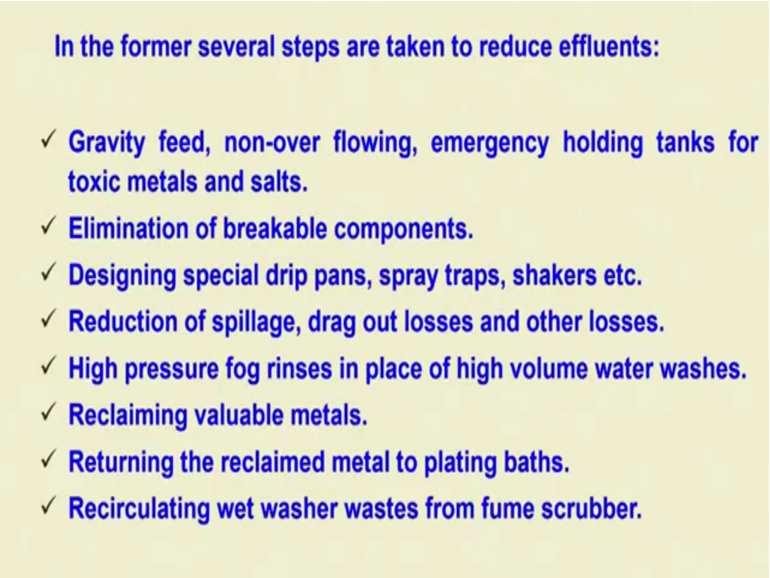

In the former several steps are taken to reduce effluents:

- ✓ Gravity feed, non-over flowing, emergency holding tanks for toxic metals and salts.
- ✓ Elimination of breakable components.
- ✓ Designing special drip pans, spray traps, shakers etc.
- ✓ Reduction of spillage, drag out losses and other losses.
- ✓ High pressure fog rinses in place of high volume water washes.
- ✓ Reclaiming valuable metals.
- ✓ Returning the reclaimed metal to plating baths.
- ✓ Recirculating wet washer wastes from fume scrubber.

Then specific steps we had discussed earlier cyanide waste treatment.

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CYANIDE WASTE TREATMENT

There are more than 10 methods of treatment:

1. Gas chlorination
2. Hypochlorites
3. ClO_2 treatment
4. Ozonation
5. Conversion to less toxic CN compounds
6. Electrolytic oxidation
7. Acidification
8. Lime-sulphur method
9. Ion exchange
10. Heat to dry

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There are number of possibilities, we need not be afraid of cyanide in the effluent.

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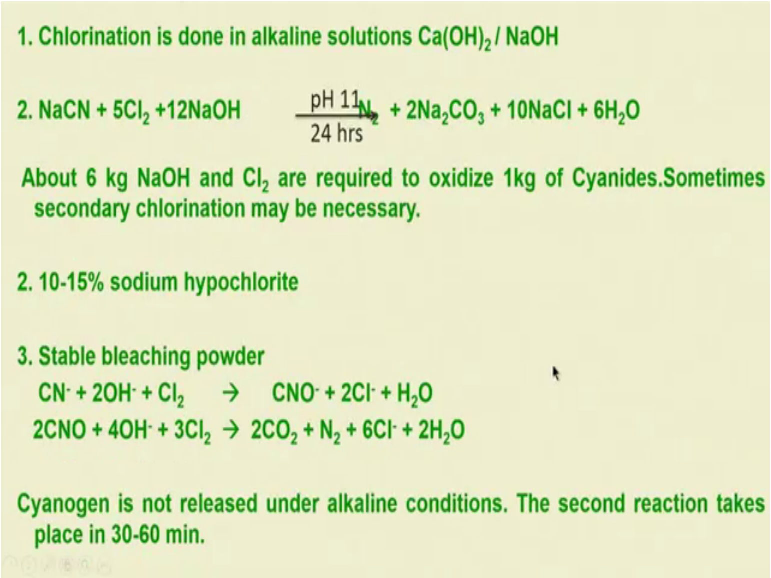

1. Chlorination is done in alkaline solutions $Ca(OH)_2$ / NaOH

2. $NaCN + 5Cl_2 + 12NaOH \xrightarrow[\text{24 hrs}]{\text{pH 11}} N_2 + 2Na_2CO_3 + 10NaCl + 6H_2O$

About 6 kg NaOH and Cl_2 are required to oxidize 1kg of Cyanides.Sometimes secondary chlorination may be necessary.

2. 10-15% sodium hypochlorite

3. Stable bleaching powder

$CN^- + 2OH^- + Cl_2 \rightarrow CNO^- + 2Cl^- + H_2O$

$2CNO + 4OH^- + 3Cl_2 \rightarrow 2CO_2 + N_2 + 6Cl^- + 2H_2O$

Cyanogen is not released under alkaline conditions. The second reaction takes place in 30-60 min.

And chlorination etcetera these I have discussed in detail.

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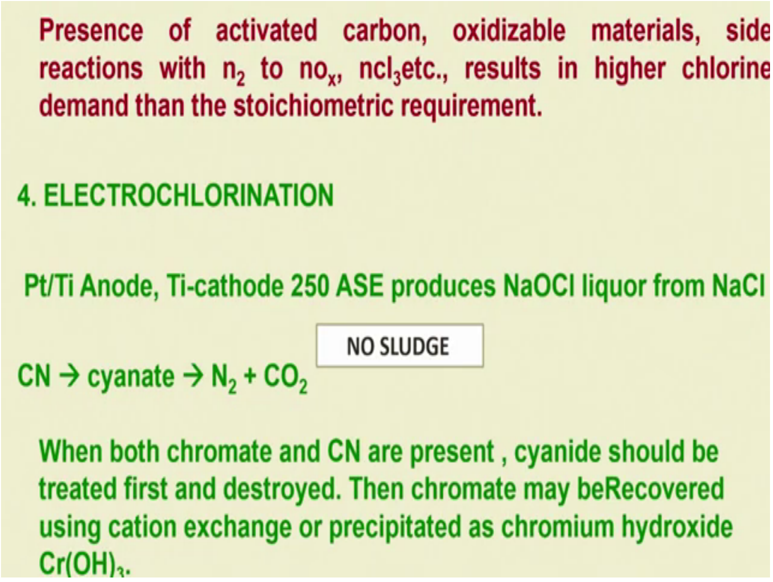

Presence of activated carbon, oxidizable materials, side reactions with n_2 to no_x, ncl_3etc., results in higher chlorine demand than the stoichiometric requirement.

4. ELECTROCHLORINATION

Pt/Ti Anode, Ti-cathode 250 ASE produces NaOCl liquor from NaCl

NO SLUDGE

CN → cyanate → N_2 + CO_2

When both chromate and CN are present , cyanide should be treated first and destroyed. Then chromate may beRecovered using cation exchange or precipitated as chromium hydroxide $Cr(OH)_3$.

Then sludge electro chlorination etcetera where there is no sludge.

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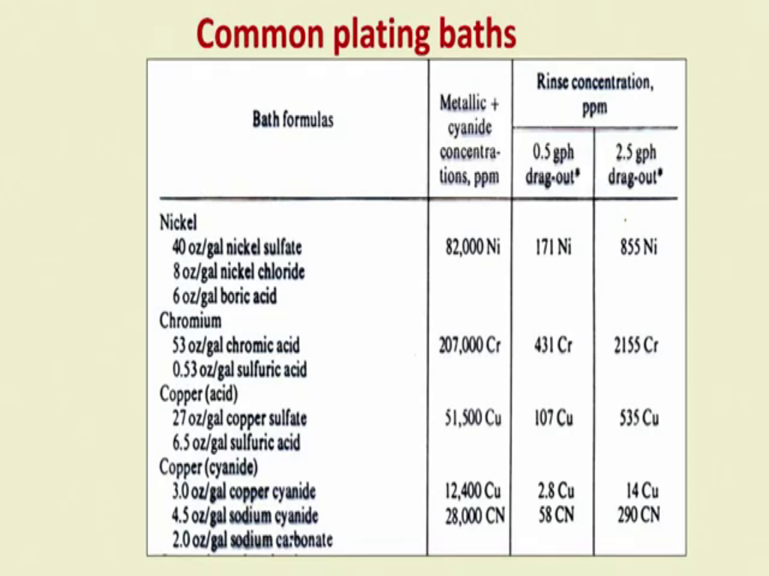

Common plating baths

Bath formulas	Metallic + cyanide concentrations, ppm	Rinse concentration, ppm	
		0.5 gph drag-out*	2.5 gph drag-out*
Nickel			
40 oz/gal nickel sulfate	82,000 Ni	171 Ni	855 Ni
8 oz/gal nickel chloride			
6 oz/gal boric acid			
Chromium			
53 oz/gal chromic acid	207,000 Cr	431 Cr	2155 Cr
0.53 oz/gal sulfuric acid			
Copper (acid)			
27 oz/gal copper sulfate	51,500 Cu	107 Cu	535 Cu
6.5 oz/gal sulfuric acid			
Copper (cyanide)			
3.0 oz/gal copper cyanide	12,400 Cu	2.8 Cu	14 Cu
4.5 oz/gal sodium cyanide	28,000 CN	58 CN	290 CN
2.0 oz/gal sodium carbonate			

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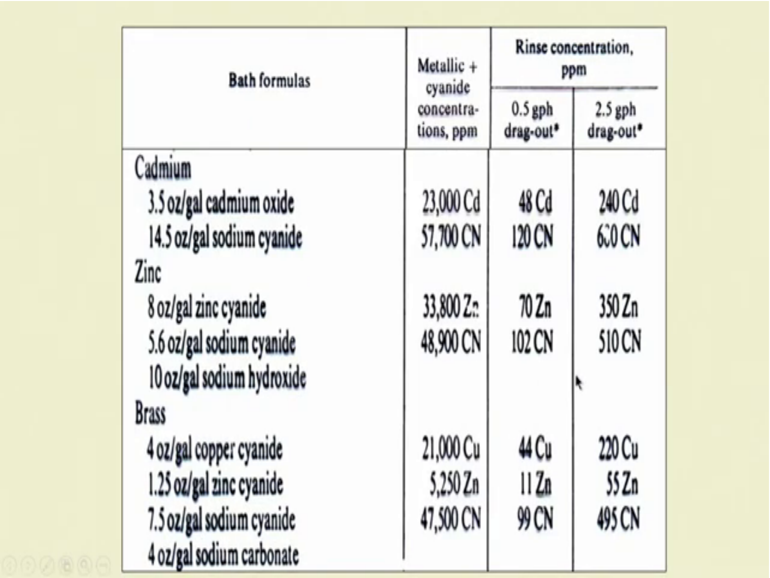

Bath formulas	Metallic + cyanide concentrations, ppm	Rinse concentration, ppm	
		0.5 gph drag-out*	2.5 gph drag-out*
Cadmium			
3.5 oz/gal cadmium oxide	23,000 Cd	48 Cd	240 Cd
14.5 oz/gal sodium cyanide	57,700 CN	120 CN	600 CN
Zinc			
8 oz/gal zinc cyanide	33,800 Zn	70 Zn	350 Zn
5.6 oz/gal sodium cyanide	48,900 CN	102 CN	510 CN
10 oz/gal sodium hydroxide			
Brass			
4 oz/gal copper cyanide	21,000 Cu	44 Cu	220 Cu
1.25 oz/gal zinc cyanide	5,250 Zn	11 Zn	55 Zn
7.5 oz/gal sodium cyanide	47,500 CN	99 CN	495 CN
4 oz/gal sodium carbonate			

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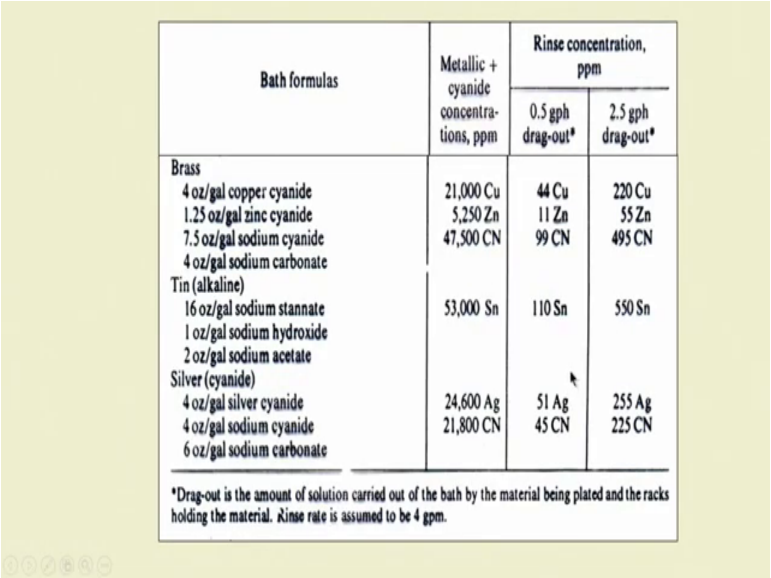

Bath formulas	Metallic + cyanide concentrations, ppm	Rinse concentration, ppm	
		0.5 gph drag-out*	2.5 gph drag-out*
Brass			
4 oz/gal copper cyanide	21,000 Cu	44 Cu	220 Cu
1.25 oz/gal zinc cyanide	5,250 Zn	11 Zn	55 Zn
7.5 oz/gal sodium cyanide	47,500 CN	99 CN	495 CN
4 oz/gal sodium carbonate			
Tin (alkaline)			
16 oz/gal sodium stannate	53,000 Sn	110 Sn	550 Sn
1 oz/gal sodium hydroxide			
2 oz/gal sodium acetate			
Silver (cyanide)			
4 oz/gal silver cyanide	24,600 Ag	51 Ag	255 Ag
4 oz/gal sodium cyanide	21,800 CN	45 CN	225 CN
6 oz/gal sodium carbonate			

*Drag-out is the amount of solution carried out of the bath by the material being plated and the racks holding the material. Rinse rate is assumed to be 4 gpm.

Then typical common plating baths, bath formulas we have discussed.

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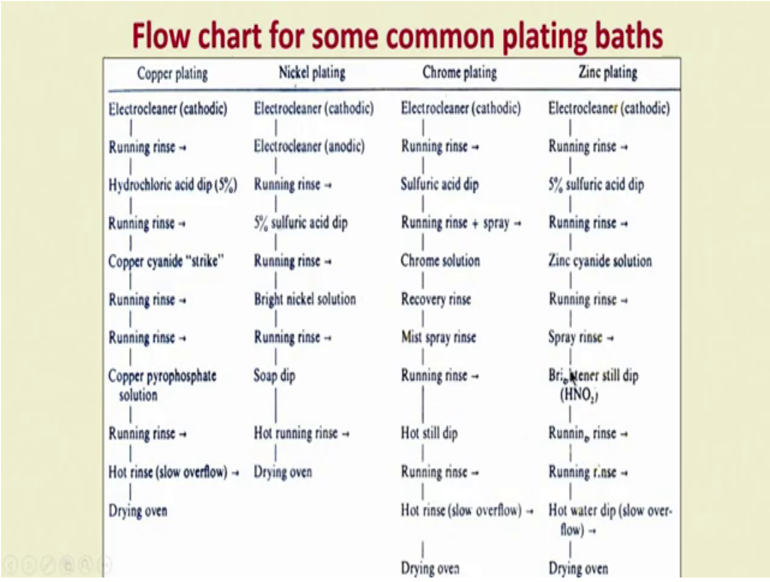

Flow chart for some common plating baths

Copper plating	Nickel plating	Chrome plating	Zinc plating
Electrocleaner (cathodic)	Electrocleaner (cathodic)	Electrocleaner (cathodic)	Electrocleaner (cathodic)
Running rinse →	Electrocleaner (anodic)	Running rinse →	Running rinse →
Hydrochloric acid dip (5%)	Running rinse →	Sulfuric acid dip	5% sulfuric acid dip
Running rinse →	5% sulfuric acid dip	Running rinse + spray →	Running rinse →
Copper cyanide "strike"	Running rinse →	Chrome solution	Zinc cyanide solution
Running rinse →	Bright nickel solution	Recovery rinse	Running rinse →
Running rinse →	Running rinse →	Mist spray rinse	Spray rinse →
Copper pyrophosphate solution	Soap dip	Running rinse →	Brightener still dip (HNO_3)
Running rinse →	Hot running rinse →	Hot still dip	Running rinse →
Hot rinse (slow overflow) →	Drying oven	Running rinse →	Running rinse →
Drying oven		Hot rinse (slow overflow) →	Hot water dip (slow overflow) →
		Drying oven	Drying oven

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PLATING-WASTE CONCENTRATIONS

Plant	pH	Cu ppm	Fe ppm	Ni ppm	Zn ppm	Cr, ppm		CN, ppm
						+6	Total	
A	3.2	16	11	0	0	0	1.0	6
A	10.4	19	3	0	0	0	0.5	14
B	4.1	58	1.2	0	0	204	246	0.2
C	2.8	11	-	0.2	-	3	7	1.2
D	2.0	300	10	0	82	0	0	0.7
E	2.4	35	8	-	-	555	612	1.2
E	10.7	14	4	19	-	32	39	2.0
F	10.5	6	2	25	39	-	-	10
G	11.3	18	18	26	-	36	-	15
G	11.9	23	21	32	-	95	-	13

Then flow chart for some of the common plating baths followed by plating wastes different kinds of industries.

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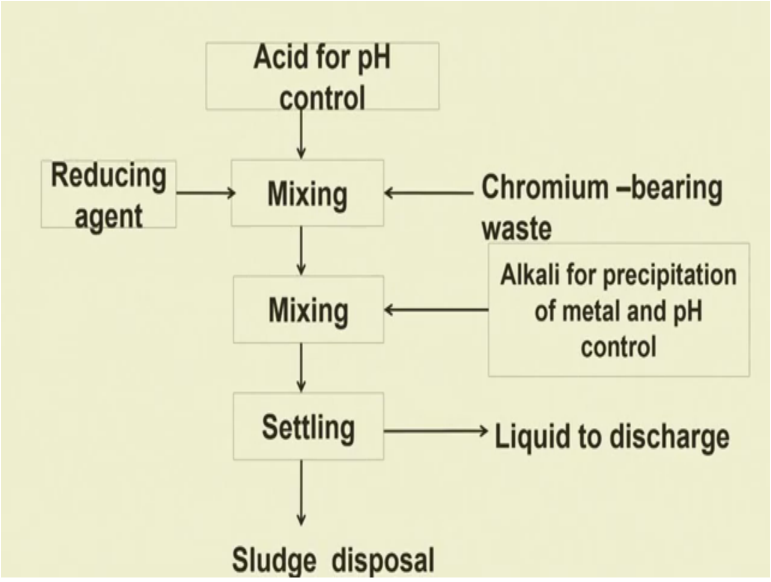

Acid for pH control

Reducing agent

Mixing

Chromium –bearing waste

Mixing

Alkali for precipitation of metal and pH control

Settling

Liquid to discharge

Sludge disposal

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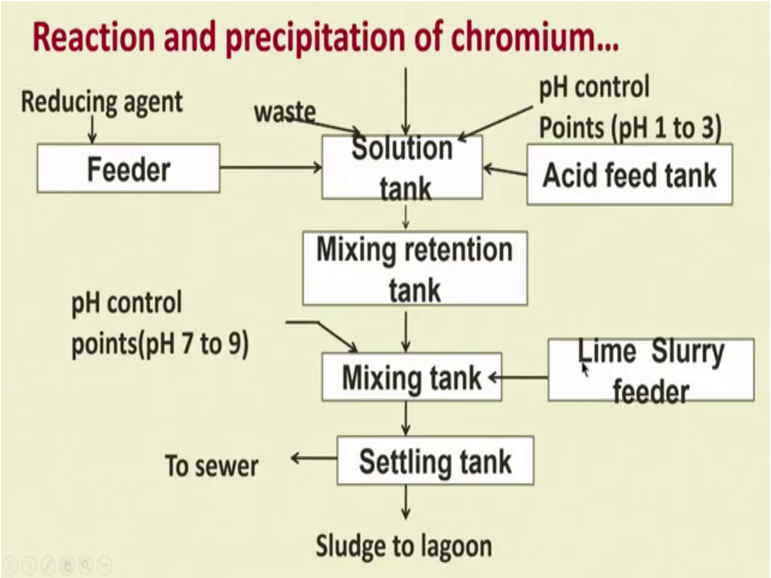

Reaction and precipitation of chromium…

Reducing agent

Feeder

waste

Solution tank

pH control Points (pH 1 to 3)

Acid feed tank

Mixing retention tank

pH control points(pH 7 to 9)

Mixing tank

Lime Slurry feeder

To sewer

Settling tank

Sludge to lagoon

Then basic treatment all these we have discussed earlier.

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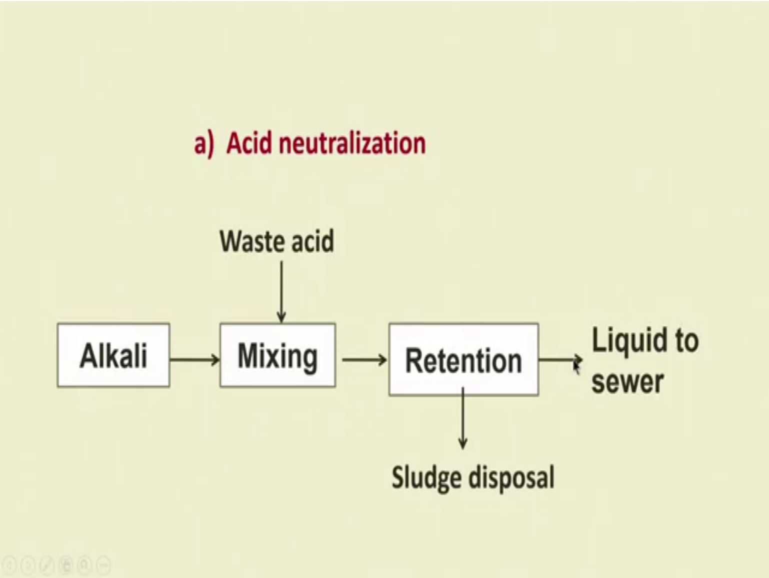

a) Acid neutralization

So, I am just reminding you quickly what are the steps involved before we proceed on to the ZLD.

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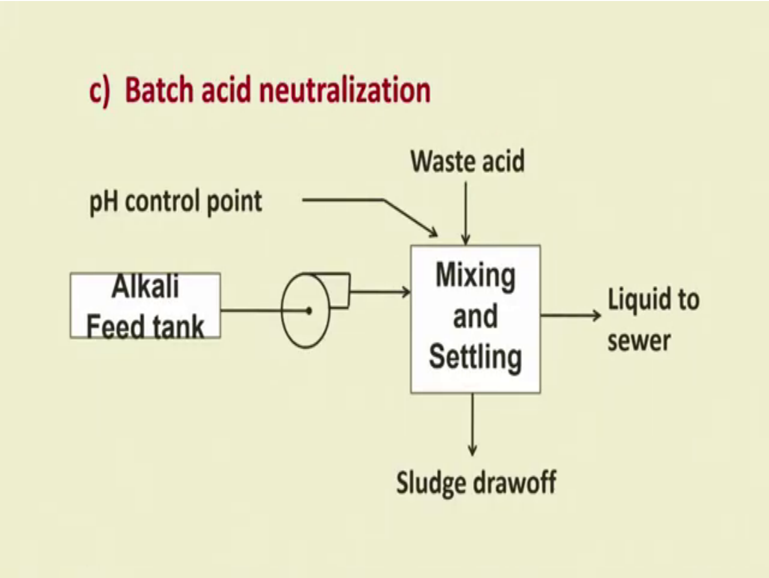

c) Batch acid neutralization

Waste acid

pH control point

Alkali Feed tank

Mixing and Settling

Liquid to sewer

Sludge drawoff

So, batch acid neutralization all these things we have already covered.

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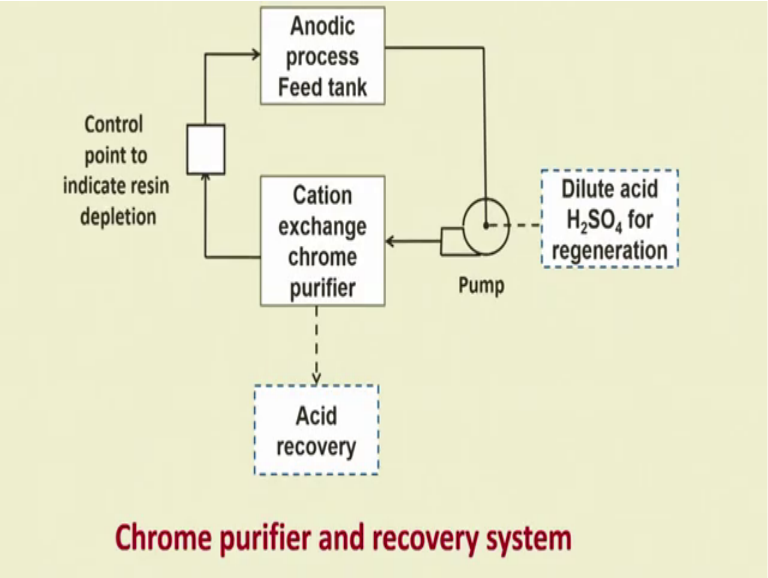

Chrome purifier and recovery system

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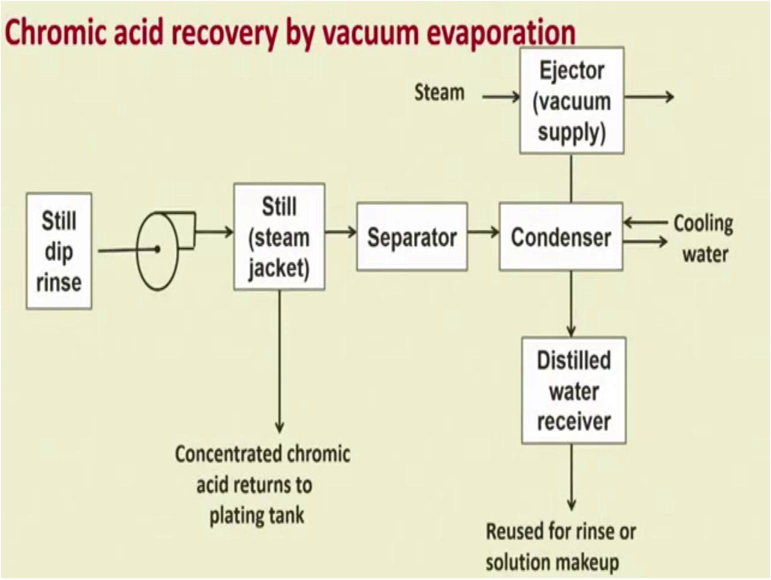

Chromic acid recovery by vacuum evaporation

Steam

Ejector (vacuum supply)

Still dip rinse

Still (steam jacket)

Separator

Condenser

Cooling water

Distilled water receiver

Concentrated chromic acid returns to plating tank

Reused for rinse or solution makeup

Chrome recovery systems.

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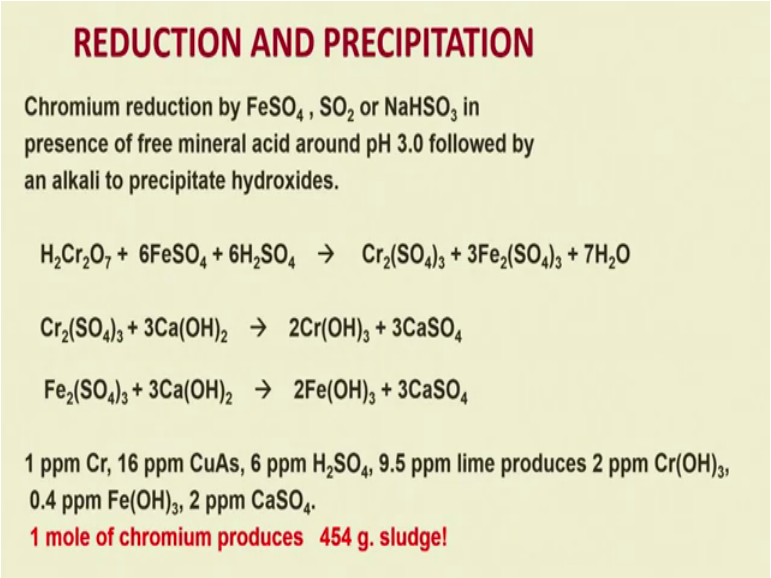

REDUCTION AND PRECIPITATION

Chromium reduction by $FeSO_4$, SO_2 or $NaHSO_3$ in presence of free mineral acid around pH 3.0 followed by an alkali to precipitate hydroxides.

$$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4$$

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_3 + 3CaSO_4$$

1 ppm Cr, 16 ppm CuAs, 6 ppm H_2SO_4, 9.5 ppm lime produces 2 ppm $Cr(OH)_3$, 0.4 ppm $Fe(OH)_3$, 2 ppm $CaSO_4$.

1 mole of chromium produces 454 g. sludge!

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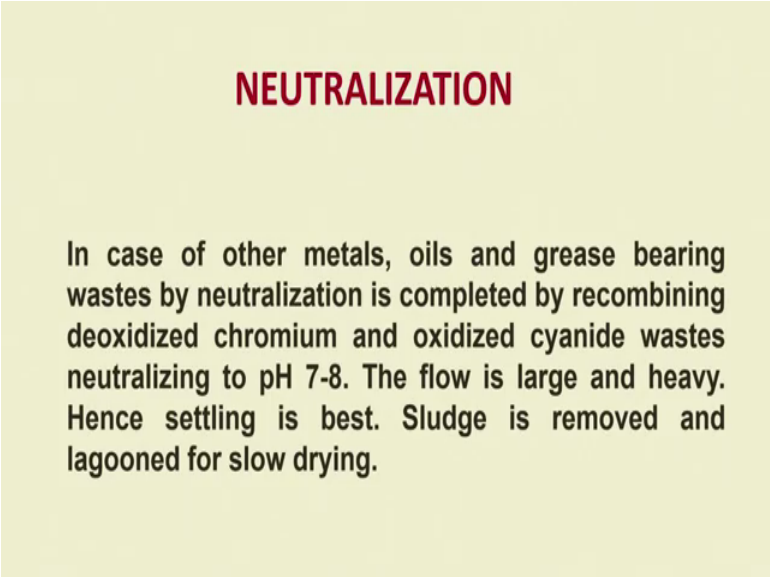

NEUTRALIZATION

In case of other metals, oils and grease bearing wastes by neutralization is completed by recombining deoxidized chromium and oxidized cyanide wastes neutralizing to pH 7-8. The flow is large and heavy. Hence settling is best. Sludge is removed and lagooned for slow drying.

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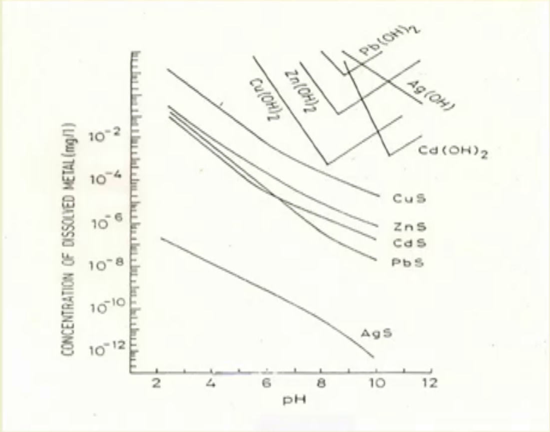

Solubility curves for hydroxides and sulphides

Vacuum evaporation, reduction precipitation followed by neutralization. And then I had discussed with you about the solubility product of the hydroxides of many of these copper, zinc, led, silver, cadmium hydroxides their solubility's are slightly minimum. Their solubility's are minimum in alkaline conditions, but solubility will increase in acidic conditions will be below pH 8. If you look at the solubility's of sulphides then also there is a possibility that we can collect them of the order of about 10 raise to minus 4 that is p p b levels.

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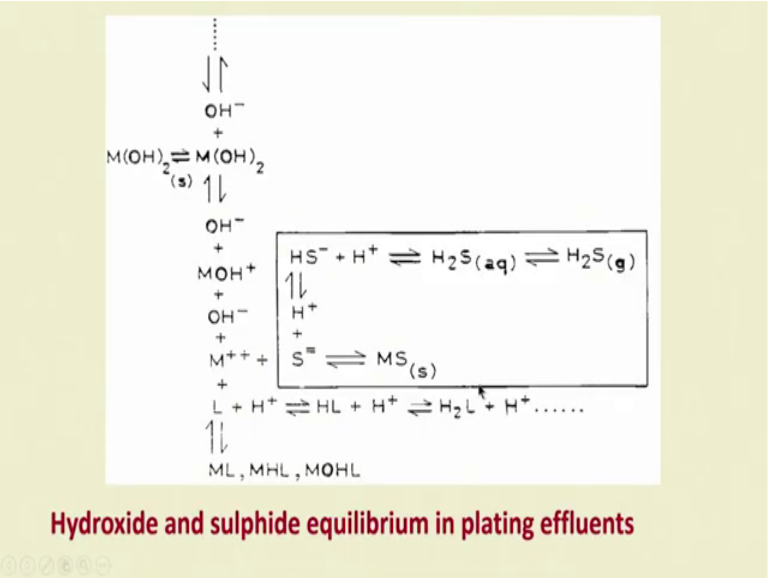

Hydroxide and sulphide equilibrium in plating effluents

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The precipitation is possible. So, these are typical reactions I had shown.

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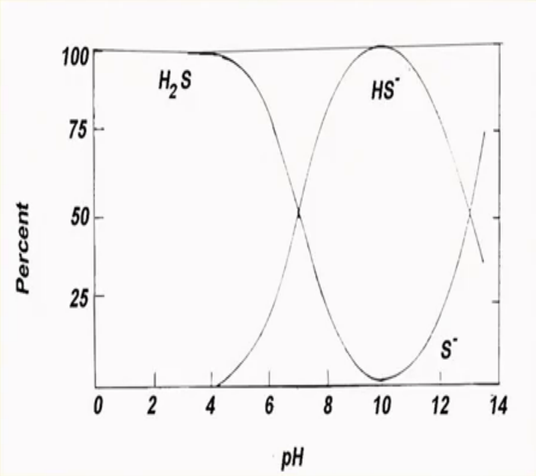

Effect of pH on hydrogen sulphide concentration

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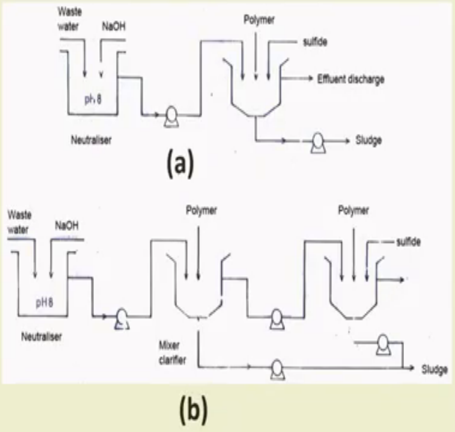

And two types of complexes with sulphide precipitation their pH effect and then a typical procedure for treatment.

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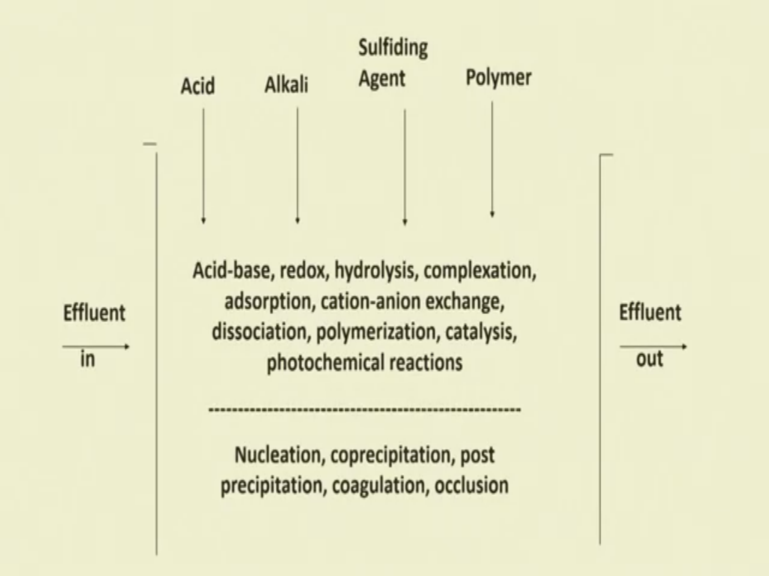

Acid-base, redox, hydrolysis, complexation, adsorption, cation-anion exchange, dissociation, polymerization, catalysis, photochemical reactions

Nucleation, coprecipitation, post precipitation, coagulation, occlusion

Then all the processes including various wastes requirement this we have discussed.

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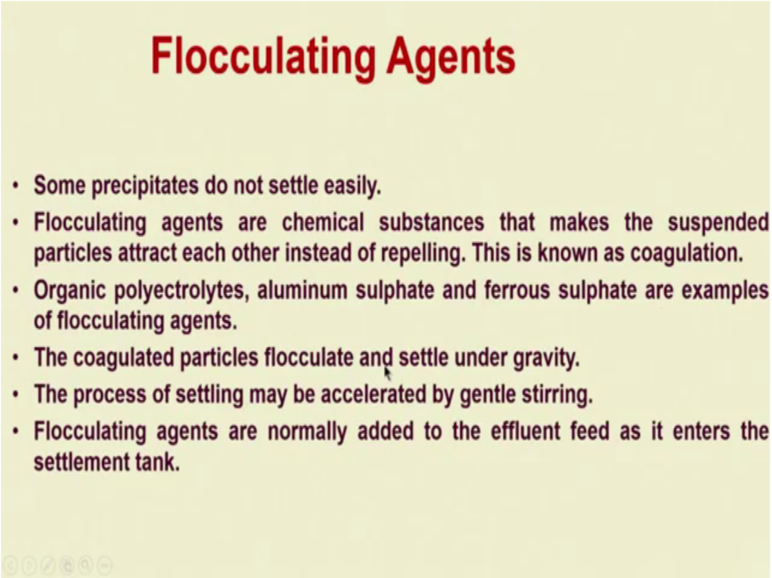

Flocculating Agents

- Some precipitates do not settle easily.
- Flocculating agents are chemical substances that makes the suspended particles attract each other instead of repelling. This is known as coagulation.
- Organic polyectrolytes, aluminum sulphate and ferrous sulphate are examples of flocculating agents.
- The coagulated particles flocculate and settle under gravity.
- The process of settling may be accelerated by gentle stirring.
- Flocculating agents are normally added to the effluent feed as it enters the settlement tank.

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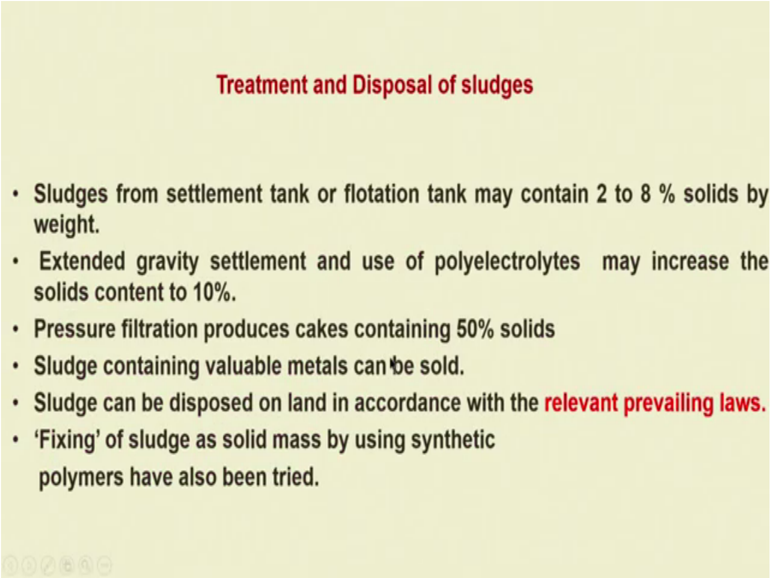

Treatment and Disposal of sludges

- Sludges from settlement tank or flotation tank may contain 2 to 8 % solids by weight.
- Extended gravity settlement and use of polyelectrolytes may increase the solids content to 10%.
- Pressure filtration produces cakes containing 50% solids
- Sludge containing valuable metals can be sold.
- Sludge can be disposed on land in accordance with the relevant prevailing laws.
- 'Fixing' of sludge as solid mass by using synthetic polymers have also been tried.

Then some flocculating agents needed for collection and precipitation of some of these sludge's. And, sludge treatment I had discussed a little bit a sludge disposal followed by sludge containment etcetera.

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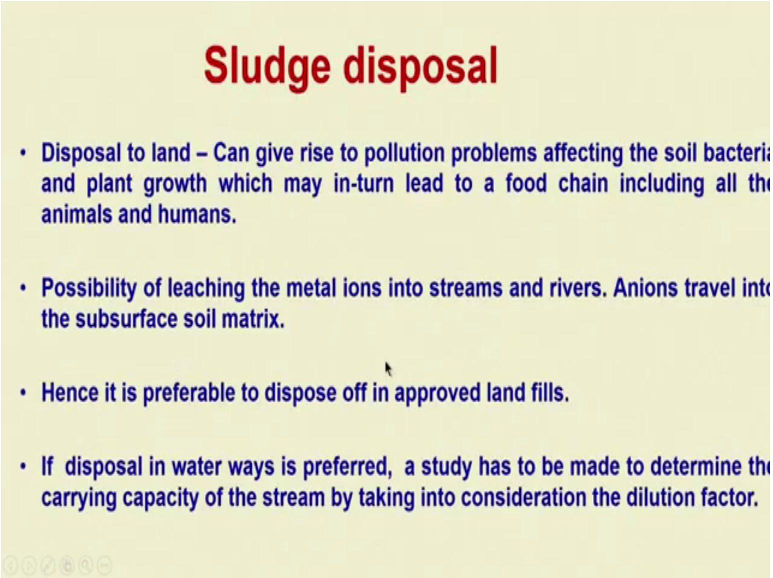

Sludge disposal

- Disposal to land – Can give rise to pollution problems affecting the soil bacteri and plant growth which may in-turn lead to a food chain including all th animals and humans.
- Possibility of leaching the metal ions into streams and rivers. Anions travel int the subsurface soil matrix.
- Hence it is preferable to dispose off in approved land fills.
- If disposal in water ways is preferred, a study has to be made to determine th carrying capacity of the stream by taking into consideration the dilution factor.

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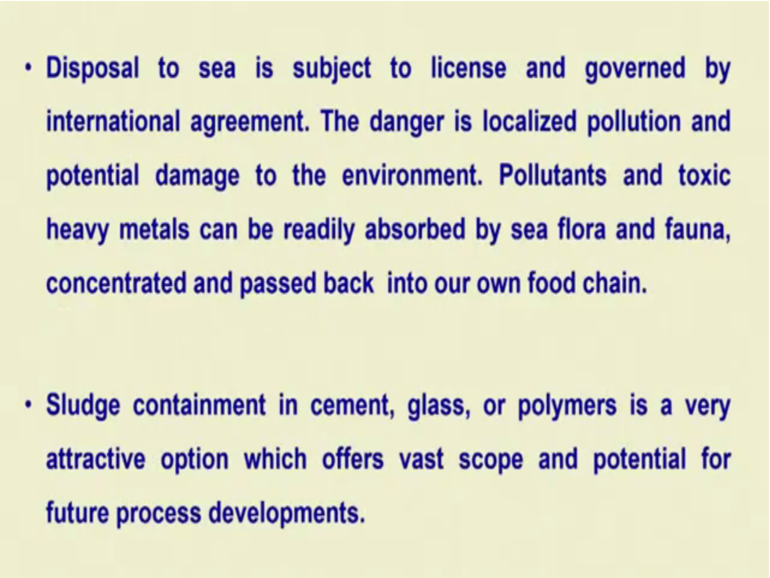

- Disposal to sea is subject to license and governed by international agreement. The danger is localized pollution and potential damage to the environment. Pollutants and toxic heavy metals can be readily absorbed by sea flora and fauna, concentrated and passed back into our own food chain.

- Sludge containment in cement, glass, or polymers is a very attractive option which offers vast scope and potential for future process developments.

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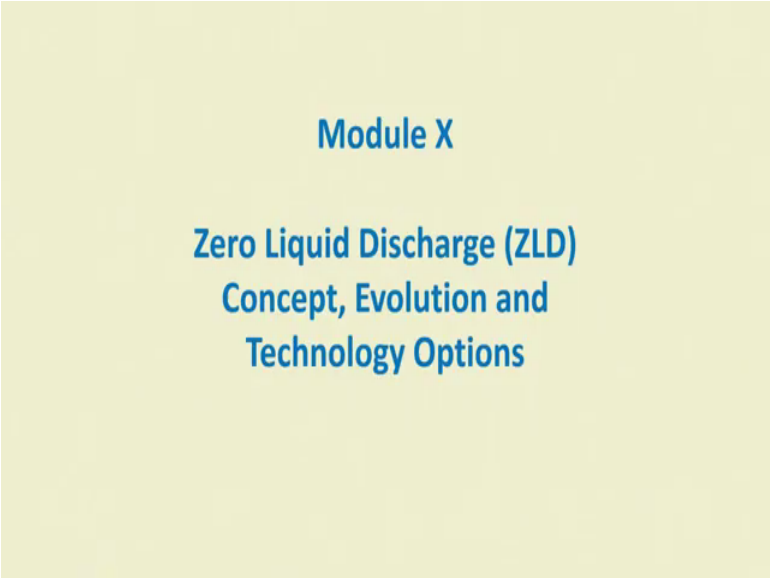

Module X

Zero Liquid Discharge (ZLD)
Concept, Evolution and
Technology Options

That brings us to the last discussion part zero liquid discharge.

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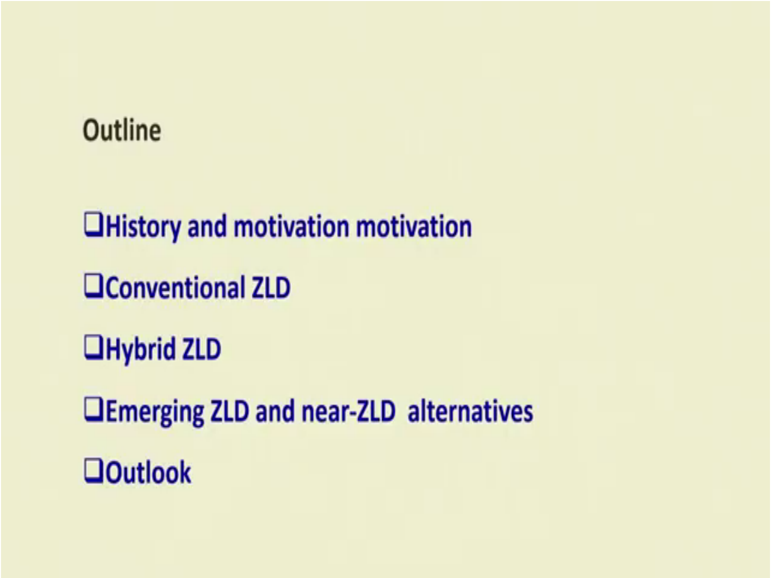

Outline

☐History and motivation motivation

☐Conventional ZLD

☐Hybrid ZLD

☐Emerging ZLD and near-ZLD alternatives

☐Outlook

What do we have here? Here I will give you a small outline of what is zero liquid discharge. And I would like to tell you at this point that zero liquid discharge is a very very important concept in the 21st century living. The basic thinking is if the effluents contain toxic substances then they have to be separated. Then if I separate would the water be reusable or not, if I separate am able to separate the pollutants would it be reusable or not the effluents treated effluents.

The answer is usually no it has to go through at least about 600 feet depth fall and about 20 kilometre flow before it collects enough oxygen from sun's rays and from the atmosphere and enough radiation from sun's rays to get natural purification, that too subject to proper dilution. So, basically the convention is a wisdom rather wisdom says do not use that so, but industries we cannot stop. So, what do we do we come out with a concept of zero liquid discharge use whatever amount of water you need, but do not discharge from the factory or industry.

Then what do you do? You either recover and reuse or you evaporate it, these are the two basic concepts of zero liquid discharge it is being applied all over India and all over the world also the concept is that has is gaining strength. And I want to introduce you to these type of treatment and it will be it will stand in good sight for you when you go to industries. So, here is the outline history and motivation conventional ZLD, hybrids ZLD, emerging ZLD and near ZLD alternatives followed by outlook what would be the final outlook.

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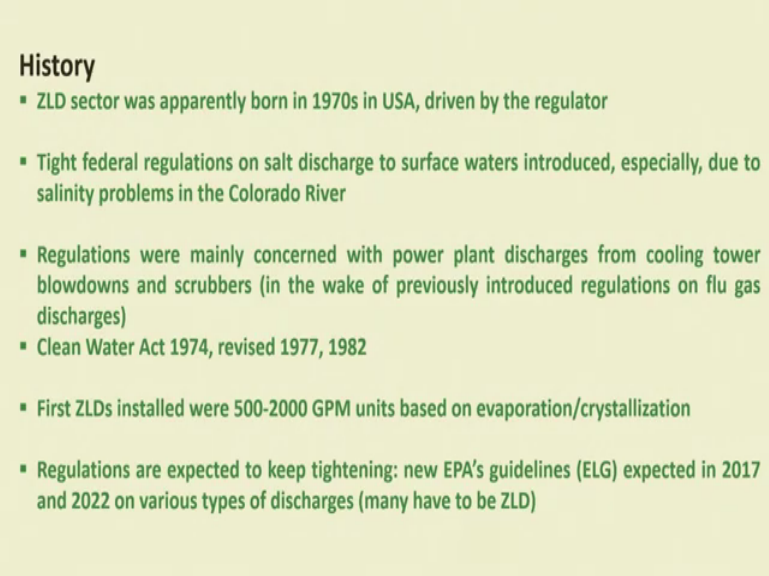

History

- ZLD sector was apparently born in 1970s in USA, driven by the regulator
- Tight federal regulations on salt discharge to surface waters introduced, especially, due to salinity problems in the Colorado River
- Regulations were mainly concerned with power plant discharges from cooling tower blowdowns and scrubbers (in the wake of previously introduced regulations on flu gas discharges)
- Clean Water Act 1974, revised 1977, 1982
- First ZLDs installed were 500-2000 GPM units based on evaporation/crystallization
- Regulations are expected to keep tightening: new EPA's guidelines (ELG) expected in 2017 and 2022 on various types of discharges (many have to be ZLD)

Then here is the history somewhere, around 1970s we started talking about it. And in America it was driven by the regulator tight federal regulations on salt discharge to surface waters were introduced especially, due to salinity problems in the Colorado River. So, regulations were mainly concerned with power plant discharges from cooling tower. Usually cooling towers have blowdown and scrubbers and clean water act came in 1974. First ZLD is installed where about 500 to 2000 GPM.

GPM means gallons per minute and based on evaporation and crystallization. If you evaporate then the water vapour in the air can be carried over by the clouds etcetera and then it can be redeposited as a pure material. There as enough dilution in the atmosphere for the water vapour to get almost purified. And then regulations are expected to keep tightening again in the coming years. And new EPA guidelines are expected in 2022 now even in India we have zero liquid discharge concept in almost all the states.

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Current Drivers and Limitations

- Presently, the major driver for using ZLD are

✓ Environmental regulation on discharge of specific solutes (salt, toxic elements, nitrate-nitrite etc)

✓ Water scarcity/water stress growing world-wide along with still negligible rate of waste water recycling

✓ Economics: Recycled water becomes more affordable as the water supply from conventional sources becomes more expensive

So, what are the current drivers? The current drivers include the major driver for using the ZLD, include environmental regulations for discharge of specific solute salts toxic elements nitrates nitrites cyanide chlorides hydroxides sulphides etcetera.

And then water scarcity is another driving force water stress in the growing world. And then economics recycled water becomes more affordable as the water supply from conventional sources becomes more expensive this is a very simple economic content.

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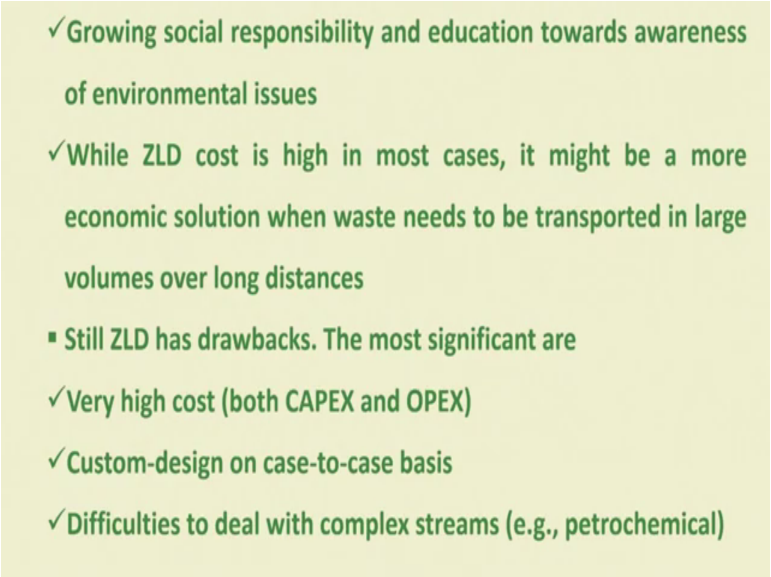

✓Growing social responsibility and education towards awareness of environmental issues

✓While ZLD cost is high in most cases, it might be a more economic solution when waste needs to be transported in large volumes over long distances

- Still ZLD has drawbacks. The most significant are

✓Very high cost (both CAPEX and OPEX)

✓Custom-design on case-to-case basis

✓Difficulties to deal with complex streams (e.g., petrochemical)

So, growing responsibility and education towards awareness of environmental issues is also one of the driving force followed by ZLD cost, that is high in most cases might become a more economic solution when waste needs to be transported in large volumes over long distance. Here I want to add that if the quantities are really large.

Then you cannot transport. So, much of liquid elsewhere, but if you go for ZLD what remains? After taking out the liquid is a very small quantity of the waste. So, that will become much cheaper in handling. So, still in spite of all these advantages ZLD has some drawbacks also. As of now it is very high highly cost type that is both CAPEX and OPEX. Capital expenditure and operating expenditure is very high as of now.

A custom design has to be made on case to basis instead of a general design then there are difficulties to deal with the complex streams. For example, petrochemical streams will have lot of problems especially, the wastes that are generated would not be common with many of the effluents that are being produced in other industries. They are all special industries where they need the sort of special treatment only.

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Current and Potential Markets for ZLD

❑Treatment and recycling of industrial waste effluents

- Power
- Petroleum and petrochemical
- Synthetic fuels
- Primary metals processing
- Petroleum and petrochemical
- Oil refining
- Primary metals processing
- Steam assisted gravity drainage (SAGD)
- Microelectronics
- Heavy oil recovery

So, the I can show you a little bit of the petrochemical problems. For example, petrochemical and petroleum synthetic fuels and petrochemicals, oil refining all these are very complex effluents. And then power sometimes if you are using power coal for power generation.

Again, complex effluents followed by these gravity drainage and micro electronics industries, which may contain toxic elements then heavy oil recovery is another aspect where current and potential markets for ZLD are sort of expected to make rapid strides in progress.

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- Cogeneration
- Pulp and paper
- Coal mining
- Fertilizer
- Solid waste (leachate and secondary sewage effluent)
- Battery manufacturing
- PVC manufacturing
- Coal liquefaction
- Ethanol production
- Uranium mining

☐ Tertiary treatment of municipal waste effluents

☐ Inland desalination desalination

So, there are other industries for example, cogeneration, pulp and paper co coal mining, fertilizer, solid waste, battery manufacturing, PVC, coal, ethanol production all these are very important industrial aspects followed by tertiary treatment of municipal wastewater effluents and inland desalination.

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Conventional Thermal ZLD Technology

- ✓The conventional ZLD is based on evaporation and crystallization operations
- ✓Evaporation (MVC or live steam) usually aims at >90% water recovery
- ✓crystallization may achieve 100% recovery
- ✓solids solids can can bebe further further dewatered dewatered onon aa filter filter-press press for landfill
- ✓Latent heat of evaporation is partly recovered (especially, for MVC)
- ✓Operational and capital costs are still very high energy consumption (20-40 kWh/m^3 vs. 2-3 kWh/m3 in desalination), use of chemicals and expensive corrosion-resistant materials

So, conventional thermal ZLD technology basically is based on evaporation and crystallization operations. Evaporation usually aims around 90 percent water recovery whereas; crystallization may achieve even hundred percent recovery. we do not mean 100 percent when we say 100 percent, but at least 99 99.99 percent should be feasible. So, solids can be further de watered on a filter press for landfill.

There are couple of mistakes here double typing has taken place. I request you to bear with me I have tried to correct it as much as possible so, but this does not make sense to have that kind of mistakes. So, latent heat of evaporation is partly recovered operational and capital costs are still very high as of in ZLD.

For example, in desalination you can see that 20 to 40 kilo Watt hour per cubic meter. The energy consumption is there compared to 2 to 3 kilo Watt hour per meter cube for desalination. So, use of chemicals and expensive corrosion materials is another aspect that is as of now a small hindrance to ZLD objective.

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See the complex ZLD operations and these are all for petrochemical industries only effluent treatment systems. So, it makes a lot of complicated engineering design, cost, treatment cost etcetera, but you can see that the wastage or effluent in the gaseous form coming out is very very less here.

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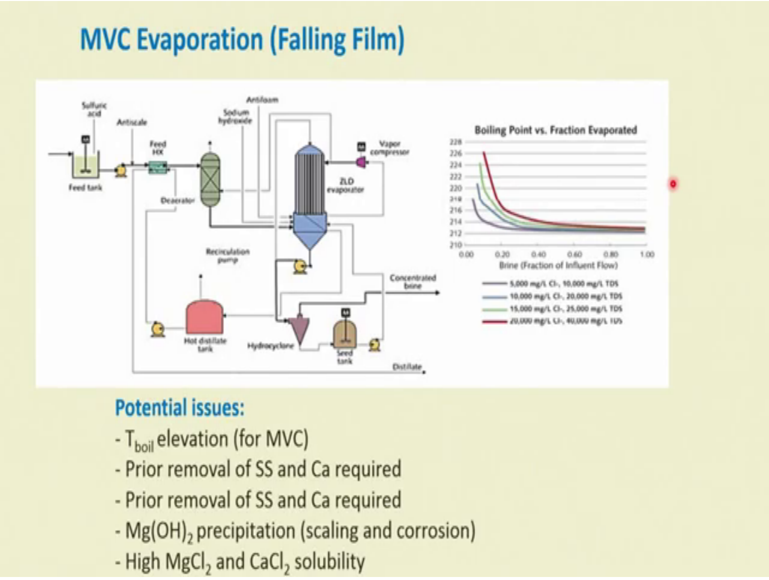

MVC Evaporation (Falling Film)

Potential issues:

- T_{boil} elevation (for MVC)
- Prior removal of SS and Ca required
- Prior removal of SS and Ca required
- $Mg(OH)_2$ precipitation (scaling and corrosion)
- High $MgCl_2$ and $CaCl_2$ solubility

Then there are other techniques for example, this MVC evaporation technique. So, here suspended solids are removed prior. And the calcium hydroxide and magnesium hydroxide precipitations are commonly employed. And here I have a boiling point diffraction evaporated etcetera some of these things if you study well you will be able to know I am know about it. And I am not going into detailed aspects because these are all very simple flows flow sheets and anyway whenever you want to design a ZLD you will have to do it case by case only.

So, I am not going into detail these are the common typically available systems.

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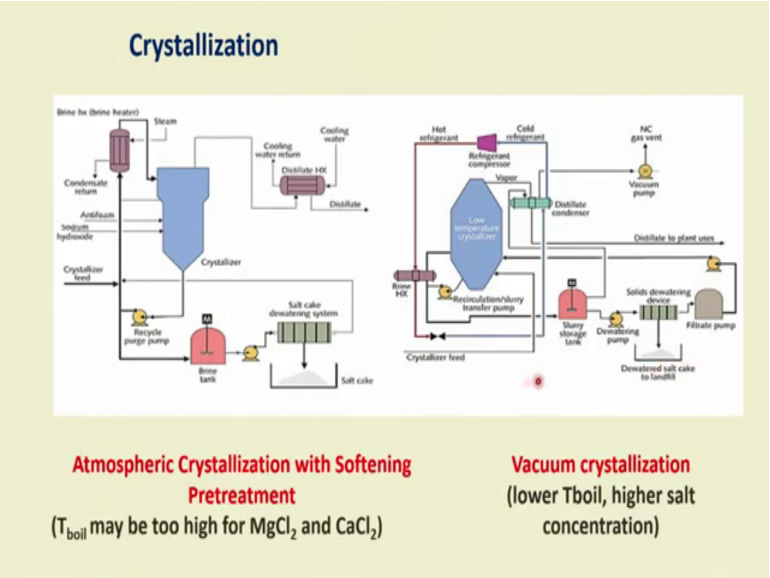

Crystallization

Atmospheric Crystallization with Softening Pretreatment
(T_{boil} may be too high for $MgCl_2$ and $CaCl_2$)

Vacuum crystallization
(lower Tboil, higher salt concentration)

So, for example, if you go for crystallization, it is not very tricky for example, here I have brine and stream is there condensate is there we add a little bit of antifoam, sodium hydroxide, neutralization and take it to crystallization. And then after crystallization filtration and collection and disposal, similarly vacuum crystallization is also another system. Here the temperature for boiling will be reduced quite a lot followed by higher salt concentration is a very typical advantage.

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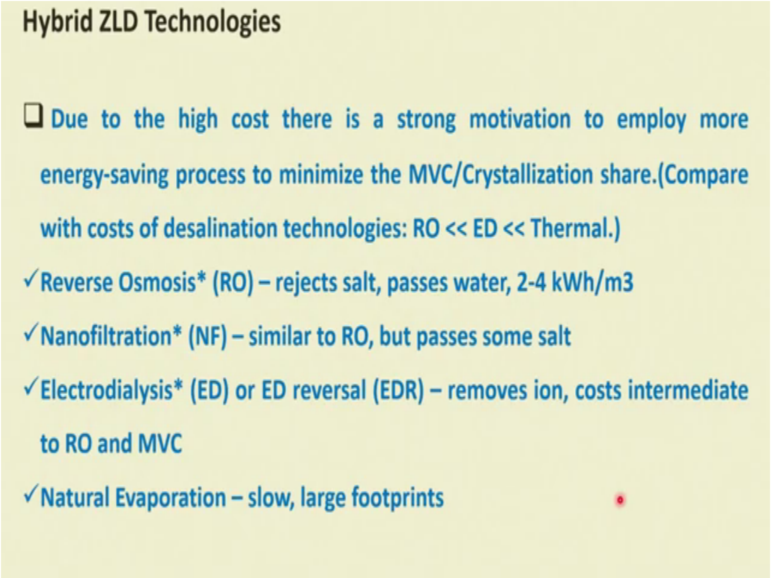

Hybrid ZLD Technologies

- ☐ Due to the high cost there is a strong motivation to employ more energy-saving process to minimize the MVC/Crystallization share.(Compare with costs of desalination technologies: RO << ED << Thermal.)
- ✓Reverse Osmosis* (RO) – rejects salt, passes water, 2-4 kWh/m3
- ✓Nanofiltration* (NF) – similar to RO, but passes some salt
- ✓Electrodialysis* (ED) or ED reversal (EDR) – removes ion, costs intermediate to RO and MVC
- ✓Natural Evaporation – slow, large footprints

Now, hybrid ZLD technologies are there a little bit mixing of the technologies. But there is strong motivation to employ energy saving processes for example, this multiple evaporator system MVC crystallization etcetera. Some of these technologies share compared with cost of desalination they are comparable for example, RO is much cheaper then ED that is much cheaper than thermal evaporation. And ED is electro dialysis. So, reverse osmosis is one part what does it do? Reverse osmosis rejects the salt passes water energy requirement is approximately 2 to 4 kilo Watt hour per cubic meter.

Then Nano filtration used to remove the salts not suspended salt not dissolved salts. Electro dialysis removes ions costs are intermediate to RO and MVC naturally evaporation again slow and large footprints again not so favoured, but any of these reverse osmosis, nano filtration, electrolysis, electro dialysis and electrode reversal all these things are quite often employed in modern day zero liquid discharge systems.

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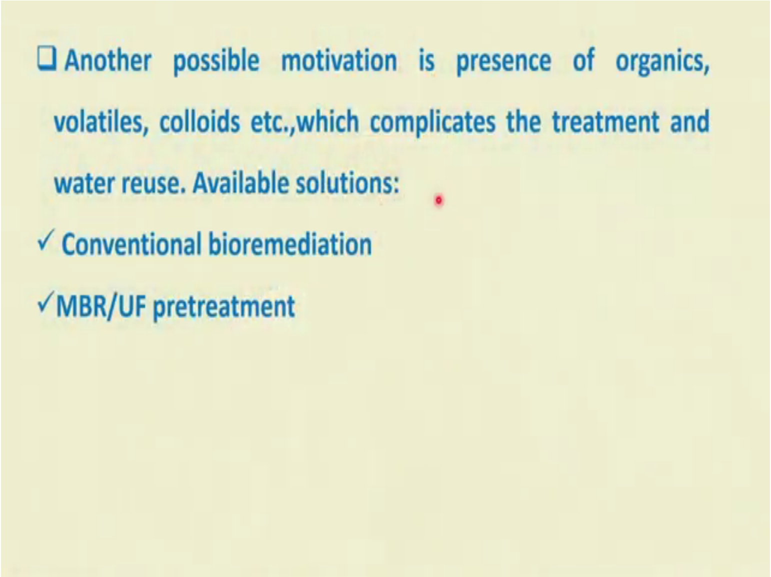

❑ Another possible motivation is presence of organics, volatiles, colloids etc.,which complicates the treatment and water reuse. Available solutions:

✓ Conventional bioremediation

✓ MBR/UF pretreatment

So, another possible motivation is the presence of organics volatiles etcetera colloids etcetera. Here what happens is many of the volatiles will not be economically recoverable if the concentration is very low. So, we go for evaporation. And then if we cannot recover if we cannot let them into the environment as vapours we can go for bio remediation. Bio remediation and then this membrane units ultrafiltration, pre-treatment, membrane biological systems these are all very typical technologies which are well established.

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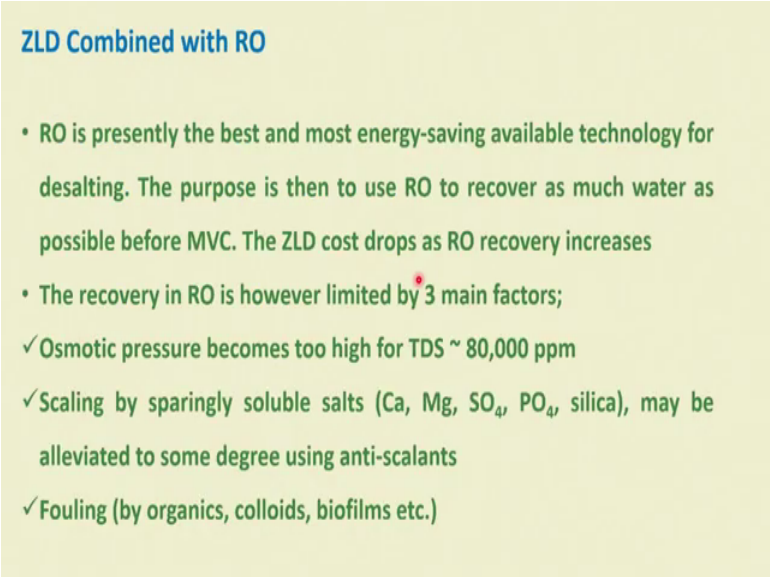

ZLD Combined with RO

- RO is presently the best and most energy-saving available technology for desalting. The purpose is then to use RO to recover as much water as possible before MVC. The ZLD cost drops as RO recovery increases
- The recovery in RO is however limited by 3 main factors;

✓Osmotic pressure becomes too high for TDS ~ 80,000 ppm

✓Scaling by sparingly soluble salts (Ca, Mg, SO_4, PO_4, silica), may be alleviated to some degree using anti-scalants

✓Fouling (by organics, colloids, biofilms etc.)

Then ZLD combined with RO is again a very attractive system. RO is presently the best and most energy saving available technology for desalting. The purpose is then to use RO to recover as much water as possible before MVC. If you wish to recover reverse osmosis water you a average ache efficiency is approximately about 50 percent, but nowadays the recovery varies from 85 to 95 percent. And some the TDS total dissolved solids osmotic pressure becomes too high for more than around 80000 PPM or something.

So, scaling may be elevated to some degree by anti-scalant. And then fouling of course, is always there. So, if there are organic substances colloids biofilms etcetera you cannot employ RO systems. If it is purely acuvue system then the RO system would work very fine. Then this is the RO system. Here I have an RO system RO product is there RO concentrate is there. And, this is a brine concentrator this can be concentrated and crystallized remove the solids and again whatever comes out can be mixed with RO product.

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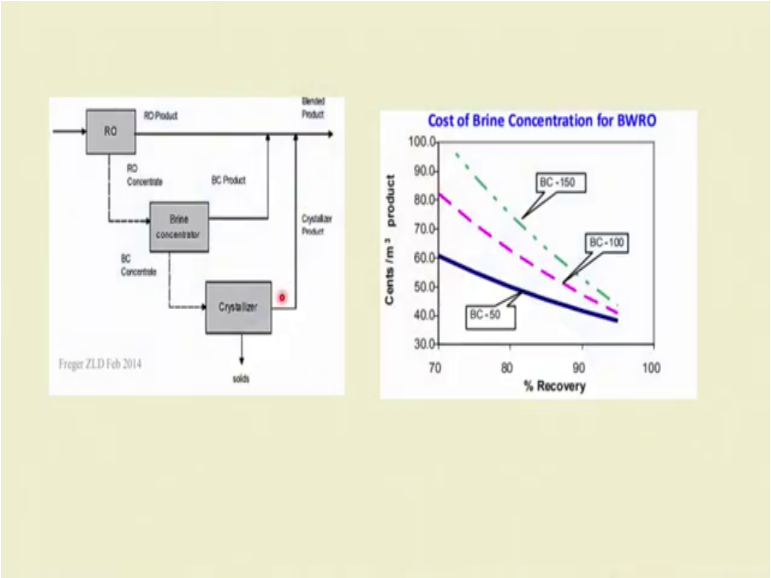

This is condensation product here. So, cost of brine come concentration for this is approximately comparable a little less when this is these are suspended solids concentration this is 50 this is 100 this is 150. The lesser and lesser suspended solids the cost will increase more.

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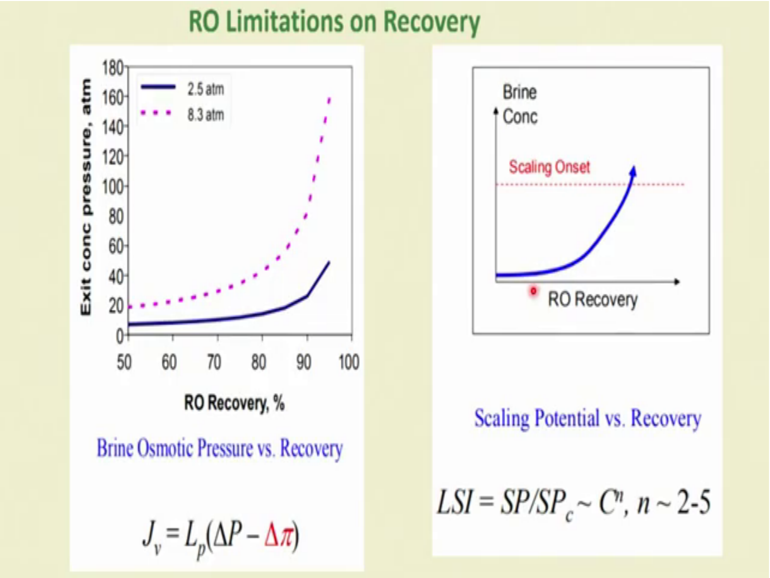

RO Limitations on Recovery

Brine Osmotic Pressure vs. Recovery

$$J_v = L_p(\Delta P - \Delta \pi)$$

Scaling Potential vs. Recovery

$$LSI = SP/SP_c \sim C^n,\ n \sim 2\text{-}5$$

So, RO limitations are there as I had already told you that if you want to recover more. Then the cost will increase exponentially here you can say this no. And the same thing is true in brine also suppose you have a salt effluent. And then you want to recover better 90 percent or something you can see that brine concentration also will increase in the reject and the cost also will become very high.

I am not going into details of these equations they are all very standard osmotic pressure and normal pressure difference etcetera they relate to the efficiency. If you wish to know more about it we will have another course on RO system separately.

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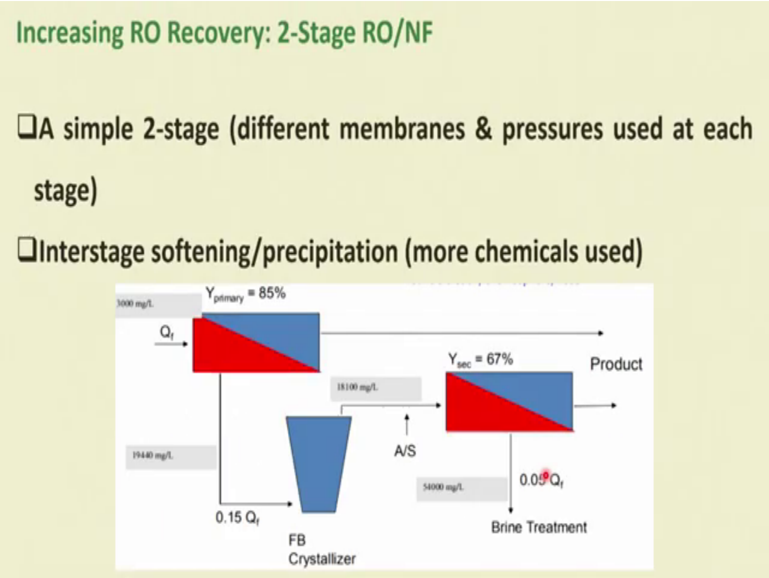

Increasing RO Recovery: 2-Stage RO/NF

- ❑A simple 2-stage (different membranes & pressures used at each stage)
- ❑Interstage softening/precipitation (more chemicals used)

Then increasing RO recovery we can go for 2 stage RO and Nano filtration. Here entire stage softening or precipitation also is quite common. And we advise people to go for this inter-stage softening and precipitation of course, it requires more chemicals to be used, but the quality of water here I have given you a simple system that is 3000 milligram per litre.

Primary separation will give you 80 percent straightaway. And remaining reject will be around 19440. And again if you can take it to a crystallization and what comes out would be the mother liquor from this would be having about 18100 followed by another RO system, where recovery would be 67 percent. And, the reject would be 54000 milligram per litre this can be evaporated and take out the salts and there you can either bury the salts or do whatever is necessary to store or dispose of in a standard TSDF that is toxic substances disposal facility.

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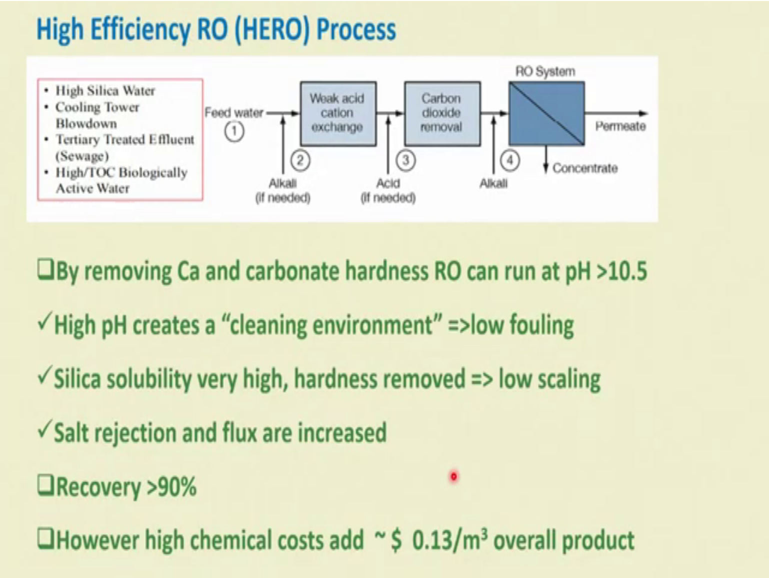

High Efficiency RO (HERO) Process

❑By removing Ca and carbonate hardness RO can run at pH >10.5

✓High pH creates a “cleaning environment” =>low fouling

✓Silica solubility very high, hardness removed => low scaling

✓Salt rejection and flux are increased

❑Recovery >90%

❑However high chemical costs add ~ \$ 0.13/m^3 overall product

Then we have RO if high efficiency RO processes are there they can we can remove the calcium and carbonate hardness. RO can run around pH 10.5 also. And high pH creates a cleaning environment that is low fouling. Then silica solubility is very high. And then hardness can be removed salt rejection and flux are increasing. And recovery will be more than 90 percent; however, cost will be proportionately higher; obviously, approximately by about 0.13 dollar per cubic meter.

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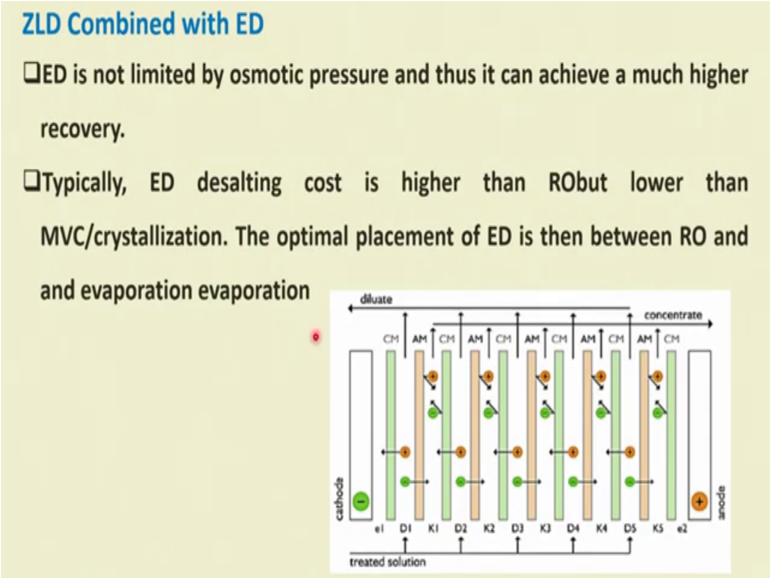

ZLD Combined with ED

- ❑ED is not limited by osmotic pressure and thus it can achieve a much higher recovery.
- ❑Typically, ED desalting cost is higher than RObut lower than MVC/crystallization. The optimal placement of ED is then between RO and and evaporation evaporation

And ZLD combined with ED electro dialysis. Here the advantage is it need not be connected automatically we can it is a choice. So, ED is not limited by osmotic pressure therefore, it can achieve much better recovery; that means, it can be removed used to remove the ions dissolved salts. So, typically ED desalting cost is higher than RO, but lower than crystallization. So, that is one of the advantage.

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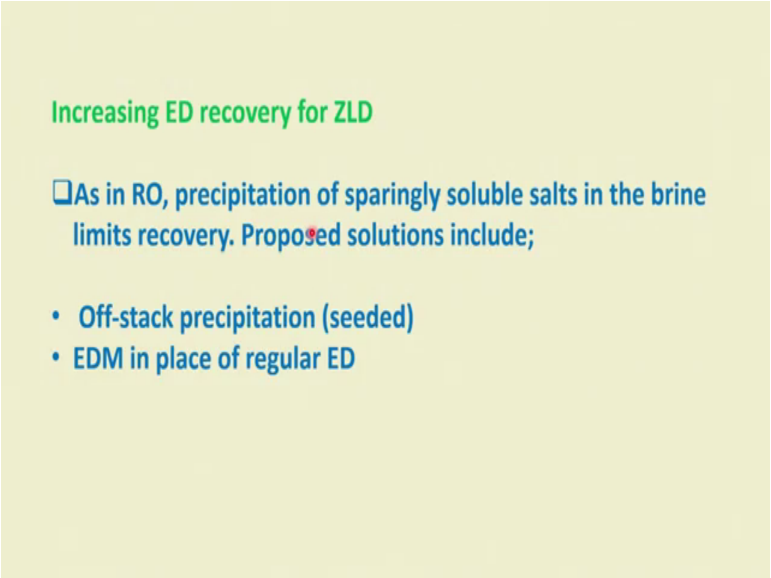

Increasing ED recovery for ZLD

❑ As in RO, precipitation of sparingly soluble salts in the brine limits recovery. Proposed solutions include;

- Off-stack precipitation (seeded)
- EDM in place of regular ED

And increasing electro then the question arises why not increase the ED itself? Electro dialysis instead of RO the point is the in RO if the quantity is very large electro dialysis becomes very costly. So, first we go for RO then followed by ED.

So, that we handle smaller quantities, but higher concentration of the dissolved salts. So, we can have go for off stack precipitation or EDM in place of regular ED.

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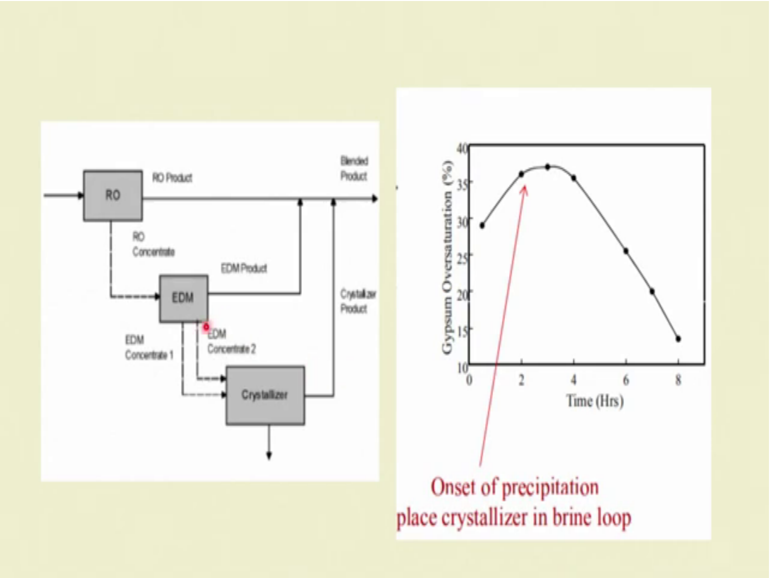

Onset of precipitation
place crystallizer in brine loop

Then these are the typical systems RO followed by EDM followed by crystallizer. And the onset of precipitation this is a typical study we have people have done for gypsum oversaturate. This is for a fertilizer industry you can see that onset of precipitation happens even within 2 hours of putting it in the crystallizer. That is interesting because the concern a salt concentration should be very high whenever you want to remove it by crystallization.

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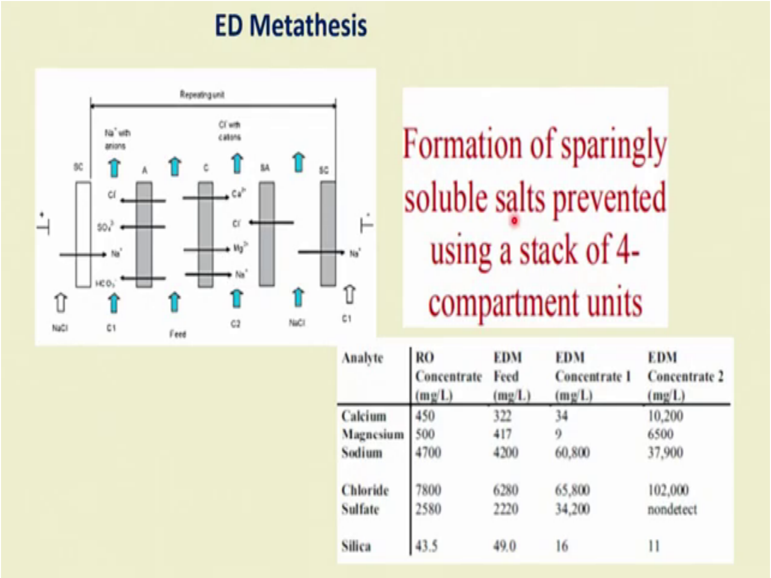

ED Metathesis

Formation of sparingly soluble salts prevented using a stack of 4-compartment units

Analyte	RO Concentrate (mg/L)	EDM Feed (mg/L)	EDM Concentrate 1 (mg/L)	EDM Concentrate 2 (mg/L)
Calcium	450	322	34	10,200
Magnesium	500	417	9	6500
Sodium	4700	4200	60,800	37,900
Chloride	7800	6280	65,800	102,000
Sulfate	2580	2220	34,200	nondetect
Silica	43.5	49.0	16	11

It has to be go to reach the super stand a super saturation level before it can start precipitation. So, the ED metathesis for example, formation of sparingly the soluble salts can be prevented very easily using 4 compartment units here we can see in the next slide. First one is RO concentrate here I have calcium, magnesium, sodium chloride, sulphide etcetera. These are the concentrations if I go to EDM take the reject of this, I end up with about these numbers that is 322, magnesium will become 417 PPM sodium will become 4200 chloride etcetera.

They all become lower then RO; that means, water will be more purer in EDM. And that is the EDM feed. And what happens to e d m concentrate? So, after EDM I get 34 PPM of calcium from 322. That is fantastic isn’t it? And then salt concentration will increase quite a lot chloride etcetera these are the rejects now. So, here you can see that EDM is much more efficient than RO alone. So, RO with EDM makes much more sense.

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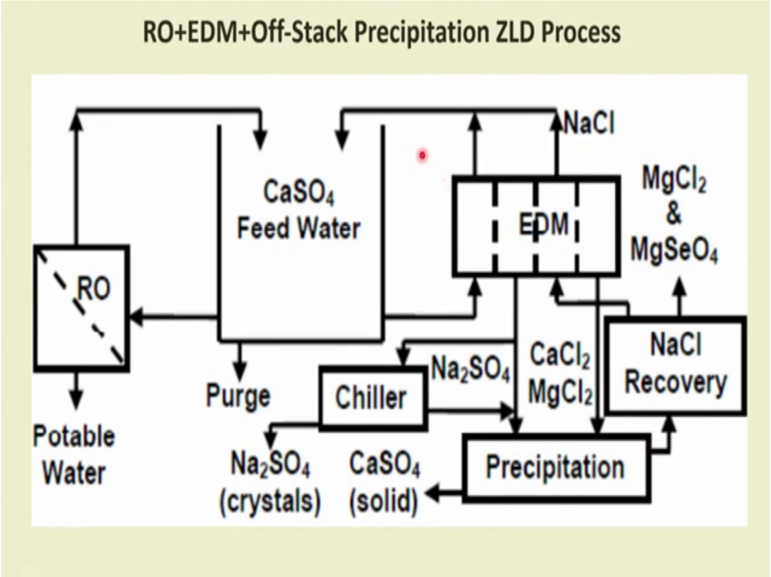

RO+EDM+Off-Stack Precipitation ZLD Process

So, this here is a presentation with RO plus EDM plus off stack precipitation. And it is a fairly simple system here I end product is potable water straightaway you can take it for drinking. And the reject goes to calcium sulphide feed water and the purge it and then add sodium. So, you from the EDM concentrate we can take it there filter and reuse the material.

So, these are all different systems for precipitation for example, in this chiller sodium sulphide can be very easily removed just by cooling the system. So, sodium chloride recovery can be done by adding magnesium chloride. So, like that there are different chemical systems available all the rejects can be added to final calcium sulphide fluid water system where it is purged. And then this can be taken back to RO for treatment. So, ZLD becomes really effective especially when you have different kinds of waste having a variety of salts.

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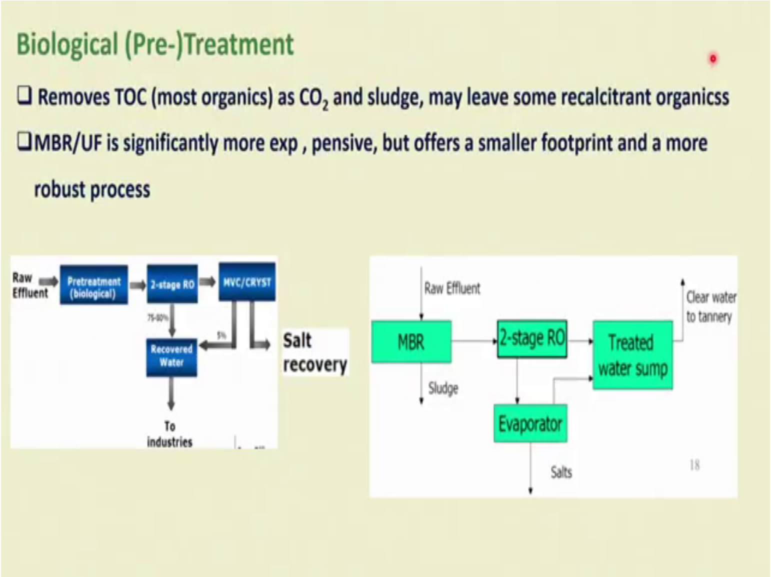

Biological (Pre-)Treatment

- ❑ Removes TOC (most organics) as CO_2 and sludge, may leave some recalcitrant organicss
- ❑MBR/UF is significantly more exp , pensive, but offers a smaller footprint and a more robust process

Then there are biological systems a couple of them. And then these things remove TOC total organics as CO 2 and sludge they may leave some recalcitrant organics, but it would not be much. And, there are methods to remove the such organics and MBR UF is significantly more expensive definitely because MBR itself is very very costly a membrane biological recovery.

So, pensive, but offers a smaller footprint and, but this MBR can be as it can be very less space consuming. So, that is one advantage we have here. So, MBR followed by 2 stage RO evaporator and treated water we get the clear water that can be taken to different systems here it is a tannery waste system.

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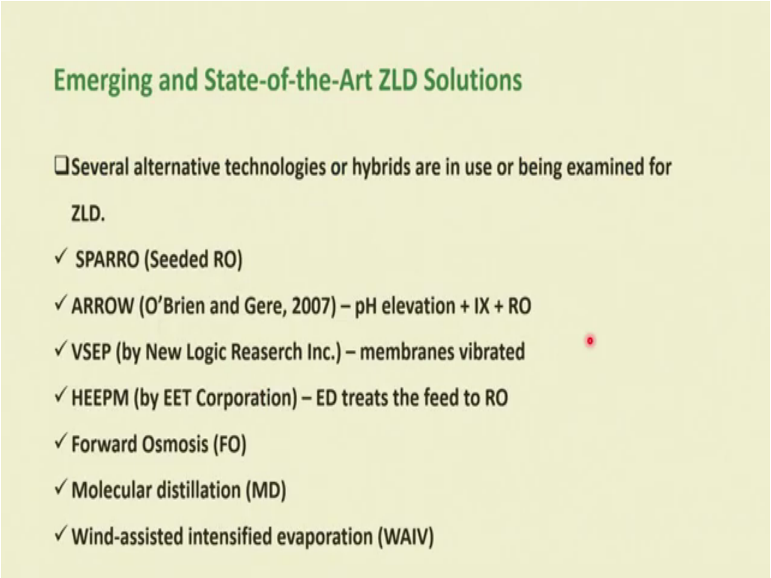

Emerging and State-of-the-Art ZLD Solutions

☐ Several alternative technologies or hybrids are in use or being examined for ZLD.

- ✓ SPARRO (Seeded RO)
- ✓ ARROW (O'Brien and Gere, 2007) – pH elevation + IX + RO
- ✓ VSEP (by New Logic Reaserch Inc.) – membranes vibrated
- ✓ HEEPM (by EET Corporation) – ED treats the feed to RO
- ✓ Forward Osmosis (FO)
- ✓ Molecular distillation (MD)
- ✓ Wind-assisted intensified evaporation (WAIV)

Then emerging and state of the art ZLD solutions I want to discuss not much to add in these. Here several alternative technologies SPARRO, ARROW and here it is pH elevation precipitation followed by RO. And then VSEP the say these are RO systems in such systems RO membranes are kept we shaking continuously. So, that there is no build-up of the falling. So, this is a very fantastic technology which I had the opportunity to review it recently, I felt a very nice 90 85 to 95 percent recovery straight away only from RO systems.

And then we have this HEEPM that is ED treats the feed to RO. Then forward osmosis again instead of reversal normal osmosis also can be employed followed by molecular distillation and wind assisted intensified evaporation etcetera WAIV it is called. These are the alternate technologies we normally explore depending upon the volume and cost.

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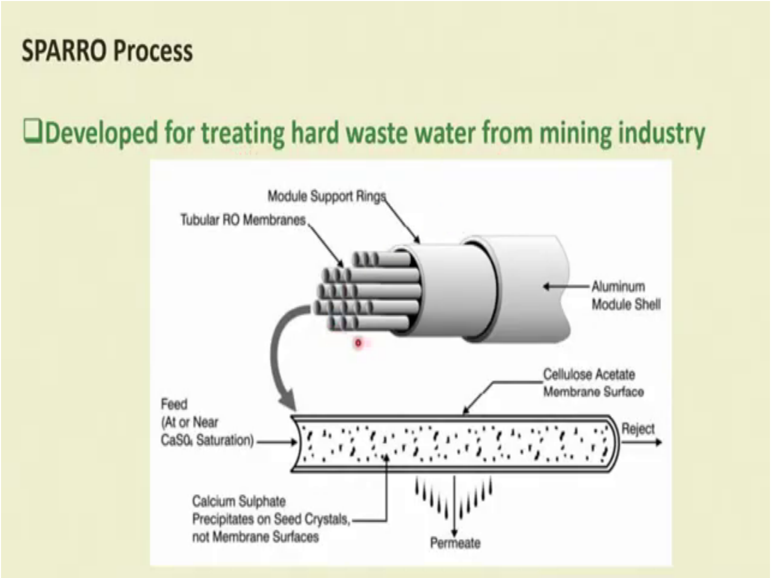

SPARRO Process

- ☐ Developed for treating hard waste water from mining industry

So, for example, in SPARRO process we have hard water from mining industry all you got to do is feed it. And then here is the calcium sulphide precipitates. And seed crystals and then not on the membrane surface, but outside, but the permeate what you get is very simple reusable water. Here it is other systems I have discussed I have described here just by notation with regarding the actual system.

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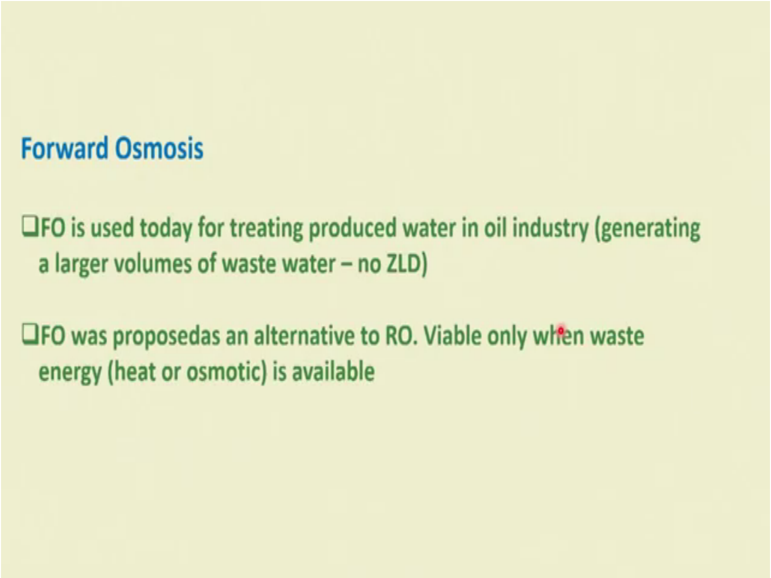

Forward Osmosis

- ❑FO is used today for treating produced water in oil industry (generating a larger volumes of waste water – no ZLD)
- ❑FO was proposedas an alternative to RO. Viable only when waste energy (heat or osmotic) is available

Then forward osmosis very useful today in oil industry. And it was proposed as an alternative to RO. It is viable only when waste energy is available.

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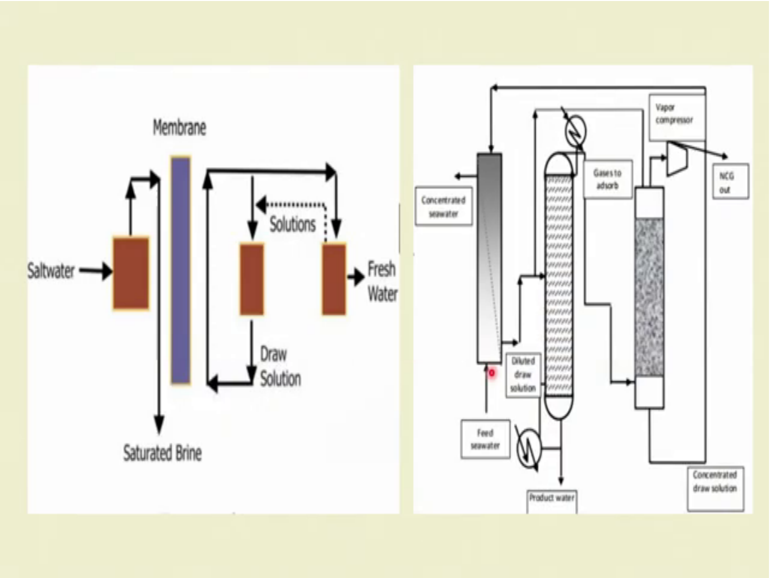

This is the forward osmosis figure. I will not go into details except you can study this yourself and come to some sort of you know understanding of the process, because I have put most of the titles here most of the components. And you can imagine what all they do each component that would be there.

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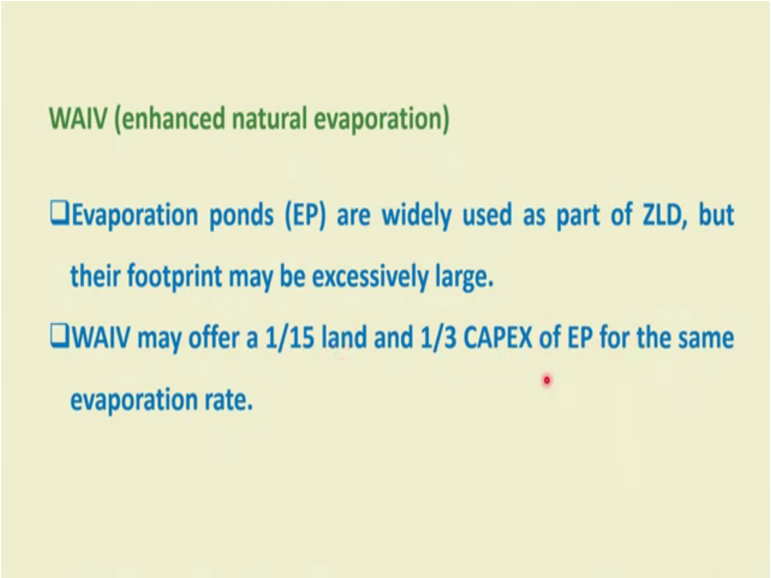

WAIV (enhanced natural evaporation)

- ❑Evaporation ponds (EP) are widely used as part of ZLD, but their footprint may be excessively large.
- ❑WAIV may offer a 1/15 land and 1/3 CAPEX of EP for the same evaporation rate.

And then enhanced a natural evaporation is again another process which was used earlier in about 20-30 years before people used to have evaporation ponds. And these are widely used as part of ZLD, but their footprint can be excessively large you know because most of the time what people do is they maintain large ponds where the water will evaporate naturally leaving the concentrate.

And the concentrate will have different layers in the pond where anaerobic and aerobic processes are in equilibrium with each other. So, normally of very complex of ways such ponds will become very useful. So, wave may offer 1 by 15 of the land and 1 3rd of the CAPEX expenditure for the same evaporation rate.

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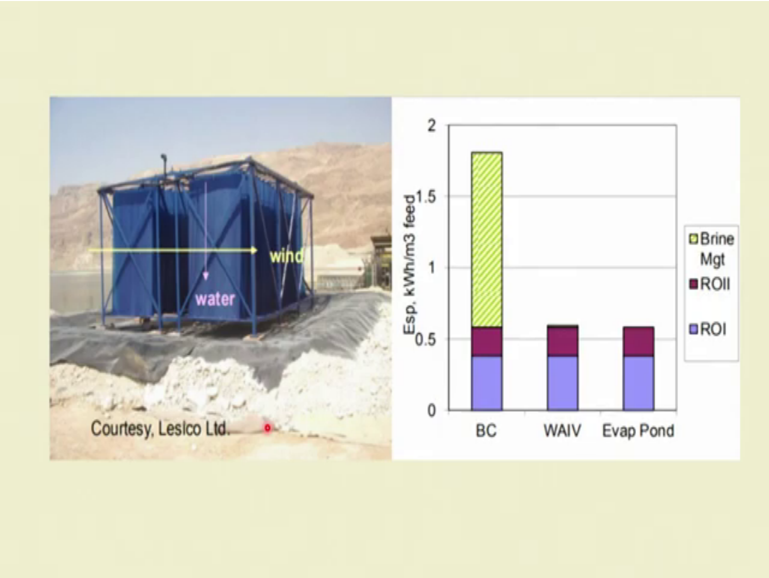

So, this is something like a typical plant. And here is the first one is the RO. RO 1,RO 2, a followed by brine treatment wave it makes a lot of sense whereas, here it is only RO 1 and RO 2.

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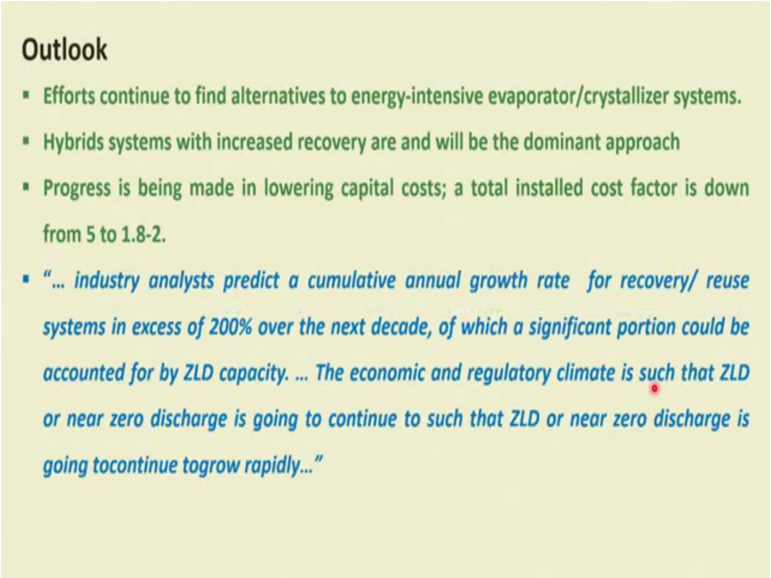

Outlook

- Efforts continue to find alternatives to energy-intensive evaporator/crystallizer systems.
- Hybrids systems with increased recovery are and will be the dominant approach
- Progress is being made in lowering capital costs; a total installed cost factor is down from 5 to 1.8-2.
- *"... industry analysts predict a cumulative annual growth rate for recovery/ reuse systems in excess of 200% over the next decade, of which a significant portion could be accounted for by ZLD capacity. ... The economic and regulatory climate is such that ZLD or near zero discharge is going to continue to such that ZLD or near zero discharge is going tocontinue togrow rapidly..."*

So, outlook industry, outlook is something like this that efforts to continue to find the alternatives to energy intensive operator hybrid systems are there with increase recovery will be the dominant approach. Progress is being made in lowering the cost. And industry analysts predict a cumulative annual growth rate of more than 200 percent in the next decade. I think it will be well for us to know more about these things as and when the opportunities rises.

And now I would like to conclude my discussion about the RO and ZLD systems. And I would like to say thank you for being with me in all these 40 41 lectures. And, I hope we had good opportunity to learn many things which I myself did not have the opportunity when I was a student, but if you need any help from me you would know how to contact me. And, I will be very happy to have you with me whenever you are in difficulty even otherwise you will all be you are all my students now you will be my good friends later thank you very much have a good career.

Thank you very much.