

Zero Liquid Discharge (ZLD) Technology Guidance Manual



Prepared for



Gujarat Pollution Control Board

by

IL&FS Academy of Applied Development



Disclaimer and conditions of use

1. *This manual is not intended as a recommendation of any particular technology, process, or method.*
2. *Mention of trade names, vendors, or commercial products do not constitute endorsement or recommendation.*
3. *It is offered for educational and informational purposes. To the extent permitted by law, the entire risk of loss, damage or unsatisfactory performance of the Program rests with the User. In no event will the Agencies be liable for damages, including any general, special, incidental or consequential damages, arising out of the use of the any material.*
4. *The numerical data and formulas contained in the Program are provided solely for the purpose of illustrating the capabilities. The Agencies give no warranty as to the accuracy, reliability, timeliness or other features of any data contained herein.*
5. *The User should rely on the User's own inquiries to determine the current status.*
6. *The words, including designations, used in the documents do not express or imply any opinion whatsoever on the part of the Agencies.*
7. *Users who re-disseminate the information should include the disclaimer and conditions of use in its current form and identify any modifications made by the user.*
8. *This material is copyrighted. Permission to copy all or in part with appropriate credit noted is freely given.*
9. *The User may modify, however, GPCB & IAAD would appreciate being informed of any modifications made by the User and being offered the opportunity to add any modifications. When making modifications, please also identify who created the material contained in the modifications. Questions should be directed to the GPCB & IAAD.*

Technical Guidance, Knowledge Content and Domain Expertise

Team IAAD:

Dr. Prasad Modak, Dean IL&FS Academy for Applied Development (IAAD)

Dr. Shrikar Dole, Head (Training, Networking & Partnerships) IAAD

Team GPCB:

Mr. Sushil Vegda (SEE), Mrs. D. P. Shah (EE), Mr. D. M. Thaker (EE),
Mr. T. C. Patel (DEE), Mrs. D. A. Tank (DEE), Mrs. Shivani Bhargav (DEE),
Mr. C. C. Bhimani (DEE), Mr. B. D. Prasad (DEE), Mr. M. G. Barad (DEE),
Mr. N. A. Shah (DEE), Mr. F. M. Modi (DEE), Mr. Sanjiv Vajnapurkar (DEE),
Mr. Ashwin Mistry (AEE), Mr. Pavankumar Sharma (AEE) and other officers of GPCB.

Field research and content production team

Ms. Vinita Dhupkar, Dr. Shrikar Dole,

Mr. Sushil Vegda and Team GPCB

This work is subject to copyright. Apart from any use as permitted under the Copyright Act 1968, the work may be reproduced in whole or in part for study or training purposes, subject to the prior permission and inclusion of an acknowledgment of the source. Reproduction for commercial use or sale requires prior written permission from GPCB & IAAD. Requests and inquiries concerning reproduction and rights should be addressed to the office of GPCB & IAAD. If you require part or all of this publication in a different format, please contact GPCB & IAAD

© GPCB & IAAD 2016

ACKNOWLEDGEMENT

It is our great pleasure to express our heartfelt and sincere gratitude to the team who assisted, supported and provided their expertise to prepare this Guidance Manual.

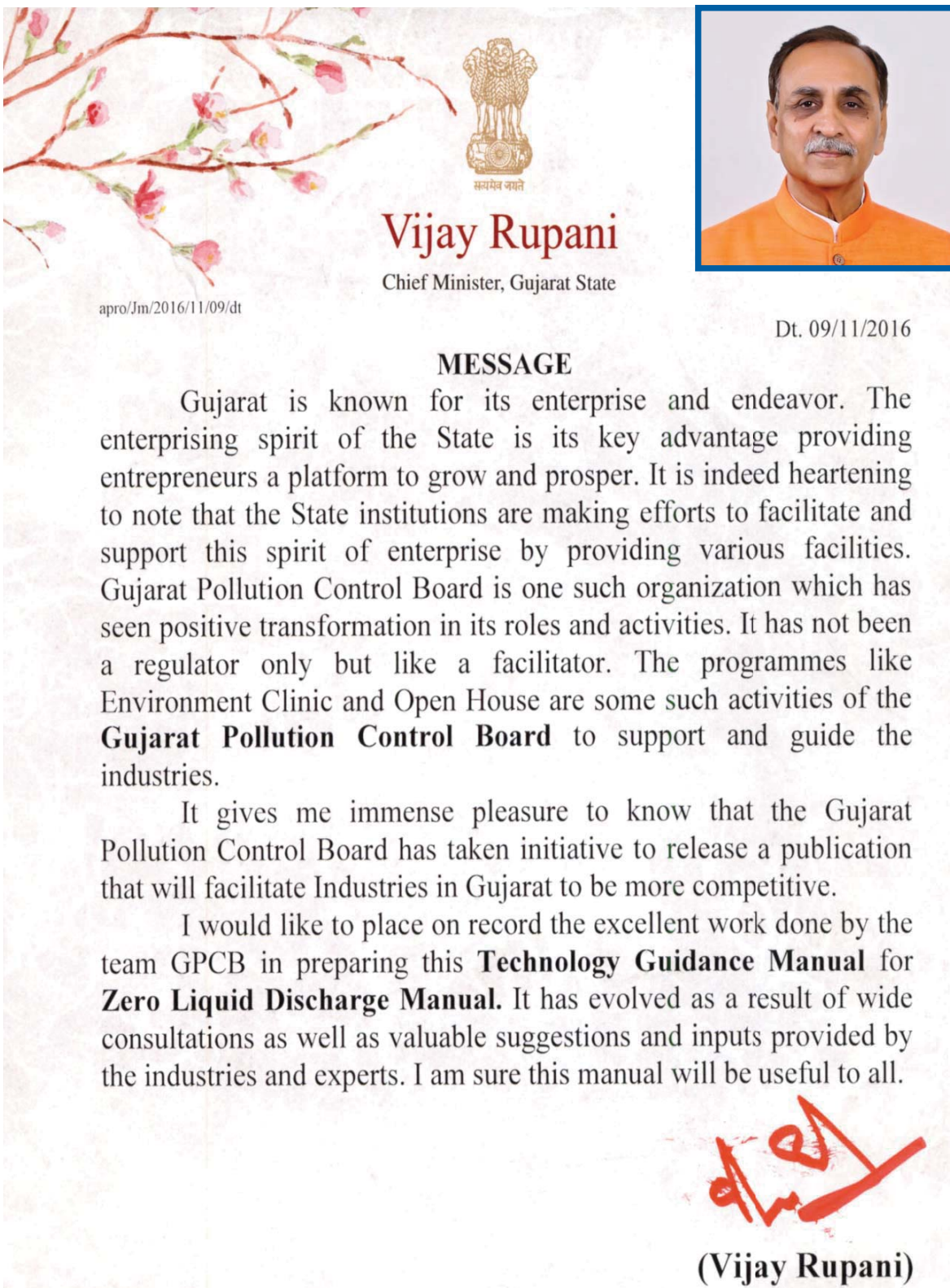
We would like to express our deepest appreciation to Team of Gujarat Pollution Control Board, led by the Member Secretary; who always challenged us and provided continuous support, guidance, directions and advices during the project.

We would like to express our sincere appreciation to the various technology providers, who provided details on their technologies and for their helpful discussions, suggestions and generous support.

We would like to sincerely acknowledge the individuals, agencies, & institutions, whose work guided us in preparing this manual. They are listed as reference.

Last but not least, we would like to record our heartfelt gratitude to all industries and CETP associations in Gujarat, who have implemented ZLD in one form or the other, and who provided us information and opportunities to visit to examine the efficacies of their systems.

Dr. Shrikar Dole
Head- Training, Networking & Partnerships
IL&FS Academy of Applied Development
Mumbai



apro/Jm/2016/11/09/dt

Dt. 09/11/2016

MESSAGE

Gujarat is known for its enterprise and endeavor. The enterprising spirit of the State is its key advantage providing entrepreneurs a platform to grow and prosper. It is indeed heartening to note that the State institutions are making efforts to facilitate and support this spirit of enterprise by providing various facilities. Gujarat Pollution Control Board is one such organization which has seen positive transformation in its roles and activities. It has not been a regulator only but like a facilitator. The programmes like Environment Clinic and Open House are some such activities of the **Gujarat Pollution Control Board** to support and guide the industries.

It gives me immense pleasure to know that the Gujarat Pollution Control Board has taken initiative to release a publication that will facilitate Industries in Gujarat to be more competitive.

I would like to place on record the excellent work done by the team GPCB in preparing this **Technology Guidance Manual for Zero Liquid Discharge Manual**. It has evolved as a result of wide consultations as well as valuable suggestions and inputs provided by the industries and experts. I am sure this manual will be useful to all.

(Vijay Rupani)

SHANKAR CHAUDHARY



No. VIP/ 3783 / 2016

**Minister of State,
Health and Family Welfare, Medical
Education, Environment (All Independent
Charge) and Urban Development,
Government of Gujarat**

Swarnim Sankul-2, 1st Floor, Sachivalaya,
Gandhinagar-382010

Office Phone No. : (079) 232 50195

Fax No. : (079) 232 50189

Date:

21 NOV 2016

Message

The Gujarat offers excellent infrastructure to industries, has abundant human capital, provides access to large markets and is an ideal place to invest in. The Government of Gujarat is extremely keen to extend this beneficial relationship with the industry and has taken many proactive steps to further attract industries.

The Ministry has initiated the process of revising the existing regulatory framework on environment to enable a greater role and ownership by industry in making the State a role model for sustainable industrial growth center.

Water is essential for industrial growth and it is in our interest to clean polluted waters, to ensure its availability for Industrial sustainability. The 'wise use' principle of water management encapsulates the linkages between this resource and livelihoods, on sustainable basis guided by ecosystem approaches.

In this context I am particularly happy to share with you the initiative of Gujarat Pollution Control Board to support and facilitate the process by bringing out a very useful publication - Technology Guidance Manual for Zero Liquid Discharge to encourage industries to become responsible corporate and be more competitive.

The publication's theme reflects the bigger and very crucial paradigm shift that the industry has to undergo from seeing 'development' and 'environment' as two ends of a spectrum, to having development while protecting environment.

The processes and guidelines have been simplified and put in a logical sequence for easy comprehension. This Manual unravels the detailed processes involved in the entire gamut of Water Management. This Manual will provide deeper understanding to the industries, officials of Departments of their roles and responsibilities. It is expected to serve as a guidebook for uniform administration of the Waste water treatment and practices.

I compliment the GPCB & IL&FS Academy of Applied development, and the team behind this noteworthy endeavor for offering invaluable assistance, support and guidance in furthering the industrial growth of the State.

I invite you to become a partner in the progress of our State.



(Shankar Chaudhary)



Arvind Agarwal IAS
Additional Chief Secretary

Government of Gujarat
Forest & Environment Department

Block No. 14, 8th Floor, Sachivalaya,
Gandhinagar-382010.



MESSAGE

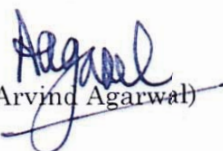
Government of Gujarat constituted the Gujarat Pollution Control Board (GPCB) in 1974, with a view to protect the environment and prevent and control pollution of water in the state of Gujarat that occupies a prominent niche in the progress and industrial development of the country.

Over the years, the Board's mandate has grown several fold, necessitating ever increasing demand for skill to handle complex laws and to cope with the challenging tasks of stringent standards of performance expected of it.

The Board has continuously made efforts at being innovative and bring about paradigm change in strategic knowledge for developing all round capabilities to protect the environment through optimum utilization of collective experience and knowledge of the GPCB team, and stakeholder engagement for informed decision-making through creating public awareness, disseminating knowledge and information for participatory action on issues of long-term nature.

I take this opportunity to congratulate the team of Gujarat Pollution Control Board as well as their knowledge partner IL&FS Academy of Applied Development for their path-breaking initiatives in bringing out a ZLD Technology Guidance Manual, a first of its kind in the country, to help the industries in Gujarat to implement the solutions for sustainable Growth.

I am sure Industry will find the manual useful in helping them solve the challenge of Water.


(Arvind Agarwal)

12th November 2016
Gandhinagar



Dr. Prasad Modak

Dean

IL&FS Academy for Applied Development (IAAD)

PROLOUGE

Water stress is a major issue that is posing a challenge to the Environment, Business and Livelihoods in India. Water is no longer easily accessible with ground water depths varying and rivers running dry. The high TDS and lowering level of groundwater due to over exploitation; water scarcity is going to be a major threat for the industry in the near future. With continuous increase in the demand of water the only option would be to reuse/recycle the water to the extent possible or achieve Zero Liquid Discharge (ZLD)

The imposition of ZLD is to ensure availability of Water for future use ensuring its sustainability. The concept of ZLD is not new to India. The recent changes in the rules and regulations have however provided the necessary impetus in a focused manner.

This Technology Guidance Manual covers a broad spectrum such as technology, economic consideration and management to facilitate the implementation of ZLD. The objective is to ensure sustainability and effectiveness of the investments made in ZLD.

In this context, I welcome the initiative taken by Gujarat Pollution Control Board of developing the Guidance Manual on ZLD. The manual will certainly guide and inspire the industries in Gujarat and help complying the ZLD mandate.

IAAD is most happy to provide support to GPCB for such endeavor and be the Knowledge Partner.



HARDIK SHAH, IAS
Member Secretary



GUJARAT POLLUTION CONTROL BOARD

PARYAVARAN BHAVAN, Sector 10-A,
Gandhinagar 382 010, Gujarat, INDIA.
Phone : (O) +91-79 2323 2152, Fax : +91-79 2322 2784
E-mail : ms-gpcb@gujarat.gov.in
Website : www.gpcb.gov.in

FOREWORD

Due to stringent regulations for disposal of waste water coupled with water stress and scarcity (in certain areas), Zero Liquid Discharge (ZLD) concept is widely accepted by Regulators and industries. There are various challenges to implement this concept such as selection of appropriate technology and techno-commercial feasibility. Based on the inputs received from the industry during the 2 day seminar cum workshop on ZLD in 2014, it was clear that conceiving, designing and implementing ZLD projects is not an easy task. There are no short cuts or solutions of simple “plug in and play” of projects. To support the sound business decisions and facilitate the industries with various options, GPCB decided to provide a ready reckoner for ZLD.

This is where the regulators, businesses, technologist, financial institutions, research & academia have to come together and develop projects/programs. The process of engagement is equally important as much the vision or the outcomes. The Board decided to facilitate the process for the benefit of the Industry. This manual will enable and guide both Regulators and industries in selection of appropriate ZLD technologies for various industrial sectors.

Hope this publication will be helpful to all stakeholders in businesses, and governments - as it conveys indicators, processes, practices and strategies that participating companies implementing ZLD, need to adopt in fulfilling their mandate under the law.

We sincerely acknowledge IAAD, our knowledge partners as well as efforts and commend the team of GPCB both at Head Office and Regional Offices, which has worked closely with the IAAD team and researchers to ensure that the manual is practical and in alignment with regulatory requirements.

Hope this publication will help all the stakeholders at large.

(Hardik Shah)

18th November 2016
Gandhinagar

Clean Gujarat Green Gujarat

ISO 9001 - 2008 & ISO 14001 - 2004 Certified

Table of Contents

Chapter	Title	Sub Titles	Page
	Table of Contents		I-II
	List of Tables		III
	List of Figures		III-IV
	Abbreviations		V
1.0	INTRODUCTION		1
1.1	<i>Zero Liquid Discharge</i>		2
1.2	<i>ZLD in India</i>		3
1.2.1		ZLD at Textile CETP Tirupur	3
1.2.2		ZLD at Tannery CETP Chennai	4
1.3	<i>ZLD in Gujarat</i>		5
1.3.1		Initiation of ZLD requirement	6
1.3.2		Gujarat Today	7
2.0	ZLD TECHNOLOGIES		8
2.1	<i>What is ZLD?</i>		8
2.2	<i>ZLD technologies</i>		10
2.2.1	Solvent Recovery		10
		Air Stripping	10
		Steam Stripping	11
		Solvent Recovery Columns	12
2.2.2	Membrane Bio Reactor (MBR)		14
		MBR Membranes	15
		Membrane types	16
		Operation of MBR	17
		Advantages of MBR System	18
		Disadvantages of MBR System	18
		Innovations in MBR technology	19
2.2.3	Filtration		20
		Membrane spectrum	20
	Ultrafiltration (UF)		21
		Types of Membrane	23
		Advantages of UF Technology	24
		Limitations of UF Technology	24
		Innovations in UF Technology	24
	Reverse Osmosis (RO)		25
		RO Membranes configurations	26
		RO system Operation	29
		Types of Fouling	29
		RO Membrane Cleaning	30
		Advantages of RO Technology	31
		Limitations of RO Technology	31
		Innovations in RO Technology	32
2.2.4	Evaporation		37
		Type of Evaporation	37
		Falling film Evaporator	37
		Forced recirculation	39
		Natural Circulation	40
		Plate type evaporator	41
	Multi effect Evaporator (MEE)		43
		Guidelines for designing MEE	45

Table of Contents

		Energy optimization in MEE	45
	Compression Evaporation		46
		TVR	46
		MVR	47
		Advantages of MVR Technology	49
		Limitations of MVR Technology	49
		Innovations in MVR technology	50
		Improvements in Evaporation technologies	52
		Selection of Evaporation technologies	53
2.2.5	Agitated Thin Film Dryer (ATFD)		55
		Key advantages	56
		Applications	57
	Crystallization		57
		Spray drier	58
		Liquid-Liquid Extraction (LLE)	58
2.3	Configuration & Comparative Assessment of ZLD Technologies		59
		ZLD Technologies Matrix	60
		Technology Maturity graph	62
		ZLD with 75% RO recovery	63
		ZLD with 90% RO recovery	64
3	INDUSTRIAL APPLICATION of ZLD		65
3.1	Pharmaceutical Industry		65
		Major Sources and characteristics of Effluents	65
		Major source of waste water from API	65
		Treatment of waste water	66
		ZLD treatment options for Pharma industry	67
3.2	Textile Industry		70
		Major Sources of waste water generation	70
		Treatment of waste water	71
		ZLD treatment options for textile industry	72
3.3	Dyes & Dye Intermediates Industry		77
		H Acid Plant	77
		H Acid Plant ZLD flow sheet	77
		Vinyl Sulphone Plant	78
		Vinyl Sulphone Plant ZLD flow sheet	78
3.4	Chemical Industry	Major Sources of Waste water generation	79
		ZLD Treatment Scheme	79
		ZLD treatment options for chemical industry	81
4	WAY FORWARD		85
		Challenges to face Technology	85
		Process Change	86
5	References		87
6	Annexure I	Technology evaluation sheet	88

List of Figures :

Sr. No.	Figure No.	Description	Page No.
1	1.1	Number of ZLD installations over the years	2
2	1.2	Location of major Industrial Estates in Gujarat	5
3	2.1	typical Air / Steam Stripper	12
4	2.2	Packed Bed Column & media	13
5	2.3	Grid Column (Tray Tower)	13
6	2.4	Membrane filtration spectrum	14
7	2.5	MBR System Flow Diagram	15
8	2.6	Types of Membranes	15
9	2.7	Hollow Fiber Membrane	16
10	2.8	External Membranes	16
11	2.9	Submerged Membranes	17
12	2.10	Innovations in MBR Technology	19
13	2.11	Membrane Spectrum	20
14	2.12	Membrane Spectrum for removal of pollutant	20
15	2.13	Pressure requirement for Membrane processes	21
16	2.14	Pressurized & Submerged UF Membranes	22
17	2.15	In to out and Out to in Membranes	22
18	2.16	Dead end filtration and Cross-flow filtration	22
19	2.17	UF membrane System module	23
20	2.18	Reverse Osmosis	25
21	2.19	RO process	25
22	2.20	RO Membranes and configurations	26
23	2.21	RO membrane materials	27
24	2.22	RO Module	27
25	2.23	stages in RO system	28
26	2.24	Typical RO system Flow Diagram	28
27	2.25	Improvement in salt rejection	32
28	2.26	Reduction in membrane cost	33
29	2.27	Reduction in energy consumption of RO	33
30	2.28	RO System guidelines	36
31	2.29	Falling film Evaporator	38
32	2.30	Forced circulation Evaporator	39
33	2.31	Natural Circulation Evaporator	40
34	2.32	Plate type Evaporator	41
35	2.33	Single Effect Evaporator	43
36	2.34	Multi Effect Evaporator	43
37	2.35	Configurations of MEE	44
38	2.36	Thermal Vapour Re-compressor	47
39	2.37	Mechanical Vapour Re-compressor	48

40	2.38	Configuration of MVR	48
41	2.39	Polymer film sheets in MVR	50
42	2.40	Polymer film sheets in evaporation technology	50
43	2.41	Selection of Evaporation Technology Option-1	53
44	2.42	Selection of Evaporation Technology Option-2	53
45	2.43	Selection of Evaporation Technology Option- 3 & 4	54
46	2.44	ZLD technologies and their interconnectivity	59
47	2.45	Technology Maturity Graph	62
48	2.46	ZLD with 75% RO recovery	63
49	2.47	ZLD with 90% RO recovery	64
50	3.1.1	Option 1 - ZLD for Pharmaceutical Industry	67
51	3.1.2	Option 2 - ZLD for Pharmaceutical Industry	67
52	3.1.3	Option 3 - ZLD for Pharmaceutical Industry	68
53	3.1.4	Selection of ZLD Treatment for Pharmaceutical Industry	69
54	3.2.1	Option 1: Textile ZLD	72
55	3.2.2	Option 2: Textile ZLD	73
56	3.2.3	Option 3: Textile ZLD	74
57	3.2.4	Typical material Balance for ZLD	75
58	3.2.5	Selection of ZLD Treatment for Textile Industry	76
59	3.3.1	H Acid Plant	77
60	3.3.2	Vinyl Sulphone Plant	78
61	3.4.1	Option 1 - ZLD for Chemical Industry	81
62	3.4.2	Option 2 - ZLD for Chemical Industry	82
63	3.4.3	Option 3 - ZLD for Chemical Industry	83
64	3.4.4	Selection of ZLD Treatment for Chemical Industry	84

List of Tables:

Sr. No.	Table No.	Description	Page No.
1	2.1	A comparison of packed & grid column in solvent stripper	12
2	2.2	Performance of ASP & MBR	17
3	2.3	MBR System comparative Data	19
4	2.4	Leading UF suppliers	24
5	2.5	SWRO membrane modules in application	35
6	2.6	Application of various Evaporation Technologies	42
7	2.7	Comparative cost of evaporation technologies	51
8	2.8	ZLD Technology Matrix	60
9	3.1	Major Sources of wastewater generation in Textile Industry	70

Abbreviations:

ASC	Acetyl Sulphonyl Chloride
ATFD	Agitated Thin Film Dryer
BOD	Biochemical Oxygen Demand
BPR	Boiling Point Rise
CA	Cellulose Acetate
CETP	Common Effluent Treatment Plant
CMC	Carboxy Methyl Cellulose
COD	Chemical Oxygen Demand
CTA	Cellulose Tri Acetate
EDR	Electro Dialysis Reversal
ETP	Effluent Treatment Plant
GIDC	Gujarat Industrial Development Corporation
GPCB	Gujrat Pollution Control Board
GWI	Global Water Intelligence
IAAD	IL&FS Academy of Applied Development
MBR	Membrane Bio Rector
MEE	Multiple Effect Evaporator
MLD	Million Liters Per Day
MLSS	Mixed Liquor Suspended Solids
MoEF	Ministry of Environment & Forests and Climate Change
MVR	Mechanical Vacuum Re-compressor
PES	Poly Ether Sulphone
PVA	Poly Vinyl Alcohol
PVDF	Poly Vinyl Dene Fluoride
RO	Reverse Osmosis
SDI	Silt Density Index
SEZ	Special Economic Zone
SPS	Sulphonated Poly Sulphone
TDS	Total Dissolved Solids
TFC	Thin Film Composites
TIPS	Thermally Induced Phase Separation
TMP	Trans-membrane Pressure
TNPCB	Tamil Nadu Pollution Control Board
TSS	Total Suspended Solids
TVR	Thermal Vapour Re-compressor
TWIC	Tamilnadu Water Investment Company Ltd. (IL&FS JV with TN Govt.)
UF	Ultra Filtration
ZLD	Zero Liquid Discharge

INTRODUCTION

Water is fundamental to life, livelihood, food security and sustainable development; it however is a finite resource. While most of the world's surface is covered by water, only about 1% is safe to drink. As our population rapidly grows, water conservation and recycling become critical priorities. Better water management is a necessity in all industries to optimize water usage, recycle water and lower manufacturing costs.

Although, water resources are 'renewable' through hydrological cycle, the externalities like pollution contamination, temporal and seasonal variations due to climate change have affected the water quality and reduced the amount of 'usable water'. The ground water levels are declining very fast due to over exploitation.

India with a growing population and rising water consumption is going to face high water stress in near future. Per capita availability of water is likely to go down from 1545 m³ per year in 2011 to 1341 m³ per year in 2025.¹

The increasing demand of water for various purposes is putting strain furthering the possibility of deepening water conflicts among different user groups as drinking water need is going to rise by 44%, irrigation need by 10%, industry need by 81% respectively.

Water is needed in virtually every industrial and manufacturing process. Regulatory restrictions on wastewater discharge, combined with corporate accountability pressures, are increasing the cost of doing business, challenging industries in all sectors to find ways to conserve, treat, and reuse the waste water. ZLD is one strategy to address this challenge.

¹UNDP's World Water Development Report, 2003 & Study by Global Water Intelligence(GWI), Dec 2009

1.1 Zero Liquid Discharge

ZLD technology was initially developed for power plants, in USA and later implemented globally. In the early seventies, increased salinity of the Colorado River (due to Power Plant discharges), created the need to impose ZLD. Regulators were mainly concerned with power plant discharges from cooling tower blowdowns and scrubbers.

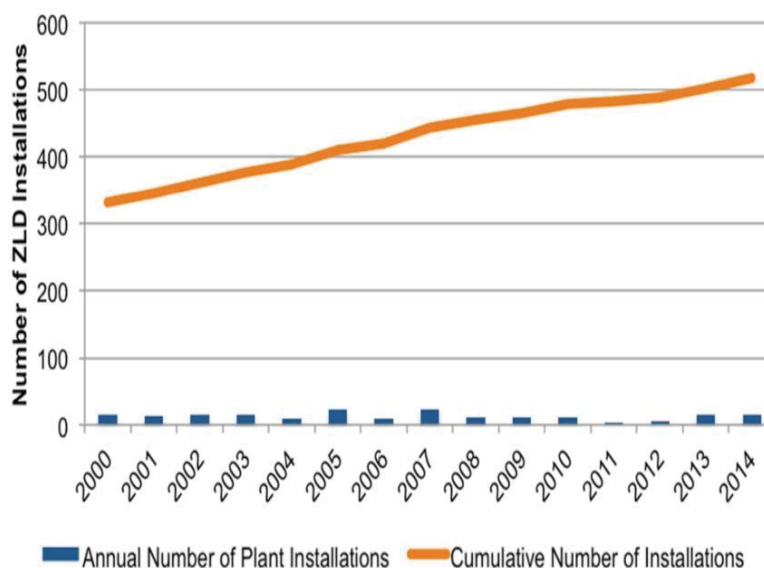
First ZLD installed was of 114-454 m³/hour units, based on evaporation / crystallization. Initially low cost ponds were used for evaporation of Reverse Osmosis (RO) reject. In Germany, stringent regulation in the 1980's resulted in ZLD systems for Coal Fired Power Plants.

Worldwide construction of ZLD plants represents an average of around 200 million USD of investment annually.² Today there are thousands of evaporator / concentrator systems around the world in a large range of industries. It is spreading widely to water scarce regions and to highly sensitive and polluted environments.

Countries like China and India, where water is scarce and the industrial water recovery ratio is very low, are potential candidates for the development of ZLD solutions. The figure 1.1 shows cumulative number of ZLD facilities between 2000 and 2014 on a global basis. This indicates that the market for ZLD is growing steadily.

The ZLD market is likely to see further increase in activity based on increased water scarcity and pressure from the regulators around brine management linked to increases in desalination.

Fig 1.1: Number of ZLD installations over the years³



² Water and wastewater International Feb/Mar (C) 2015. Penn Well Corp.

³ Cumulative ZLD Reference Facilities based on reference plant data from Aquatech, GE Water and Veolia.
URL: <http://www.bluetechresearch.com/streams/themes/zeroliquiddischarge/> accessed on 5.05.2015

1.2 ZLD in India

Several States in India are water stressed. In addition, competing demands for water from agriculture and domestic use reduce the availability of water for industrial use, impacting industrial growth. Water scarcity, water economics and regulatory pressures are main drivers of ZLD in India.

Tamil Nadu has taken a lead on ZLD due to absence of fully flowing perennial-river. Most rivers originate from neighboring states and water sharing is always in disputes. Tirupur Textile CETPs and Tannery CETPs at Chennai have adopted ZLD concept on large scale. Other States such as Gujarat and Karnataka are also implementing ZLD.

1.2.1 ZLD at Textile CETP Tirupur

Tirupur is a dry region with no perennial rivers. Exports from Tirupur hosiery and knit wear industry contributes a major chunk of foreign exchange earnings of the country. Based on the directions of the Madras High Court and Tamilnadu Pollution Control Board in 2005, the bleaching and dyeing units in Tirupur implemented CETP. Later the court asked to meet the ZLD requirements and accordingly directions were issued by TNPCB.

In all 450 units collectively have set up 20 CETPs with total investment of around Rs. 8 billion (800 crores) for 20 CETPs, while balance 150 units have set up their own individual effluent treatment plants (ETPs). This investment was financed by the bleaching and dyeing units (20 to 30%) with balance arranged through commercial banks as loans (70 to 80%).

Tamilnadu Water Investment Company Limited (TWIC - a JV of Tamilnadu state and IL&FS) was engaged by 9 CETPs for operation. The total effluent treatment capacity of these nine CETPs is 53,000 m³ per day, forming the majority of the effluents generated in Tirupur. The cost of this project was Rs. 4.2 billion (420 crores). The Pre- treatment Section and R.O. successfully commissioned and operated since October 2008 in TWIC CETPs. Evaporators were commissioned in Jan 2010.

The evaporator which has been installed did not meet the desired requirements and consequently industries had been facing difficulty in operating the ZLD project to full capacity. TWIC developed alternate solution which would reduce load on the evaporator. In August 2010, a petition of contempt of court was filed in the Madras High Court. While disposing of the case after various hearings Madras High Court closed all the industries in Tirupur in January 2011

TWIC made a presentation to GoTN in June 2011 on ZLD based on “brine reuse technology”. This was accepted by GoTN and necessary orders for demonstration at Arulpuram CETP and also funding for 20 CETPs was announced. All the units were closed by High Court Order of 31 January, 2011. Units were reopened with demonstration of modified “Brine Technology” and providing additional units in existing treatment.

1.2.2 ZLD at Tannery CETP Chennai

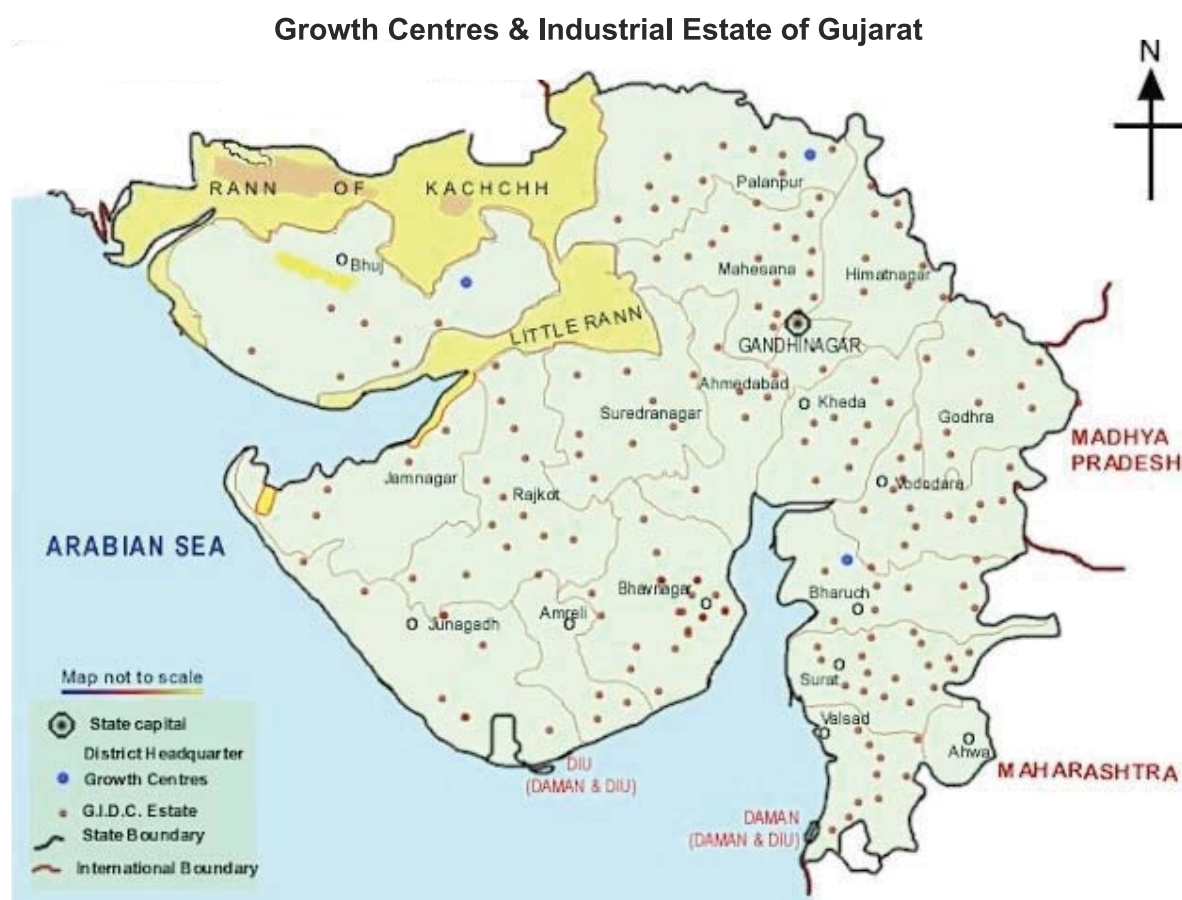
Ambur Economic Development Organization Limited has installed three CETPs for tannery waste water with capacities ranging from 1 MLD to 4 MLD (combined capacity of 7.2 MLD) in Ambur and Vaniyambadi Tannery cluster. These CETPs have Membrane Bio-Reactor as pre-treatment for RO systems and Evaporator for RO reject management.

The project cost of approx. Rs. 1 billion (100 crore) was financed through a blend of Government grant (50%) commercial loans (25%) and industry contribution (25%).

1.3 ZLD in Gujarat

Gujarat State is one of the economically developed States of the country and is a leader in industrial development. Investor friendly policies of the state have resulted in rapid industrialization with large number of small and medium scale industries. The State has more than 3 million industries located across 257 industrial estates developed by GIDC.

Fig 1.2: Location of major Industrial Estates in Gujarat⁴



To overcome operational problems of ETPs of individual industries, Common Effluent Treatment Plant (CETPs) were introduced for industrial clusters in 1990. Currently 33 CETPs are operational in the State, while 4 CETPs are in construction / commissioning stage.

⁴ Gujarat Pollution Control Board, Annual report 2013-14, Green Gujarat- Ecological and Industrial Balance

1.3.1 Initiation of ZLD requirements

Gujarat State has concentration of industrial units in certain areas, with heavy pollution load. In 1997, through an order, Hon'ble High Court on a PIL for pollution of chemical industries in Ahmedabad, introduced Environmental Audit Scheme for polluting industries; making yearly Environmental Audit by recognized auditors was made mandatory.

In 2010, after declaration of critically polluted areas by MoEF, GPCB heightened its enforcement and expanded its infrastructure, emphasizing pollution control at source. Action Plan was prepared for declared critically polluted areas, mainly Ankleshwar, Vapi, Ahmedabad, and Vatva. Action Plans were implemented in consultation with stakeholders and necessary directions were issued.

Zero Liquid Discharge (ZLD) concept was introduced in Action Plans where:

- Large units (discharge > 100 KLD) to have their own incinerator / evaporator / dryer / solvent distillation plant, acid handling/recovery plant etc. to make the treated waste reusable or to reduce the load on ETP/CETP.
- All units including zero discharge units to have pH correction and SS removal system, so that they cannot discharge any acidic effluent to CETP or to any unauthorized point of disposal. In cases, where spent or mixed acid is generated in large quantity, its recovery or re-use should be planned. Only the residues may be sent to authorized facilities for treatment and disposal.
- CETP are required for each industrial cluster for effluent treatment and safe disposal. No direct discharge in GIDC pipeline or any disposal point is permitted.

Such a time bound action plan directed the concerned industries to install multiple effect evaporator (MEE) / RO system / Incinerator System / New technologies including cleaner production and cleaner technology.

In order to educate industries, a seminar was organized by GPCB on 27-28 January 2014 at Gandhinagar jointly with IL&FS Academy of Applied Development (IAAD) on “Zero Liquid Discharge – Policy Experience and Emerging Technologies”. This seminar was attended by more than 450 industry representatives, enabling the Board to exchange the knowledge on ZLD with industry.

1.3.2 Gujarat Today

GPCB has already taken concrete steps to implement recycling, reusing and recovering product from industrial waste water. Currently 33 CETPs in GIDC industrial estates are operational in the State, while 4 more CETPs are at construction / commissioning stage. Many industries have been directed to segregate high strength waste water and treat it separately. CETPs are also going for ZLD technologies e.g. Naroda CETP, Ankaleshwar CETP, Zydus SEZ CETP, etc.

All pharmaceutical (API manufacturing) industries, Dyes & Dye intermediates industries and pesticide / chemical manufacturing industries are directed to install captive incinerator to process high strength waste. In addition to these efforts, 8 common hazardous waste incinerators and 89 captive incinerators in various industries have been installed.

Going beyond pollution compliance, emphasis is given on recovery and recycling of useful material from waste. Due to water scarcity, strong enforcement of environmental regulations, unavailability of suitable disposal points, many industries have started adopting ZLD. By adopting ZLD, industries are saving water, recover valuable products and at the same time protecting environment.

A relatively new technology, Multiple Effect Evaporator (MEE) has found its place in ETPs in the last few years. Gujarat has widely accepted this concept and industries are using MEE for concentrated streams by reducing load to ETP. There are 170 captive MEE units in industries, which itself is a great initiative, towards recycling and recovery of water.

Another concept adopted is co-processing of hazardous waste in cement industry as supplementary resources or for energy recovery. GPCB has taken initiative and directed many industries to send their wastes for co-processing at cement plants. Cement plants were also convinced to come forward for more and more co-processing of waste in their kilns. Till March, 2016; 75,78,645 MT waste have been processed in cement industry (GPCB annual report 2015-16). Authorities of the Cement plants in the State have prepared action plan targeting 10 % fuel requirements substitution in the next three years. This strategy has also helped in achieving ZLD.

Spent acid recovery plant is another initiative in Gujarat. Spent sulphuric acid is generated in the industrial units manufacturing dyes, dye-intermediates and other chemicals where sulphuric acid or oleum is used as raw material.

The concentration of sulphuric acid in the spent acid is normally in the range of 10-30%. Individual industries find it difficult to store, handle or treat it effectively.

Here, spent acids are segregated and collected in different tanks depending on the concentration of sulphuric acid and other properties for its proper reuse/utilization.

Treatment of spent acid results in production of Gypsum which is supplied to the cement manufacturing plants for use as blending material reducing consumption of mined natural material such as limestone.

ZLD TECHNOLOGIES

2.1 What is ZLD?

Zero Liquid Discharge (ZLD) refers to the recycling and treatment process in which the plant discharges no liquid effluent into surface waters, completely eliminating the environmental pollution to water bodies. ZLD process makes effective use of waste water treatment, recycling, and reuse, thereby contributing to water conservation through reduced intake of the fresh water.

This Guidance manual presents various treatment methods, the prospect of ZLD, the benefits & challenges and equipment overviews. Zero liquid discharge solutions can be accomplished by concentrating the effluent using various techniques, including membrane-based and multiple effect evaporation-based systems for recovery and recycling of water.

CPCB Draft Guidelines, January, 2015; defines 'ZLD' as:

“Zero Liquid discharge refers to installation of facilities and system which enables industrial effluent for absolute recycling of permeate and converting solute (dissolved organic and in-organic compounds/salts) into residue in the solid form by adopting method of concentration and thermal evaporation.”

ZLD is recognized and approved based on two broad parameters that are, water consumption versus waste water re-used or recycled (permeate) and corresponding solids recovered. In the above ZLD definition, domestic waste water from industry is separated from industrial waste water and treated separately. However, recycle / disposal of domestic waste water is not mentioned or stipulated.

ZLD is applicable to industries generating waste water of high BOD/COD load, colour, metals, pesticides, toxic / hazardous constituents, solvents and High TDS bearing effluents. However, considering water scarcity and reject water / sludge disposal cost, many industries are adopting ZLD as a long term strategy.

Drivers of ZLD

- ✓ Stringent Environmental regulations on discharge of specific pollutants
- ✓ Water scarcity in the area of operation
- ✓ Economics : Recycled water becomes more economical than disposal of water and buying fresh water
- ✓ Recovery of useful materials
- ✓ Growing social responsibilities towards environmental issues

Challenges for ZLD

- ❖ Stringent regulations are forcing industries to install ZLD, however, Technical guidance is not available for industries.
- ❖ Technology selection is a big challenge. ZLD plant varies from industry to industry. Therefore, technical experts are required for customized design for successful ZLD operations.
- ❖ Difficulty in dealing with very complex streams from petrochemical or pharmaceutical industries.
- ❖ Need of integration of suitable technologies to achieve reduce, recycle, recovery, and re-use.
- ❖ Industries are reluctant due to high capital cost and operational cost (CAPEX and OPEX). A financial feasibility model need to be developed to overcome this problem.

2.2 ZLD Technologies

Zero Liquid Discharge refers to processes that fully removes water from the concentrate stream (in other words, no liquid is left in the discharge). The end product of a ZLD system is a solid residue of precipitate salts that needs to be reused or transferred to a designated solid waste disposal facility for incineration/ landfill.

ZLD systems range from simple to highly complex system depending on the complexities in waste water streams. Ultimate aim of ZLD system is to recover useful products, and salts from rejects, apart from recovery of maximum water for recycle. Following are the major ZLD technologies that are used in various combinations as per the requirement:

- ✓ Solvent Extraction / Stripper
- ✓ Membrane Bio Reactor Technology (MBR)
- ✓ Ultra Filtration (UF)/Reverse Osmosis (RO)
- ✓ Evaporation Technologies - Multi Effect Evaporators-(MEE) / Mechanical Vacuum Re-compressor (MVR)
- ✓ Agitated Thin Film Dryer (ATFD)/ Crystallization
- ✓ Incinerator

2.2.1 Solvent Recovery

Solvent recovery from industrial waste water is usually carried out by two methods:

- ❖ Air stripping
- ❖ Steam Stripping

Objectives of treatment is either recovery of solvent or removal of solvents from waste water to facilitate easy treatment and disposal.

Air Stripping

Many organic solvents are removed from waste water by air stripping. This applies particularly to solvents that have low solubility in water or a high volatility with respect to water. It is essential to provide air stripping before biological treatment for better efficiency of treatment. Solvent removed from water by air stripping is recovered by adsorption on activated carbon.

This method is used only when less quantity of solvent is present in water. Air stripping batch reduces solvent content of water to less than 100mg/ltrs (w/w) and many cases up to 20mg/ltrs. Presence of inorganic salts may affect the efficiency of air stripping. To reduce solvent concentration by 1 mg/ltrs (from 21mg/ltrs to 20mg/ltrs), one m³ air is required for one m³ of water.

Steam Stripping

Low concentration of solvent in effluent air, makes it difficult to capture the solvent through air stripping. Steam stripping requires relatively simple equipment for trapping the stripped solvent.

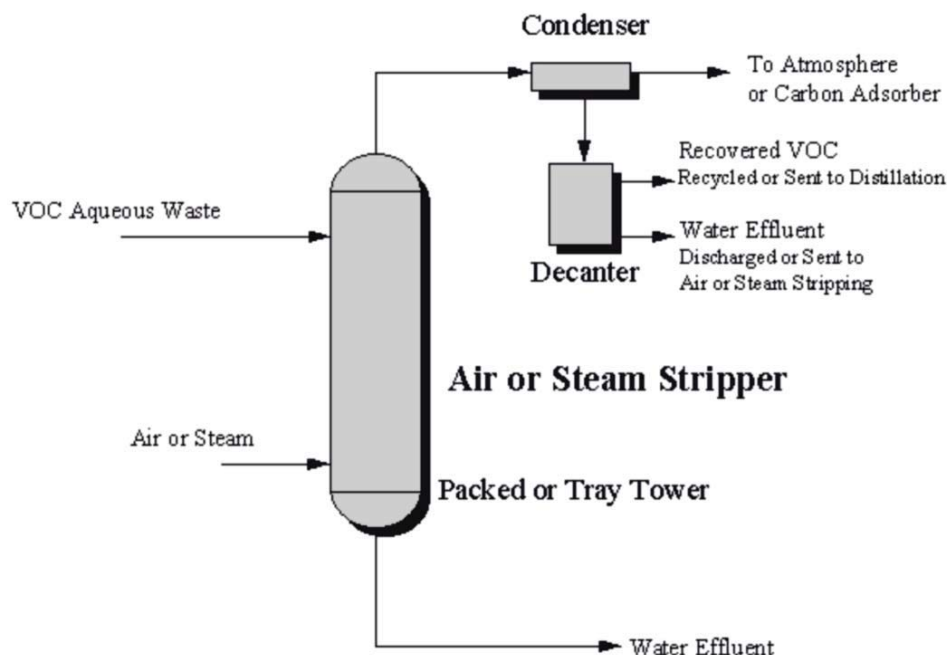
In steam stripping, a waste water stream is heated and put in intimate contact with steam in a packed or tray tower. The combined effects of the steam and heat, or temperature causes organic material to transfer from the liquid to the vapour phase. Steam costs are modest provided that good heat exchange is maintained between hot stripped water being discharged and feed to stripper. It is easy to strip VOC's by this method if they have lower boiling points than water or have limited solubility in water. The concentrated organic product generated by the steam stripping operation is a distillate stream.

Combination of effluent clean-up and solvent distillation is considered in the design of steam stripper. For water miscible solvents like methanol, acetone, etc. the conversion of the stripping column into a fractionating column give rise to few problems. Similarly, the solvents that are sparingly water miscible can be passed through decanter and the water phase returned to stripper feed. Combination of stripper and distillation unit is favored when very consistent flows of effluent both quality and quantity are to be processed.

Steam stripping is not suitable for water miscible solvents with high boiling points. Steam stripping may give rise to scaling problems at the end of the stripper column. A facility to clean scaling or bypassing scaling needs to be provided.

Three factors contribute to economics of solvent stripping in ZLD process:

- ✓ Treated water reuse/ recycle potential,
- ✓ Value of recovered solvent and
- ✓ Treatment cost (CAPEX/OPEX).

Figure 2.1 Typical Air / Steam Stripper

Solvent Recovery Columns: There are two types of columns used in steam stripper.

- ✦ Packed column
- ✦ Grid Column(Tray Tower)

Table 2.1 show a comparison of packed column v/s Grid Column

Table 2.1: comparison of solvent strippers

S. No.	Packed Column	Grid Column
1	As only one feed inlet is possible, the column needs to operate at design conditions, giving no flexibility	The column can have multiple feed inlets, providing operational flexibility depending on variation in the feed condition
2.	Being a packed column, the pressure drop is greater and results in higher steam requirement	The pressure drop is comparatively lower than in the packed column. Hence, less steam is consumed
3	Packed columns have a narrower operating range	Tray columns have a wider operating range
4	If liquid flow rate is too low, the wetting of the packing material may not be adequate	If the liquid flow rate is too high, treatment in tray columns is more economical
5	If solid particles are present in the liquid, cleaning the packing section is complicated and expensive	Tray columns can handle suspended solids without performance being affected
6	When stressed by temperature variations and pressure, the packing elements are easily breakable	Trays made up of SS316, therefore breaking due to temperature and pressure will not occur
7	Packed columns do not possess special design elements for addressing TSS handling	Tray columns are specially designed for more effectiveness

Fig. 2.2 & 2.3 show the media and packaging details

Fig 2.2 Packed Bed Column & media

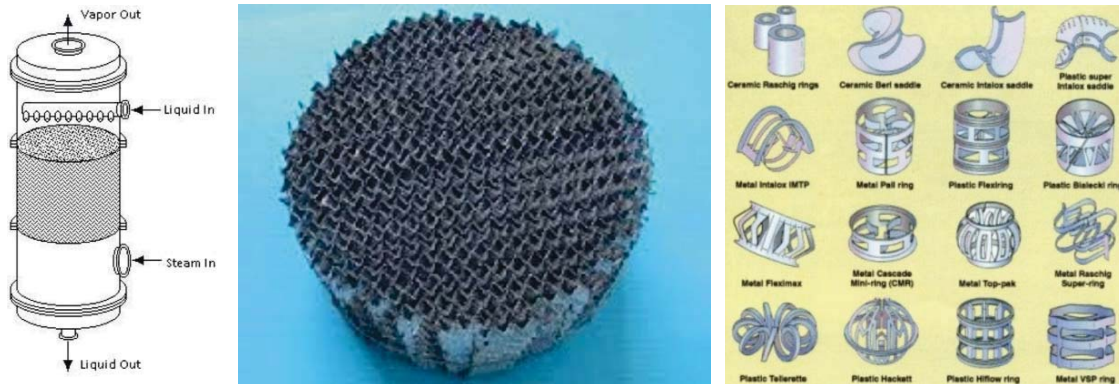
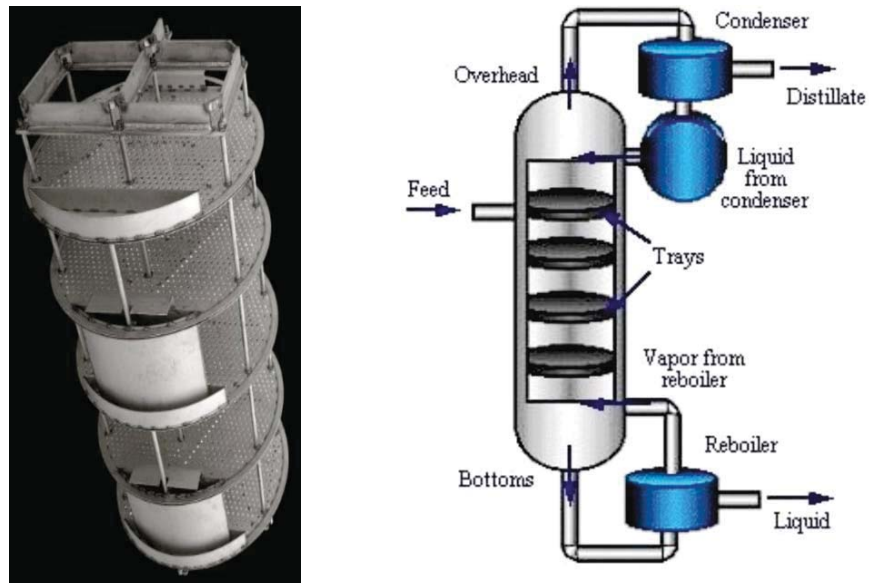


Fig 2.3 Grid Column (Tray Tower)



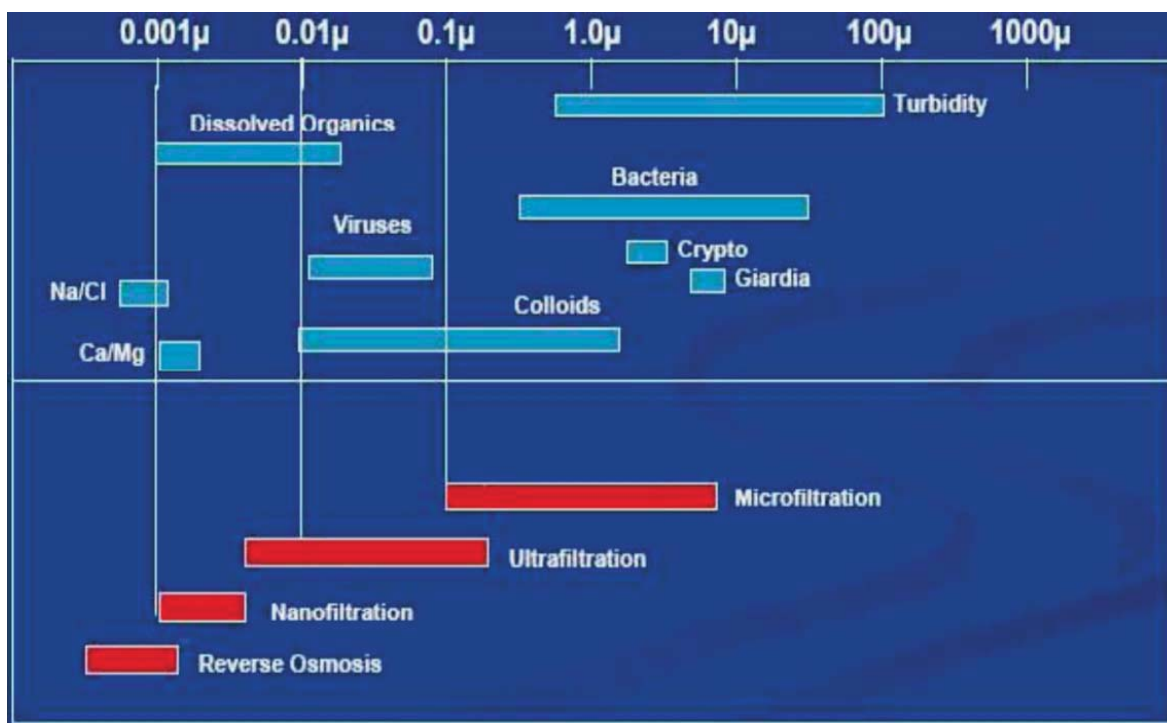
2. 2.2 Membrane Bio-Reactor (MBR)

Membrane filtration is a vital resource for the treatment and reuse of municipal water and wastewater, most notably for the treatment of surface, brackish, or seawater water for production of drinking water.

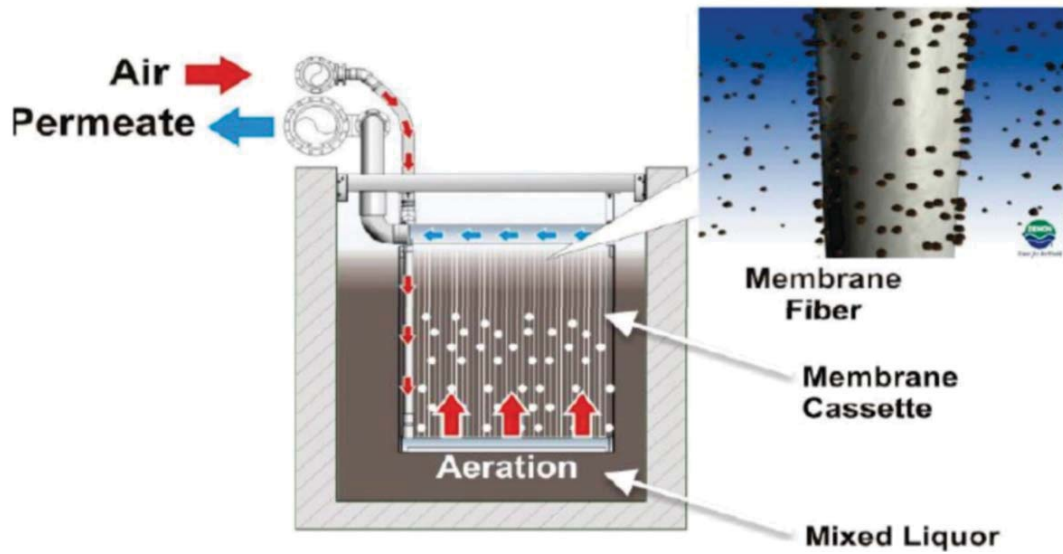
Membrane Bio Reactor (MBR) is a process where Microfiltration (MF) /ultrafiltration (UF) membrane is used. MF/UF are low pressure driven processes, where feed water is driven through a micro-porous synthetic membrane and divided into permeate, which passes through the membrane, and retentate/reject containing the non-permeating species. In waste water treatment applications, these membranes process are more effective in removal of particles and micro-organisms.

Fig 2.4 gives spectrum of Membrane filtration systems illustrating the size range of various impurities and the application range of the membrane processes.

Fig 2.4 Membrane filtration spectrum



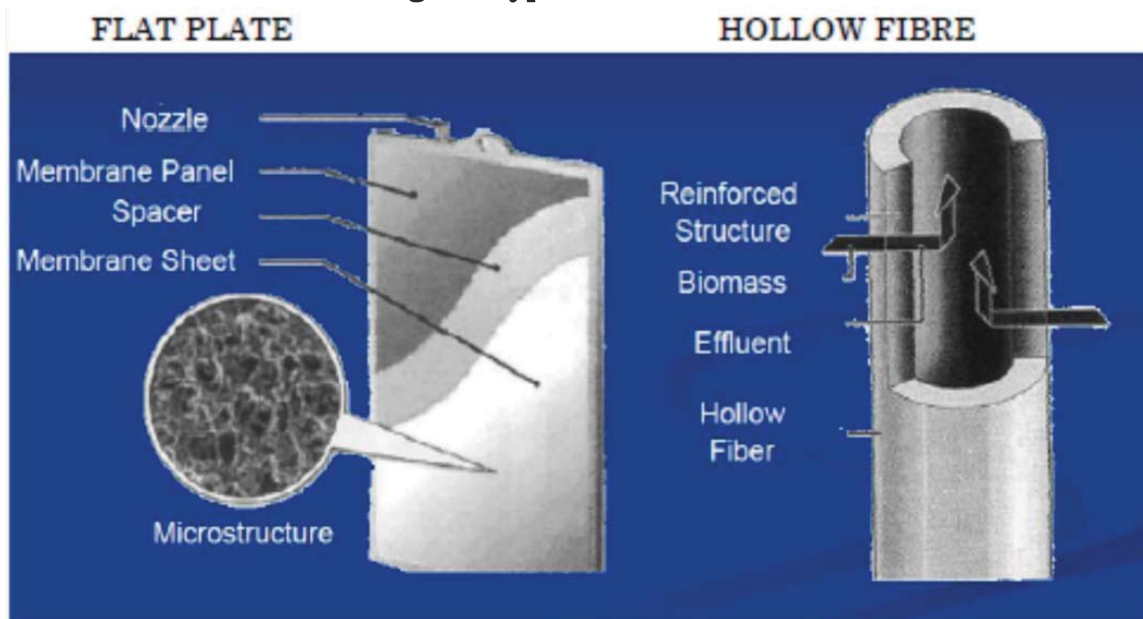
MBR systems essentially consists of combination of membrane and biological reactor systems. These systems are the emerging technologies, currently developed for a variety of advanced waste water treatment processes. MBR system is essentially an aerobic biological system where air is provided through diffuser membranes for growth of biomass (MLSS – Mixed Liquor Suspended Solids). See fig 2.5

Fig 2.5 MBR System Flow Diagram

When waste water passes through MBR membranes, secondary clarifier is not required. Treated water quality is as good as filtered water from sand filters.

MBR Membranes

MBR membrane's pores form barrier to impurities (Suspended, colloidal particles bacteria, and viruses) while allowing water molecules to pass through. Water is drawn through the pores using a gentle suction. There are two types of membranes. Flat Plate and Hollow Fiber membranes. Flat plate membrane sheet is placed on flat plate, while hollow fiber membranes have reinforced structure in the form of fiber. See fig 2.6 and 2.7

Fig 2.6 Types of Membranes

Hollow fiber membranes (HFMs) are a class of artificial membranes containing a semi-permeable barrier in the form of a hollow fiber. Originally developed in the 1960s for reverse osmosis applications, hollow fiber membranes have since become prevalent in water treatment, desalination, etc. Most commercial hollow fiber membranes are packed into cartridges.

Fig 2.7 Hollow Fiber Membrane

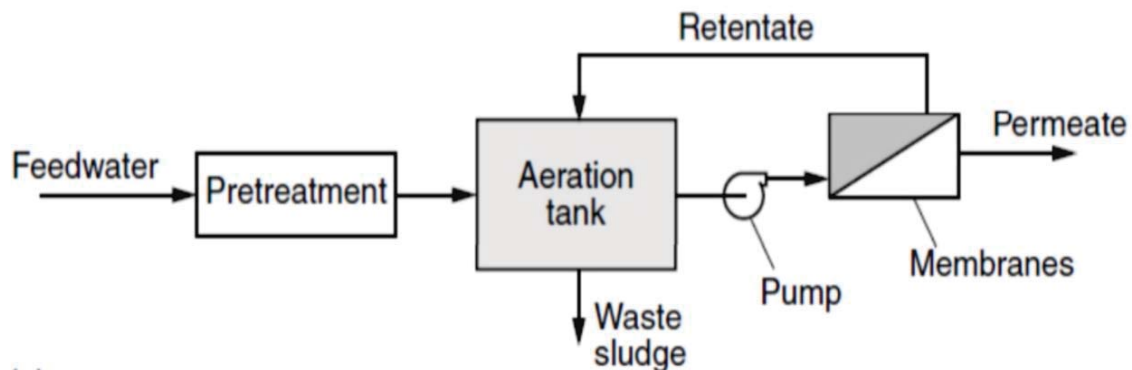


Membrane Types: There are two configurations of MBR membranes:

- External Membranes
- Submerged membraness

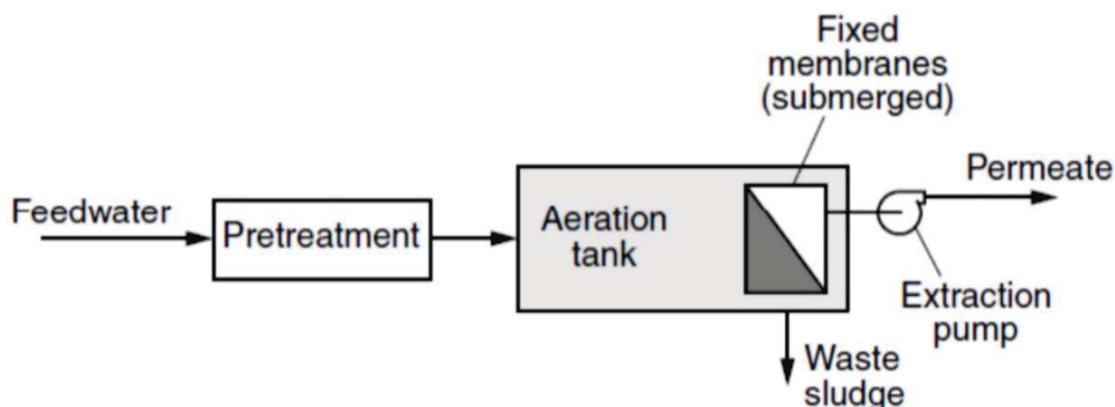
External Membranes: External membranes are pressure driven and commonly come in tubular form. They are placed outside the aeration tank.

Fig 2.8



Submerged Membranes: Submerged membranes are submerged inside the aeration tank and are usually vacuum driven.

Fig 2.9



Operation of MBR

MBR can be operated on either constant trans-membrane pressure (TMP) or constant flux through membrane (constant flow). Constant flux is preferred, since it gives consistent outlet flow.

Vacuum less than 0.5kg/cm. sq. (< 50 kPa) draws water through membrane, solids are retained in the reactor. At the base of the module, there is an air distribution manifold. Air provides oxygen, which helps to maintain TSS in suspension within the bioreactor and cleans exterior of membrane surface.

While operating MBR system, continuous backwash is required for membranes after every 10-15 min, and this is carried out by in-built control program of MBR system. Periodical cleaning of membranes through chemicals dosing system is required. MBR operates at higher MLSS concentration in MBR Aeration tank than the conventional Activated Sludge Process (ASP).

- ✓ Mixed Liquor Suspended Solids (MLSS) in MBR Tank: 5000 to 16000mg/l
- ✓ Treated water Quality:
 - BOD – <5mg/l
 - TSS - <1mg/l
 - Turbidity - <0.2mg/l

Table 2.2: Performance of ASP and MBR

	ASP Treated effluent	MBR Treated effluent
TSS, mg/l	<30	ND(<2)
Turbidity, NTU	2 to >10	<0.2
Total Coliform, no/100ml	10,000 to 1,00,000	ND to 100
BOD, mg/l	<10 to 30	ND to <5mg/l

Note: MBR process does not remove TDS of waste water. Therefore, TDS of inlet wastewater remains unchanged. Membrane flux rate (L/sq. m. and hour) is an important design and operation parameter. Lower flux rates at higher MLSS is desirable. Fine air bubble diffusers or coarse bubble aeration system is used as per technology provider's design.

Advantages of MBR System

- ❖ Secondary clarifier is not required
- ❖ Smaller foot print than conventional ASP, SBR systems.
- ❖ Complete retention of suspended solids and most soluble compounds.
- ❖ Post treatment of sand filters can be eliminated
- ❖ Independent control of hydraulic and solid retention times
- ❖ Ability for slow-growing species to grow (nitrifying bacteria, etc.)
- ❖ High loading rate capability
- ❖ Combined COD, solids and nutrients removal
- ❖ Low sludge production and high SRT
- ❖ Eliminates problems of sludge settling, etc.
- ❖ High biomass (MLSS) concentrations
- ❖ Bulking or rising sludge is not a problem
- ❖ Effluent disinfection takes place due to removal of bacteria and viruses

Disadvantages of MBR System

- ❖ Energy consumption is 2-3 higher than conventional treatment.
- ❖ Membrane costs are very high, therefore MBR system CAPEX is high.
- ❖ Operational problems due to Membrane complexity and fouling
- ❖ Pretreatment of feed - flushing with water/air or chemical cleaning.
- ❖ Operation and maintenance
 - High Energy costs due to high recirculation of inlet flow
 - High cost of membranes replacement
 - Aeration limitations

International Leading Manufacturers and comparative data

- 1) Zenon Environmental Inc. (CANADA) (Hollow Fiber)
- 2) General Electric (Hollow Fibre)
- 3) Mitsubishi Rayon Cooperation (JAPAN) (Flat Plate)
- 4) Kubota Cooperation (JAPAN) (Flat Plate)
- 5) US Filter (USA) (Flat Plate)
- 6) Koch Membranes (Hollow Fiber)
- 7) Hydranautics

Table 2.3 provides a comparative data of some of the manufacturer's

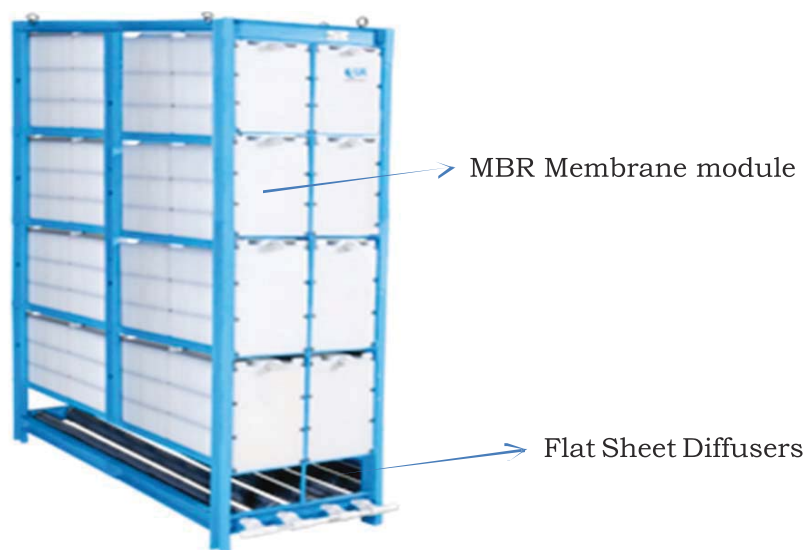
Table 2.3: MBR systems comparative data

	Zenon	Kubota	Mitsubishi	US Filter
Membrane				
Type	Hollow fiber	Plate	Hollow fiber	Hollow fiber
Configuration	Vertical	Vertical	Horizontal	Vertical
Pore size	0.04 μm	0.4 μm	0.04 μm	0.04 μm
Module size	31.6 m^2	0.8 m^2	105 m^2	9.3 m^2
Location	Cell compartment	Throughout basin	Throughout basin	Cell compartment
Screening size	$\leq 2 \text{ mm}$	$\leq 3 \text{ mm}$	$\leq 2 \text{ mm}$	$\leq 2 \text{ mm}$
Flux management				
$\text{m}^3/\text{m}^2\text{h}$	0.37	0.53	0.73	0.18
Aeration cycle	10 sec on 10 sec off	Constant	Constant	Constant
Flux rate				
Average, $\text{l}/\text{m}^2, \text{h}$	17-25	17-25	8.5-12	17-25
Peak hour ($\leq 6 \text{ hrs}$) $\text{l}/\text{m}^2\text{h}$	<42	<59	equalize	<51
Maintenance				
Clean				
Type	Backpulse and relax hourly	Backpulse	Relax	Backpulse or relax 1 min/15min
Frequency		1 min/15min	2 min/12 min	
Recovery clean				
Type	Chem. Soak	Chlorine Backwash	Chlorine Backwash	Chem. Soak
Location	Drained cell	In situ	In situ	Drained cell
Frequency	$\geq 3 \text{ months}$	$\geq 6 \text{ months}$	$\geq 3 \text{ months}$	$\geq 3 \text{ months}$
Biological Parameters				
SRT, days	10-15	15	20	10-15
MLSS, mg/l	$\leq 10\,000$	$\leq 10\,000$	$\leq 10\,000$	$\leq 10\,000$

Innovations in MBR Technology

Continuous backwashing to avoid membrane fouling is an operational problem. To overcome this, new membrane material reducing frequency of membrane backwash to once in a week are developed. Flat membrane diffusers are used in many cases in place of tubular membranes. Flat membrane diffusers along with membrane cage reduces height of unit. See fig. 2.10

Fig 2.10: Innovations in MBR Technology



2.2.3 Filtration

Filtration is a process of removing particulate matter from water by forcing the water through a porous media. This porous media can be natural, like sand, gravel and clay, or it can be made of various materials. The size of materials that can be removed during filtration depends upon the size of the pores of the filter. In membrane filtration, Figure 2.11 summarizes various separation processes and pore sizes and material removed from membranes.

Fig. 2.11: Membrane Spectrum

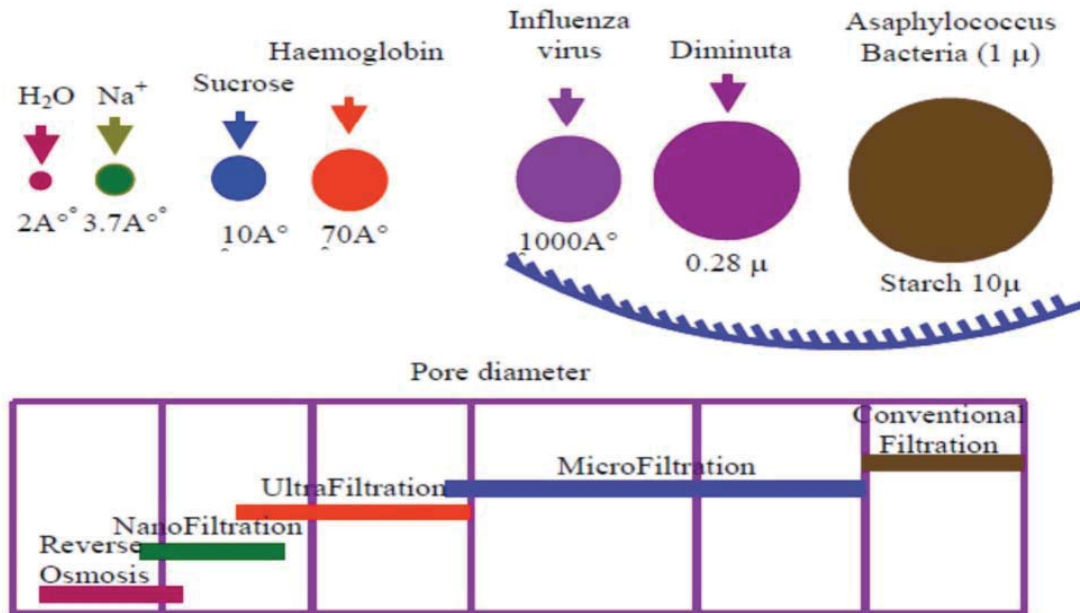


Fig. 2.12: Membrane Spectrum for removal of various pollutants

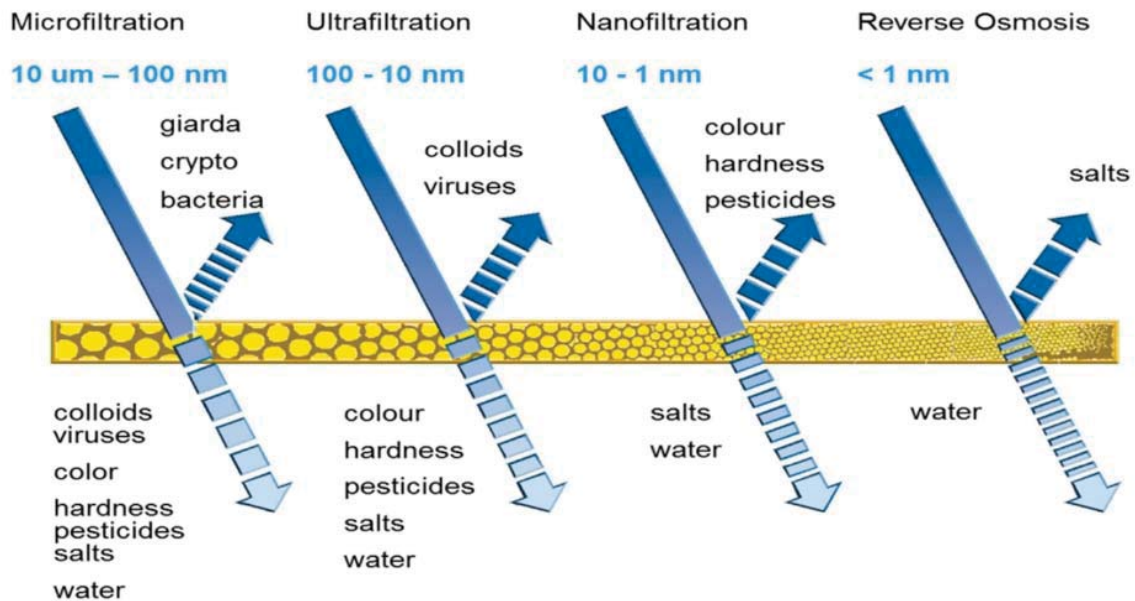


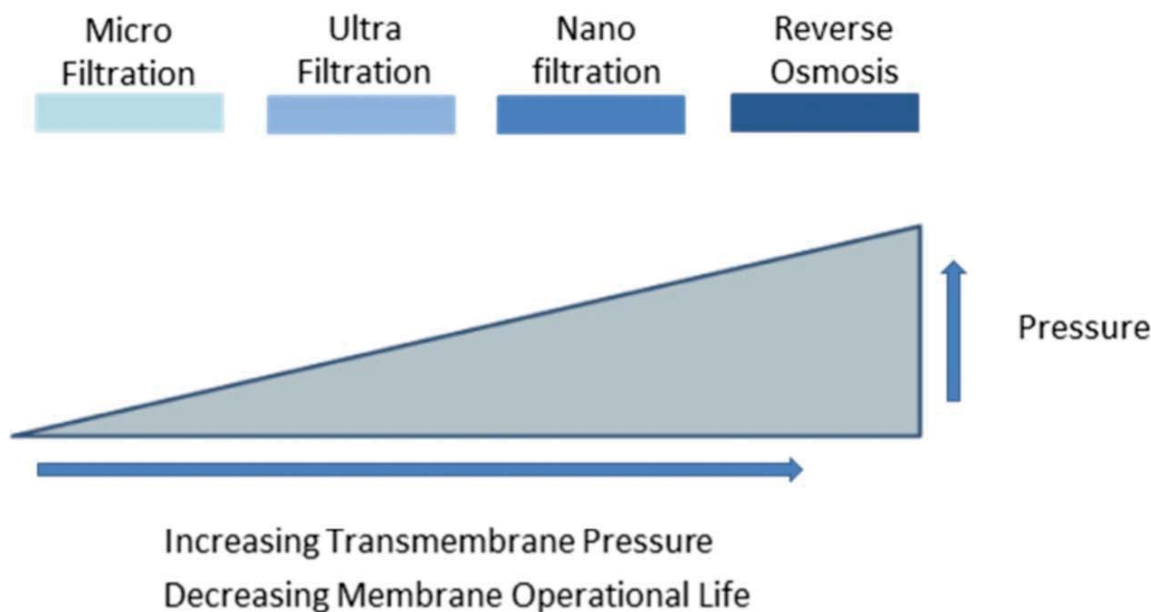
Fig. 2.13: Pressure requirement for Membrane processes

Figure 2.13 shows increase in pressure requirement for membrane processes as we go on reducing pore size of membrane.

Ultrafiltration (UF)

Ultra filtration (UF) is a low pressure membrane filtration process which removes bacteria, protozoa and some viruses from the water. Along with this there is removal of colloidal particles from wastewater. It is mostly used as pre-treatment to RO.

A pressure is applied to waste water to pass through semi-permeable membrane. By using ultrafiltration, multimedia filtration process can be eliminated. Ultrafiltration is also used for applications in industrial wastes for recovery.

Metal industry $\Rightarrow$ Separation of water-oil emulsions

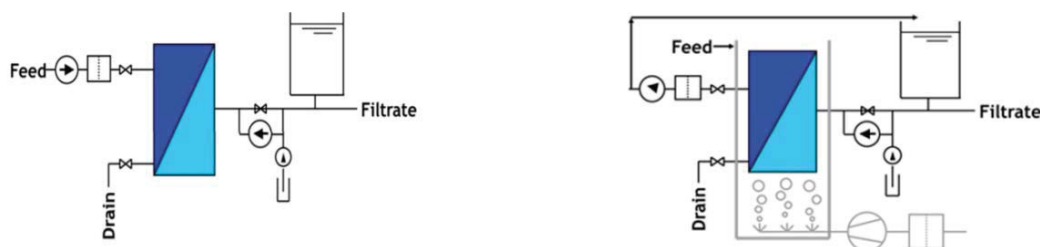
Automotive painting industry $\Rightarrow$ Separation of dye from washing water

Pharmaceutical industry $\Rightarrow$ Separation of enzymes

Food industry $\Rightarrow$ Cheese waste

UF membranes are of two types: Submerged membranes & pressurized membranes. See fig, 2.14 and 2.15

Fig. 2.14 Pressurized & Submerged UF Membranes



There are two types of membranes as far as filtration mode is concerned:
In to out and Out to in

Fig. 2.15

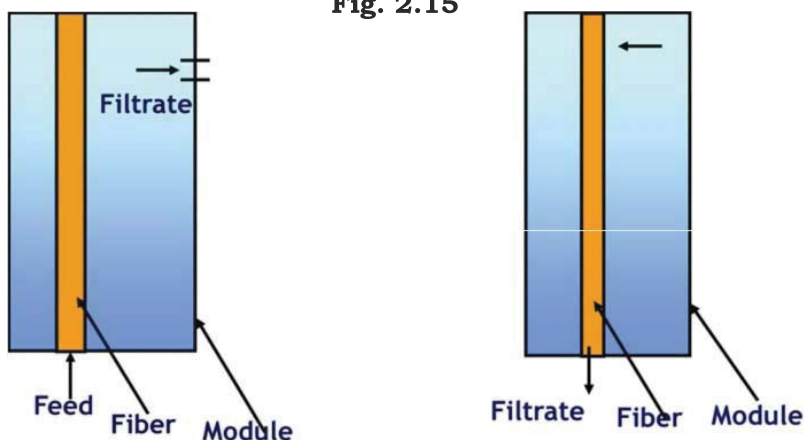
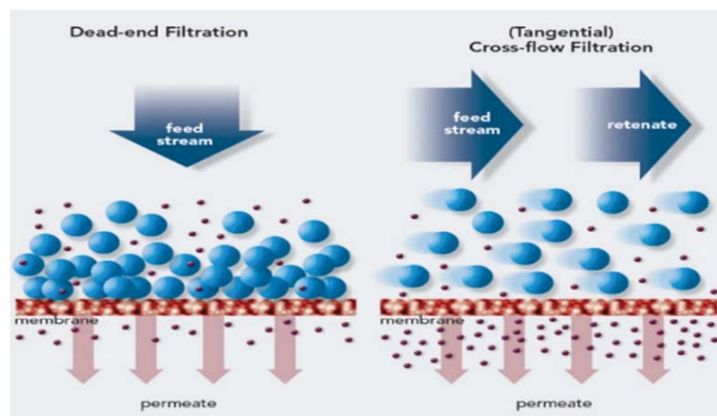


Fig. 2.16: Dead end filtration and Cross-flow filtration



Dead end Filtration: Operating Flux- 70-130 L/sq. m. and hour,
Recovery: 90-98%
Cross flow Filtration: Used for Turbidity > 10 NTU /20ppm,
Operating flux: 40 - 70 Lmh,
Recovery: 75-90%,
Cross flow recommended for very high solid loading (e.g. MBR)

Fig. 2.17 shows typical modules of UF membrane System

Fig. 2.17: UF membrane system module



Membrane



Module



Rack



Types of Membranes:

Hollow fiber capillary membranes

Operating parameters for UF:

Filtration pressure: 0.1 to 0.6 kg/cm²

Temperature range: 0 - 40°C

pH range in filtration: 4 – 11

Flux: 50-90 l/mh

Recovery: 85 to 94%

Energy requirement: 0.02 to 0.05 KWH/m³ (UF as a pre-treatment to RO)

Filtration rate (flux) depends on water quality, pre-treatment, temperature of waste water.

Material of Construction: Polyethersulphone (PES)/Polyvinylidene fluoride (PVDF)

Treated water quality

Particles: > 1 µm > 6 log

SDI Permeate: < 3

Virus: > 4 log

Giardia: > 5 log

Cryptosporidium: > 5 log

Turbidity Permeate: < 0.1 NTU

COD Removal: 0 to 25 %

COD removal with coagulant: 25 to 50 %

Note: The above are estimates that are applicable for a wide range of waste water flows. For individual or specific cases, the range may differ.

Advantages of UF Technology:

- It is one of the best technologies for pre-treatment of RO
- It eliminates pressure sand filtration, Dual media filtration, microfiltration or any other filtration methods for removal colloidal suspended particles.
- Very low pressure and energy requirement
- Very less foot print area as compared to dual media/sand filtration
- Removes small colloids, bacteria, viruses and suspended organics from the waste water

Limitations of UF Technology:

- ❖ Capital cost is comparatively high
- ❖ Membrane replacement required after 3-5 years depending on application
- ❖ Membrane backwashing and cleaning is required
- ❖ Cleaning chemical dosing system is to be provided

Innovations in UF Technology:

- ✓ Multi bore system by providing superior mechanical strength, which avoids fiber breakages
- ✓ Composite fibers to facilitate better collection system and free flow
- ✓ Two stage UF system by diverting backwash water to second stage, thus improving recovery to more than 95% (Inlet COD < 150 mg/ltr)
- ✓ Micro porous, crystalline structure resulting from Thermally Induced Phase Separation (TIPS) provides increased chemical resistance and increased mechanical strength. Thus reduces maintenance by reducing backwash frequency and membrane replacement frequency

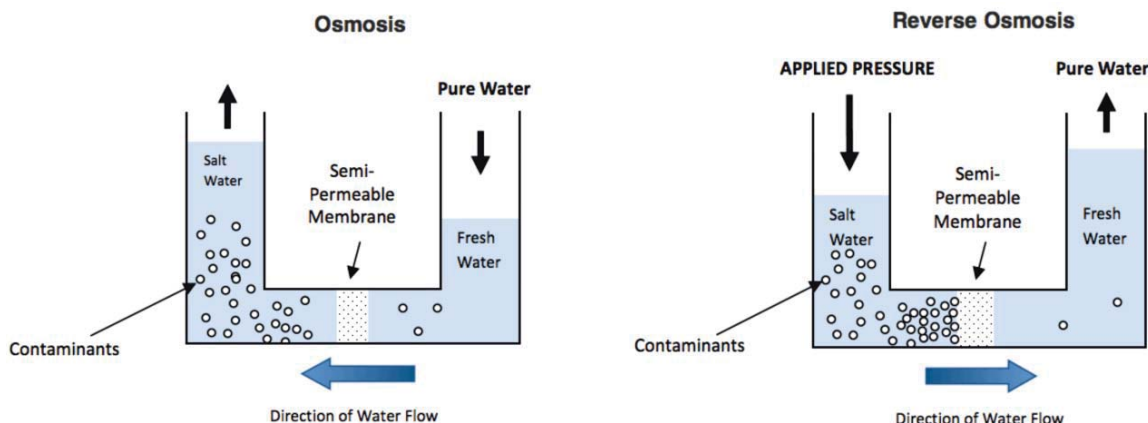
Table 2.4 lists some of the leading UF suppliers

Table 2.4: leading UF suppliers

Manufacturer	Membrane Material of Construction
Aquasource	Polysulfone Cellulose Acetate
Hydranautics	Polyethersulfone
Inge	Polyethersulfone
Koch	Polysulfone
Pall	Polyacrylonitrile Polyvinylidenefluoride
TriSep - SpiraSep	Polyethersulfone
US Filter	Polypropylene Polyvinylidenefluoride
X-Flow	Polyethersulfone / Polyvinylpyrrolidone Blend
Zenon	Laminated Polysulfone

Reverse Osmosis (RO)

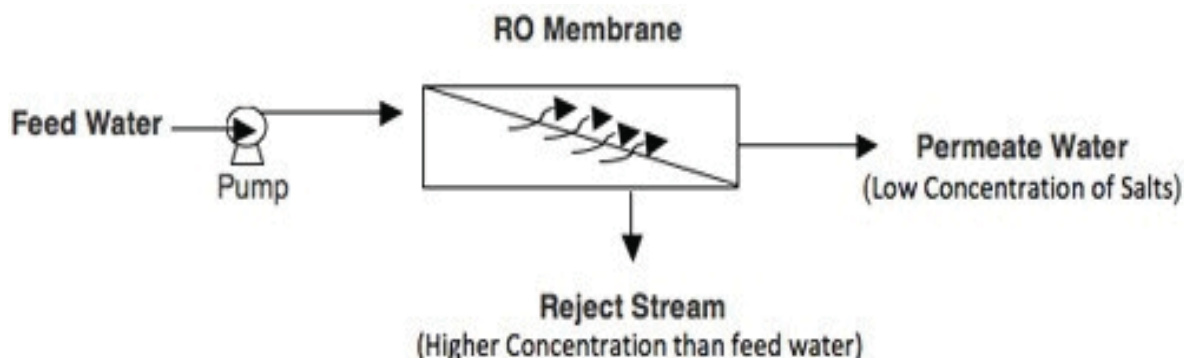
Since the development of the first practical cellulose acetate membranes in the early 1960's and the subsequent development of thin-film, composite membranes, the uses of reverse osmosis have expanded to include not only the traditional desalination process but also a wide variety of waste water treatment applications.

Fig. 2.18

Reverse Osmosis (RO) works by using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required, depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure. The desalinated water that is de-mineralized or de-ionized, is called permeate (or product) water.

Reverse Osmosis (RO) works by using a high pressure pump to increase the pressure on the salt side of the RO and force the water across the semi-permeable RO membrane, leaving almost all (around 95% to 99%) of dissolved salts behind in the reject stream. The amount of pressure required, depends on the salt concentration of the feed water. The more concentrated the feed water, the more pressure is required to overcome the osmotic pressure. The desalinated water that is de-mineralized or de-ionized, is called permeate (or product) water.

The water stream that carries the concentrated contaminants that did not pass through the RO membrane is called the reject (or concentrate) stream. See fig. 2.19

Fig. 2.19

RO system employs cross filtration rather than standard filtration where the contaminants are collected within the filter media. With cross filtration, the solution passes through the filter, or crosses the filter, with two outlets.

To avoid build-up of contaminants, cross flow filtration allows water to sweep away contaminant build up and also allow enough turbulence to keep the membrane surface clean. RO is capable of removing up to >99% of the dissolved salts (ions), particles, colloids, organics, bacteria and pyrogens from the feed water.

Any contaminant that has a molecular weight greater than 200 is likely to be rejected by a properly running RO system. Similarly greater the ionic charge of the contaminant, the more likely it will be unable to pass through the RO membrane. For example, a sodium ion (one charge -monovalent) or calcium (two charges) are not rejected by the RO membrane.

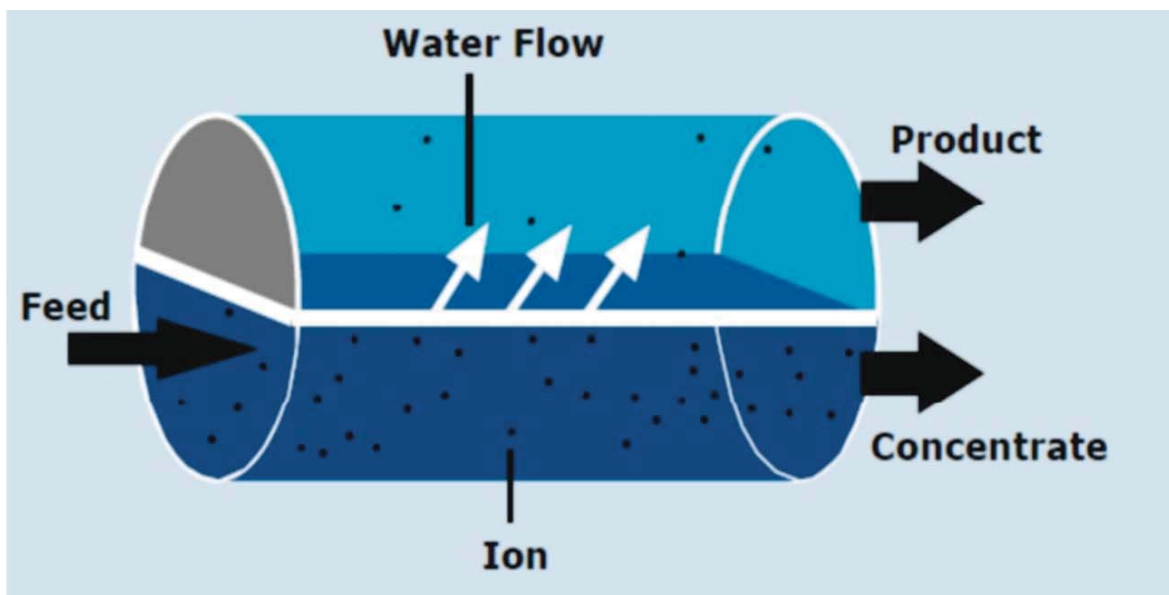
That is also why RO system does not remove gases such as carbon dioxide very well because they are not highly ionized (charged) while in solution & have a very low molecular weight. Because an RO system does not remove gases, the permeate water can have a slightly lower than normal pH level depending on carbon dioxide levels in the feed water as the carbon dioxide is converted into carbonic acid.

RO is very effective in treating brackish, surface and ground water for both large and small flows applications. Some examples of industries that use RO water include pharmaceutical, boiler feed water, food and beverage, metal finishing and semiconductor manufacturing etc.

RO Membranes and configurations:

To reduce the rate of membrane fouling significantly, RO systems employ cross-flow filtration (see Fig2.20), that allows water to pass through the membrane while separate flow of concentrate sweeps rejected salts away from the membrane surface.

Fig. 2.20



Common membrane materials include polyamide Thin Film Composites (TFC), Cellulose Acetate (CA) and Cellulose Tri Acetate (CTA) with the membrane material being spiral wound around a tube. TFC membranes have superior strength and durability as well as higher rejection rates than CA/CTA membranes. They also are more resistant to microbial attack, high pH and high TDS. CA/CTA's have a better ability to tolerate chlorine. See fig 2.21 and 2.22

RO membranes are rated for their ability to reject compounds from contaminated water. Rejection rate (% rejection) is calculated for each specific ion or contaminant and for reduction of Total Dissolved Solids (TDS).

Fig. 2.21

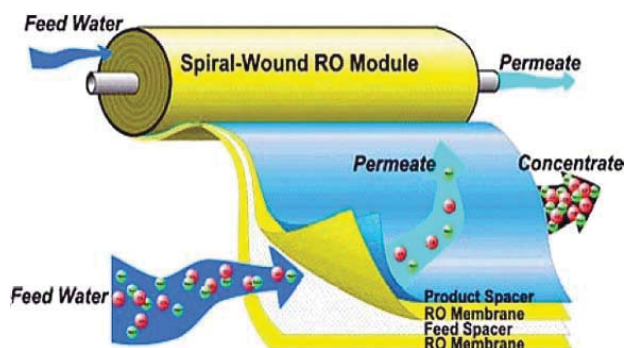


Fig. 2.22



RO system configuration varies as per inlet quality and recovery of water. To increase recovery percentage, reject of first stage RO is subjected to second stage RO and thus overall recovery is increased. Again second stage RO reject can be subjected to third stage.

No. of stages in RO system depends on reject TDS, silica, etc. The cost of RO system increases with increase in number of stages. See fig 2.23 and 2.24

Fig. 2.23

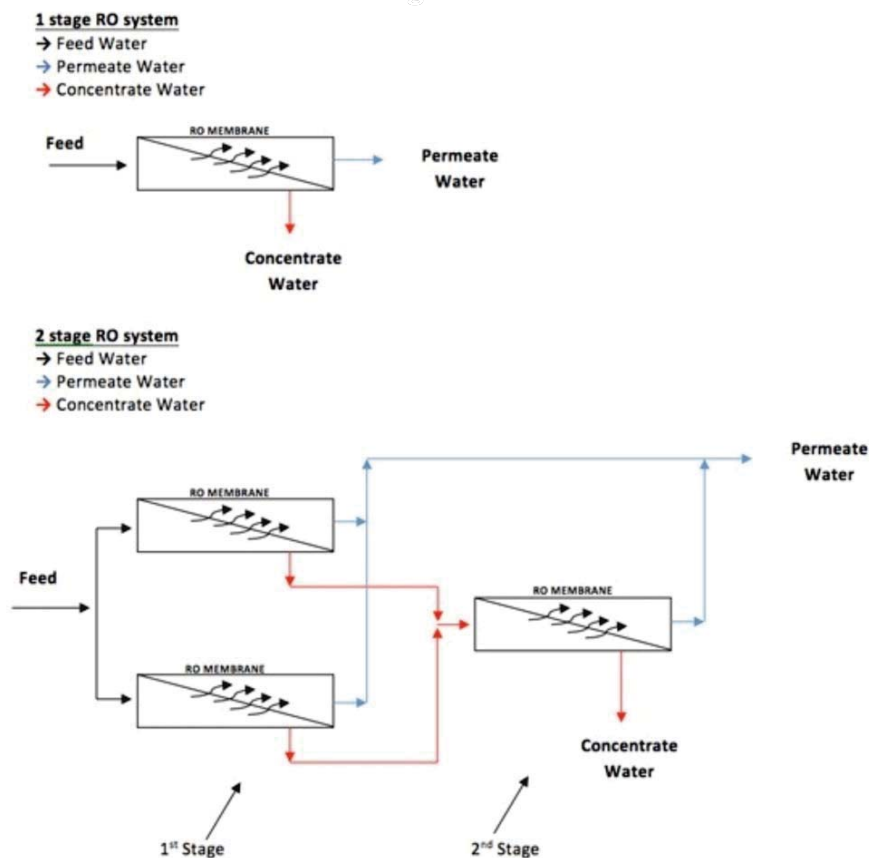
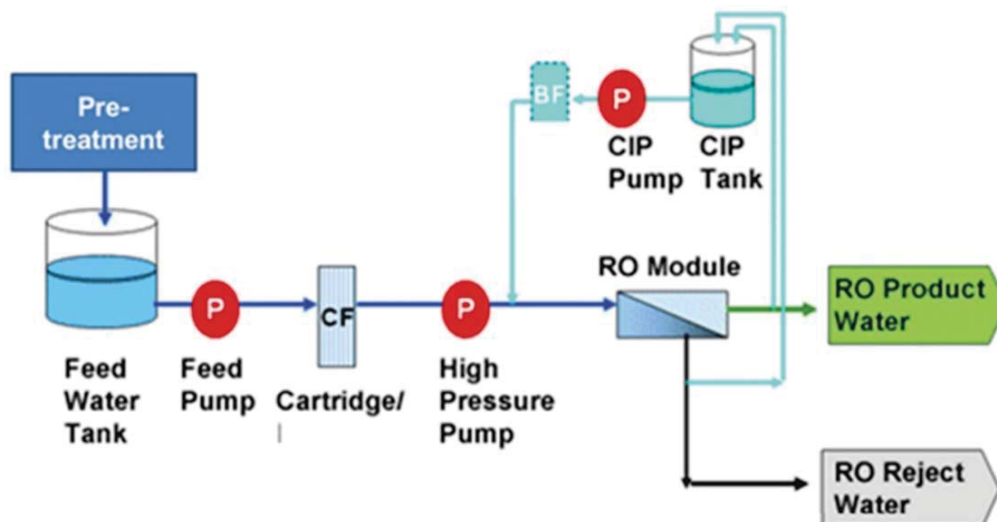


Fig. 2.24: Typical RO system Flow Diagram



RO System operation:

Preparing pre-treatment using both mechanical and chemical treatments is critical for an RO system to prevent fouling and premature RO membrane failure as well as frequent cleaning requirements. UF before RO is best solution to avoid frequent fouling. Silt Density Index (SDI) before RO should be <3. The performance of RO system depends on factors such as membrane type, flow control, feed water quality, temperature and pressure. Fouling is a major factor affecting performance of the system.

Types of Fouling

Bio-fouling: Fouling can be formed due to the following-

- Particulate or colloidal mater (dirt, silt, clay, etc.)
- Organics (humic/fulvic acids, etc.)
- Microorganisms (bacteria, etc.).

Bacterial presence is one of the most common fouling problem, since RO membranes in use today cannot tolerate a disinfectant such as chlorine. Hence micro-organisms are often able to thrive and multiply on the biofilms that cover the membrane surface which results in heavy fouling.

- Breakthrough of filter media upstream of the RO unit.
- GAC carbon beds and softener beds may develop an under drain leak
- Inadequate post filtration in place the media can foul the RO system.

Damage to membranes can be limited by controlling these substances by use of microfiltration or UF before RO

Scaling: Scaling can occur as certain dissolved (inorganic) compounds become more concentrated, exceeding their solubility limits and precipitate on the membrane surface as scale. The results of scaling are higher pressure drop across the system, higher salt passage (less salt rejection), low permeate flow and lower permeate water quality. An example of a common scale that tends to form on RO membrane is calcium carbonate. Scaling can be reduced by limiting salt content (by adding acid) to limit formation of calcium carbonate and by addition of anti-scaling chemicals.

Chemical Attack: Modern thin film composite membranes are not tolerant to chlorine or chloramines. Oxidizers such as chlorine will 'burn' holes in the membrane pores and can cause irreparable damage. The result of chemical attack on RO membrane is a higher permeate flow and higher salt passage (poorer quality permeate water). This is why micro-organism growth tends to foul RO membranes easily as there is no biocide to prevent its growth.

Mechanical Damage: Part of the treatment scheme should be pre and post RO plumbing and controls. If 'hard start' occurs, mechanical damage to the membranes can occur. Likewise, if there is too much backpressure on the RO system then also mechanical damage to the RO membranes can occur. These can be addressed by using variable frequency drive motors to start high pressure pumps for RO systems and by installing check valve(s) and/or pressure relief valves to prevent excessive back pressure on the RO unit that can cause permanent membrane damage.

RO Membrane Cleaning

RO membranes inevitably require periodic cleaning, anywhere from 1 to 4 times a year, depending on the feed water quality. As a general rule, if the normalized pressure drop or the normalized salt passage has increased by 15%, then it is time to clean the RO membranes. If the normalized permeate flow has decreased by 15% then also it is time to clean the RO membranes.

You can either clean the RO membranes in place or have them removed from the RO system and cleaned off-site by a specialized service provider. RO membrane cleaning involves low and high pH cleaners to remove contaminants from the membrane. Scaling is addressed with low pH cleaners and organics, colloidal and biofouling is treated with a high pH cleaner.

Cleaning RO membranes is not about using the appropriate chemicals only. There are many other factors involved such as flows, water temperature & quality, properly designed & sized cleaning skids and many other factors that a service provider must address in order to properly clean RO membranes.

RO Operating parameters:

Feed water SDI - <3

Feed pressure – As per membrane type and make

For brackish water – 10.5 to 42kg/cm² (150-600psi)

For sea water – 56-70kg/cm² (800-1000psi)

Salt rejection >99%

% recovery for one stage - 50%-70%

Sea water membranes:

Inlet TDS – 10,000 to 40,000mg/ltrs

Feed pressure – up to 70kg/cm² max (1000psi)

Brackish water membranes:

Inlet TDS - <10,000mg/ltrs

Feed pressure – up to 42 kg/cm² (600psi)

Advantages of RO Technology

- ❖ RO system is very attractive where there is water scarcity and permeate water is recycled/reused in industry
- ❖ Treated water quality is consistent and water is reused for industrial processes
- ❖ RO systems are modular in nature, making expansion of the systems easy
- ❖ Simple to design and operation,
- ❖ Low day to day maintenance

RO technology considerably reduces the volume of waste streams allowing it to be treated more efficiently and cost effectively by other processes such as MEE or Incineration

Limitations of RO Technology

- ❖ RO processes have limited recovery (50- 85%) dictated by the presence of large concentrations of sparingly soluble salts in the feed water
- ❖ Reject disposal challenges
- ❖ High capital cost
- ❖ High operating cost due to higher energy consumption due to high pressure pumps
- ❖ Replacement of membranes is required after 3 years depending on application

If pre-treatment is not proper, membrane fouling results into poor performance of the system, resulting into frequent cleaning and damage of membranes. Skilled system operation and monitoring is required to maintain the consistent performance

Innovations in RO Technology

Continuous process improvements such as developments in membrane materials and module design, process design, feed pre-treatment, and energy recovery, or reduction in energy consumption in RO technology has resulted in significant cost reductions.

The enhanced mechanical, biological and chemical strength of RO membranes, as well as increased permeability, have reduced the membrane cost per unit volume of water produced by more than 10 times since 1978. The combined impact of effort to minimize fouling and concentration polarization, along with efforts to maximize permeate flux and energy recovery, has decreased the energy consumption from 12 kWh/m³ in the 1970s to less than 2 kWh/m³ in 2006.

There is seven fold increase in salt rejection performance over 30 years. See fig. 2.25 that shows a study by University of BATH, UK

Fig. 2.25: Improvement in salt rejection

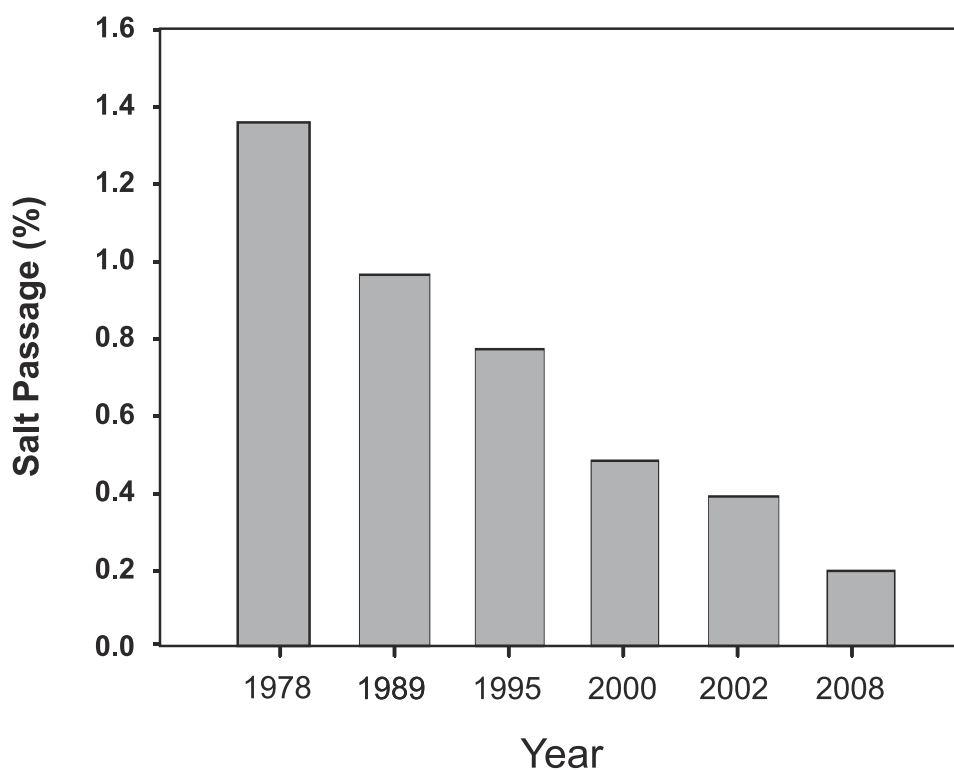


Fig 2.26 and 2.27 show the reduction in capital (membrane) and operation (energy) costs

Fig. 2.26: Reduction in membrane cost

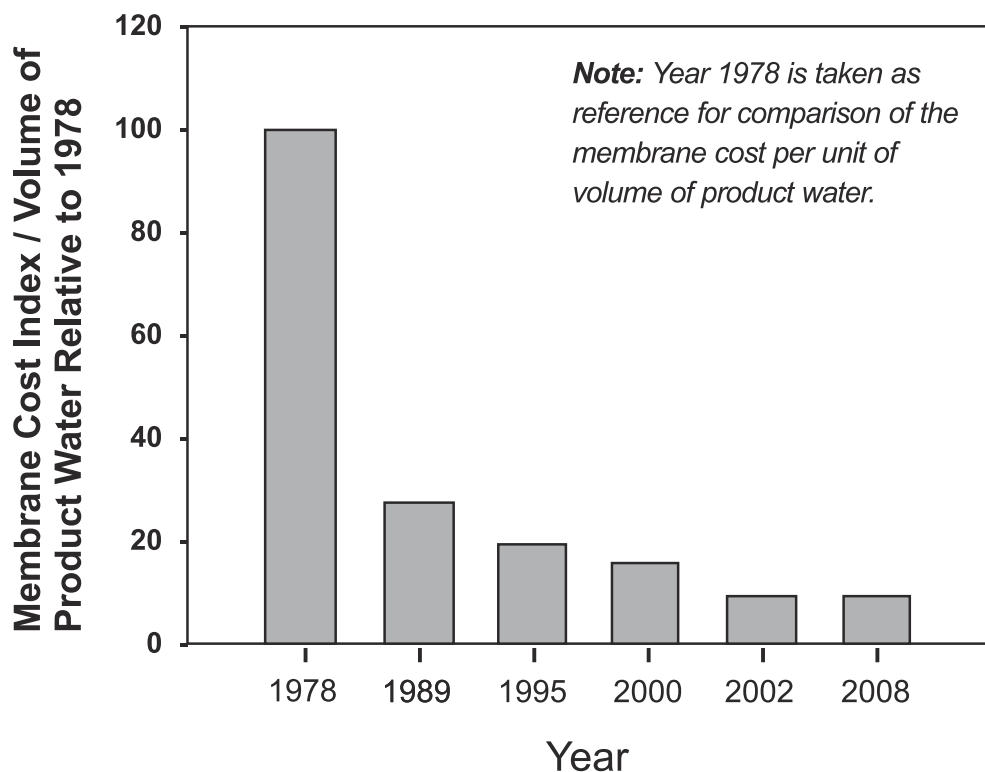
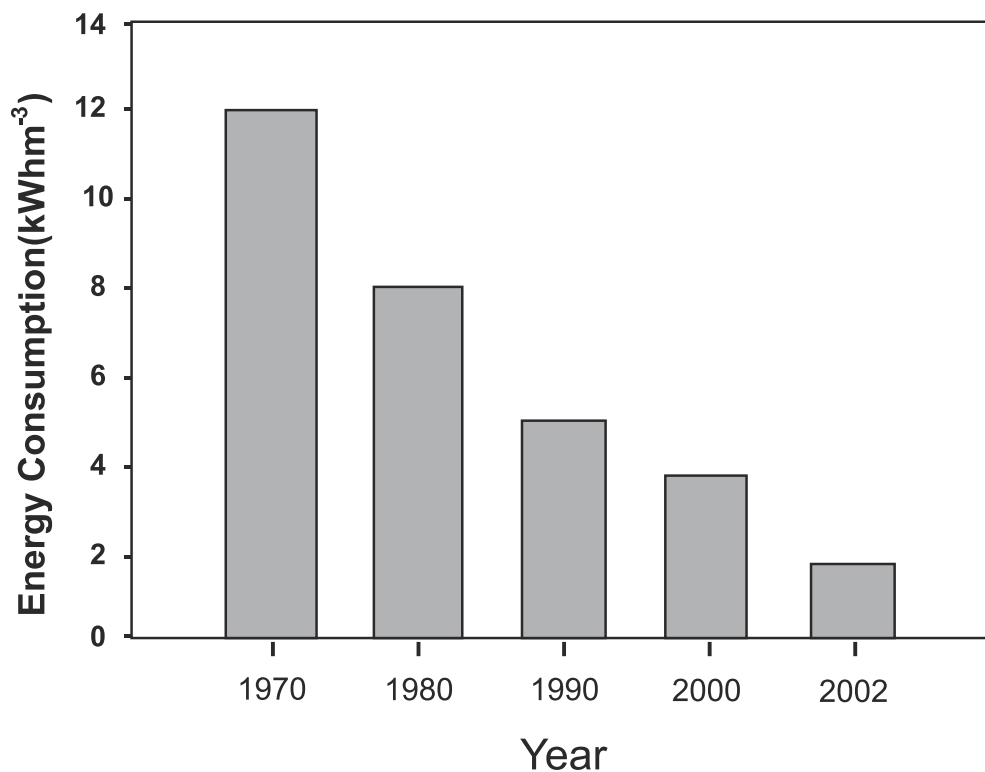


Fig. 2.27: Reduction in energy consumption of RO



Following are the advanced membranes and improvements:

- ✓ Sulphonated poly sulphone membranes (SPS) are chlorine tolerant and can withstand higher pHs and are best used where the feed water is soft and high pH or where high nitrates are of concern.
- ✓ Low fouling membranes are developed by manufacturers, which are neutrally charged (Unlike negatively charged normal membranes). Low fouling membranes can operate at feed COD of 100-200mg/ltrs.
- ✓ Low differential membranes with longer life, more productivity and low fouling have been developed
- ✓ Another innovation is using spacer with sanitizer to avoid fouling in membranes
- ✓ Improved spacer design to prevent trapping of small colloidal particles

The enhanced chemistry of membrane elements helps minimize pressure and energy consumption and provide reliable, long-term permeate quality for single, double pass and inter stage desalination systems.

EDR membranes: Electro Dialysis Reversal (EDR) membranes recover more water from high Total Suspended Solids (TSS) and high silica source water. Because of the polarity reversal design, EDR is a self-cleaning, durable membrane system ideal for turbid waste water reuse.

The current RO membrane market is dominated by Thin Film Composite (TFC) polyamide membranes. The spiral wound membrane module configuration is the most extensively used design in RO desalination.

This configuration offers high specific membrane surface area, easy scale up operation, inter-changeability, low replacement costs and, most importantly, it is the least expensive module configuration produced from flat sheet TFC membrane.

Although the spiral-wound configuration was developed decades ago, improvements in the dimensions of spacers, feed channels and vessels, as well as the materials of construction, have optimized the inter-connection between module design and fluidic transport characteristics, thereby decreasing both fouling and pressure losses.

There are many membrane/module suppliers who provide RO membranes for large scale desalination plants, some of the leading names are DOW, Toray, Hydranautics and Toyobo. See table 2.5

Table 2.5: SWRO membrane modules in application

Membrane module brand name	Material & module	Permeate flux ($\text{m}^3 \text{ day}^{-1}$)	Salt rejection (%)	Specific energy consumption ^[d] (kWh m^{-3})
DOW FILMTEC™ 8 inch SW30HRLE	TFC crosslinked fully aromatic polyamide spiral wound	28.0 ^[a]	99.60 – 99.75 ^[a]	3.40 (2.32) ^[e] at Perth SWRO Plant, Australia [30]
Hydranautics 8 inch SWC4+	TFC crosslinked fully aromatic polyamide spiral wound	24.6 ^[b]	99.70 – 99.80 ^[b]	4.17 (2.88) ^[e] at Llobregat SWRO Plant, Spain [30, 33]
Toray 8 inch TM820C	TFC crosslinked fully aromatic polyamide spiral wound	19.7 – 24.6 ^[a]	99.50 – 99.75 ^[a]	4.35 at Tuas SWRO Plant, Singapore [31]
Toyobo 16 inch HB10255	Asymmetric cellulose tri-acetate hollow fibre	60.0 – 67.0 ^[c]	99.40 – 99.60 ^[c]	5.00 at Fukuoka SWRO Plant, Japan [32]

Note: [a] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 8 and 8 % recovery [29, 35];

[b] Test condition: 32 g L⁻¹ NaCl solution, 55 bar, 25 °C, pH 7 and 10 % recovery [34];

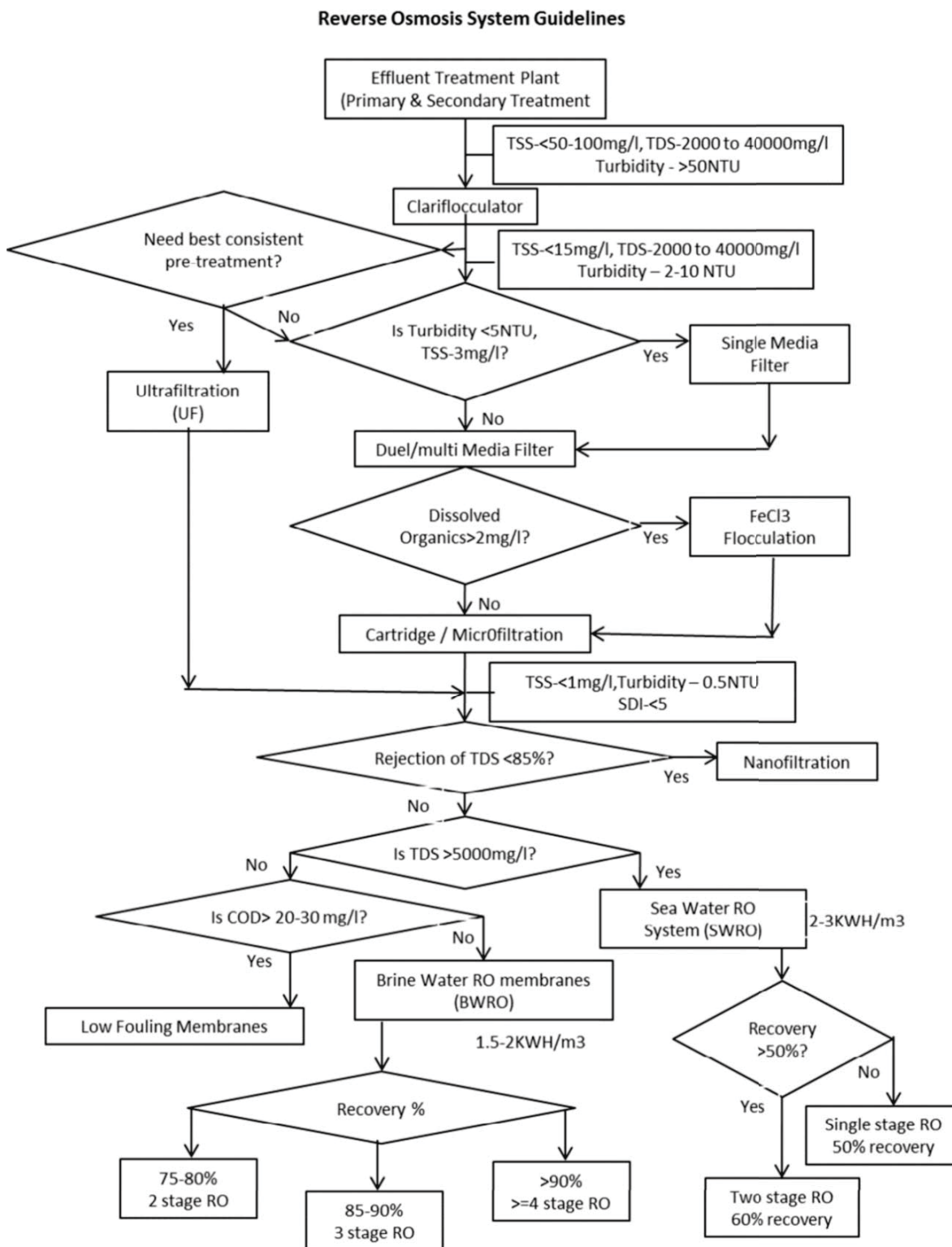
[c] Test condition: 35 g L⁻¹ NaCl solution, 54 bar, 25 °C and 30 % recovery [36];

[d] These numbers should not be compared explicitly because of different operating parameters (*e.g.* feed water quality, recovery, pre-treatment processes, process design, etc.) at different desalination plants.

[e] The number in brackets is the energy consumption for the RO unit.

Fig 2.28 provides guidelines to select RO system

Fig. 2.28



2.2.4 Evaporation Technologies

The ultimate objective of ZLD is not discharging waste water outside the industry. This objective is achieved by evaporation or crystallization of rejects from previous treatments. During these processes (ultrafiltration and reverse osmosis), the condensate (treated water) is recovered while contaminated elements are separated as solid waste with some moisture in it. Typically, the effluent is a salty solution and the thermal separation is the final step of ZLD.

Evaporation of reject water is most commonly used treatment for reduction of waste volume, recovery of salts and to recycle the condensate in process. Evaporation plants are used are thermal separation technology, for the concentration or separation of liquid solutions, suspensions and emulsions.

Ideally the evaporator design should have:

- Minimum surface area with highest heat transfer
- Efficient vapour liquid separation.
- Efficient energy utilization – steam/power/thermic.
- Purer condensate/water recovery
- Optimum capital cost
- Optimum material of construction with economic life cycle.
- Least maintenance cost
- Easy operation

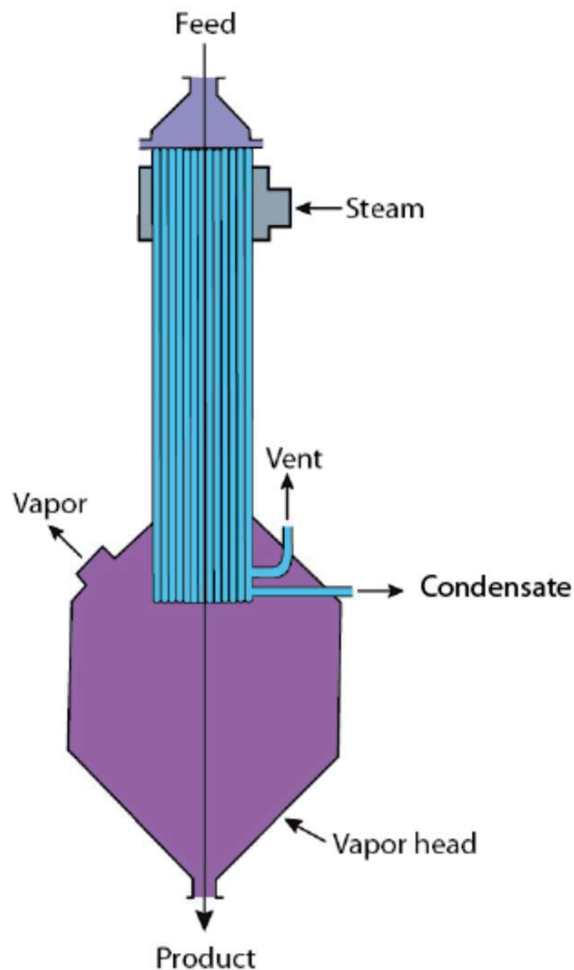
Types of evaporators:

Falling film Evaporator: This technology is particularly suited for energy -saving. It only requires a very small operating temperature and thus allows it to be easily controlled. It is fast to start up and shut down due to a minimal liquid hold-up. Falling film technology is the right solution for streams which are viscous in nature and contain small concentrations of suspended solids.

A falling film evaporator can be used as a pre-concentrator in a combined multiple-effect plant. It has the capacity to treat streams with small to large flow rates. Unlike rising film, Liquid is fed at the top of long tubes and allowed to fall down the film walls. Evaporation occurs on the surface of the highly turbulent film and not on the tube surface. This requires that temperature differences be relatively low.

Many times rising film and falling film evaporators are combined into single unit. When a high ratio of evaporation to feed is required and the concentrated liquid is viscous. A tube bundle is divided into two sections with the first section functioning as a rising film evaporator and the second section serving as a falling film evaporator. See fig. 2.29

Fig. 2.29: Falling Film Evaporator



Advantages

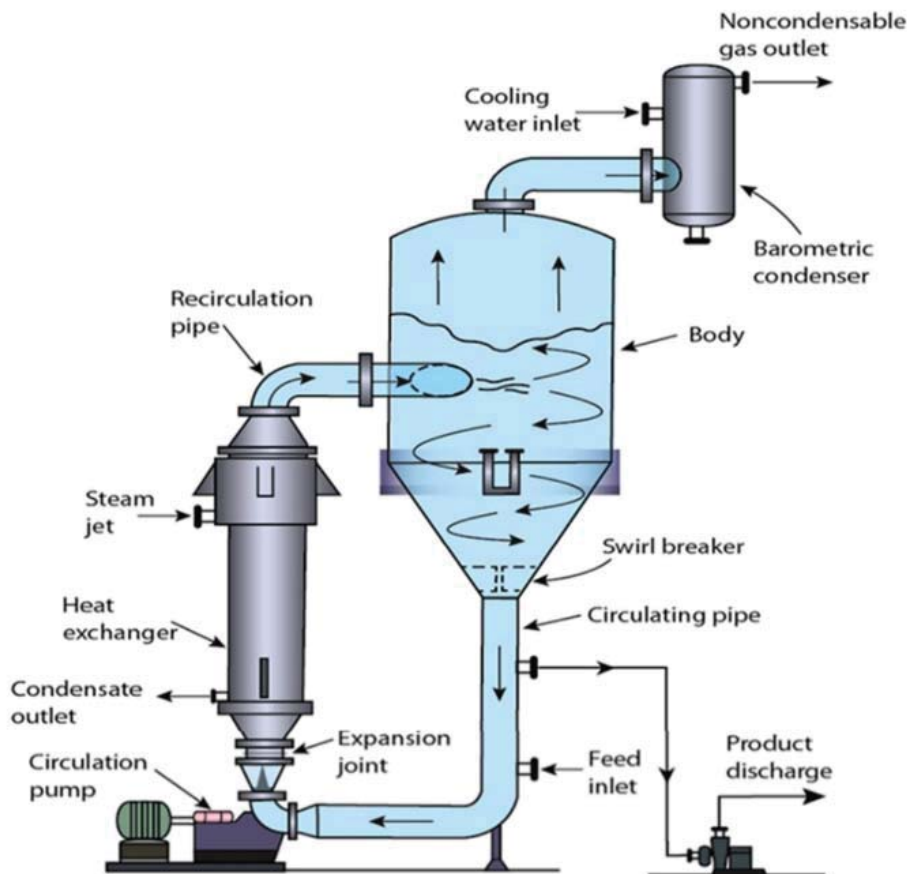
- ✓ Low power requirement
- ✓ Low pressure drop
- ✓ High heat transfer rate
- ✓ Less capital cost

Limitations

- ❖ Very sensitive to saturation of ions present in liquid
- ❖ Not suitable if any of the component gets saturated during evaporation
- ❖ Frequent scaling in case of effluent and crystalline product
- ❖ More down time
- ❖ Higher cleaning frequency

Forced circulation: The forced circulation evaporator is used for processing liquors which are susceptible to scaling or crystallizing. Liquid is circulated at a high rate through the heat exchanger, boiling being prevented within the unit by virtue of a hydrostatic head maintained above the top tube plate. As the liquid enters the separator where the absolute pressure is slightly less than in the tube bundle, the liquid flashes to form a vapour. See fig. 2.30

Fig. 2.30: Forced Circulation Evaporator



Advantages

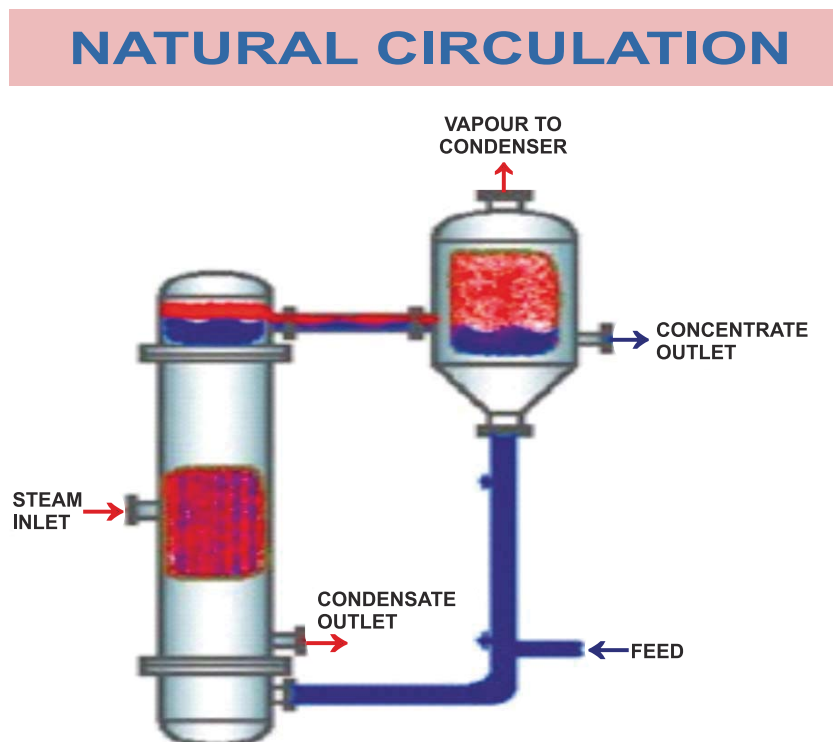
- ✓ Suitable for crystalline product
- ✓ Can handle slurry
- ✓ Very less fouling
- ✓ Minimum down time
- ✓ Very high heat transfer rate
- ✓ Extended cleaning cycle
- ✓ Most rugged kind of evaporator

Limitations

- ❖ Higher power requirement
- ❖ Higher capital cost

Natural Circulation: Evaporation by natural circulation is achieved through the use of a short tube bundle or by having an external shell and tube heater outside of the main vessel. The external heater has the advantage that its size is not dependent upon the size or shape of the vessel itself. As a result, larger evaporation capacities can be obtained. The most common application for this type of unit is as a re-boiler at the base of a distillation column. See fig. 2.31

Fig. 2.31: Evaporation based on natural Circulation



Advantages

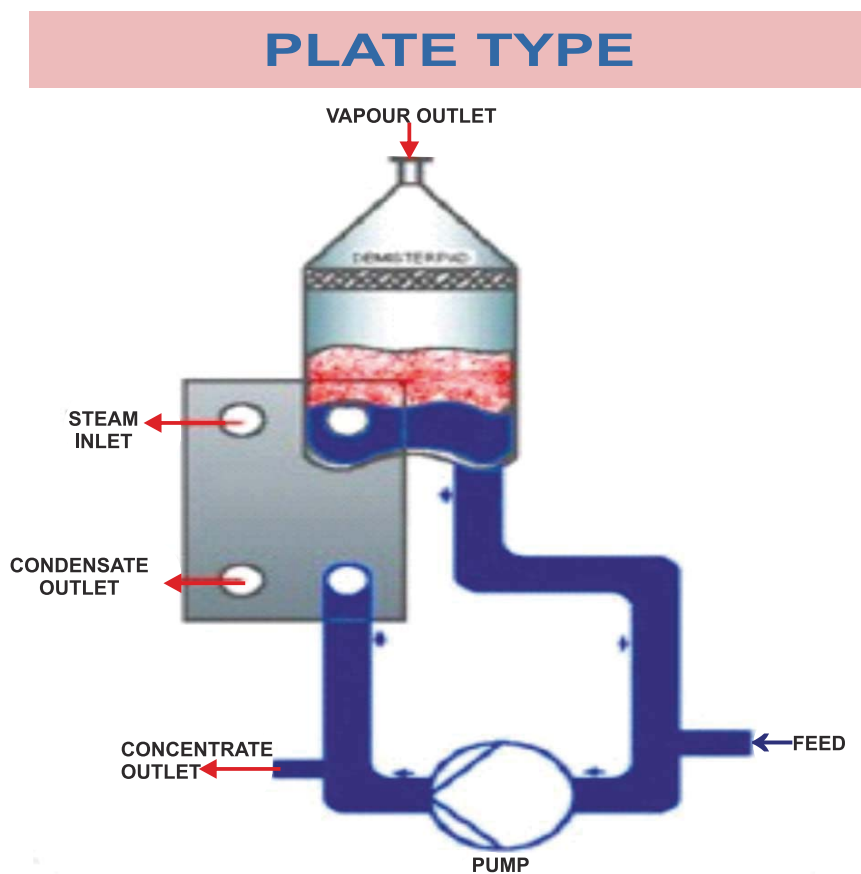
- ✓ Minimum power cost
- ✓ Easy operation
- ✓ Can handle viscous material

Limitations

- ❖ Very sensitive to saturation of ions present in liquid
- ❖ Not suitable if any of the component gets saturated during evaporation
- ❖ Frequent scaling in case of effluent and crystalline product
- ❖ Higher cleaning frequency
- ❖ Low heat transfer coefficients
- ❖ Higher capital cost

Plate type evaporator: Principally, plate evaporators are similar to falling film & forced recirculation tubular evaporators. The plate evaporator offers full accessibility to the heat transfer surfaces. It also provides flexible capacity merely by adding more plate units. Because of shorter product residence time, superior quality concentrate is obtained. It is a more compact design with low headroom requirements, and low installation cost. See fig. 2.32

Fig. 2.32: Plate Type Evaporator



Advantages

- ✓ Less pressure drop on liquid side
- ✓ High heat transfer co-efficient
- ✓ Less height required
- ✓ Compact construction
- ✓ Less capital cost
- ✓ Physical cleaning is easy

Limitations

- ❖ Gaskets required to replace periodically
- ❖ Not suitable for slurry and crystalline products

Table 2.6 summarizes various applications of different type of evaporation technologies

Table 2.6: Application of various Evaporation Technologies

S.N.	Technology	Application
1	Forced Recirculation	➤ Suitable for evaporation applications containing high levels of hardness, silica, suspended solids & Crystalline slurries ➤ Salt recoveries like NaCl, Na₂SO₄, NH₄Cl, (NH₄)₂SO₄, ZnSO₄, K₂SO₄, KCl, & CaCl₂, etc.
2	Falling film	➤ Suitable for clear liquors, feeds with low hardness and non- crystalline concentrates with low viscosities ➤ Useful for concentrating milk, fruit juices, if hardness is <150ppm
4	Natural Recirculation	➤ Suitable for concentration of viscous liquids below saturation without hardness ➤ Solid slurry with high viscous ➤ liquid, where solids will settle down and clear liquid is recirculated
5	Plate Type	➤ Application is same as Forced recirculation and falling film designs. Used for low level installations

Above evaporation methods are applied separately or in combination for overall evaporation system depending on application, saving energy and availability of excess heat or steam.

Multiple Effect Evaporator (MEE)

A multiple-effect evaporator is an evaporator system in which the vapour from one effect is used as the heating medium for a subsequent effect boiling at a lower pressure. Effects can be staged when concentrations of the liquids in the effects permits; staging is two or more sections operating at different concentrations in a single effect. The term evaporator denotes the entire system of effects, not necessarily one body or one effect.

A multiple-effect system may be considered as a number of resistances (effects), in series, to the flow of heat. The driving force causing heat to flow is the difference in temperatures of the steam condensing in the first effect and the temperature of the heat sink, often cooling water. Some of the available driving force is lost when the liquid exhibits a boiling-point elevation, the total loss equal to the sum of the boiling-point elevations in all the effect.

Figures 2.33 and 2.34 presents schematics of single effect and multiple effect evaporators

Fig. 2.33: Single Effect Evaporator

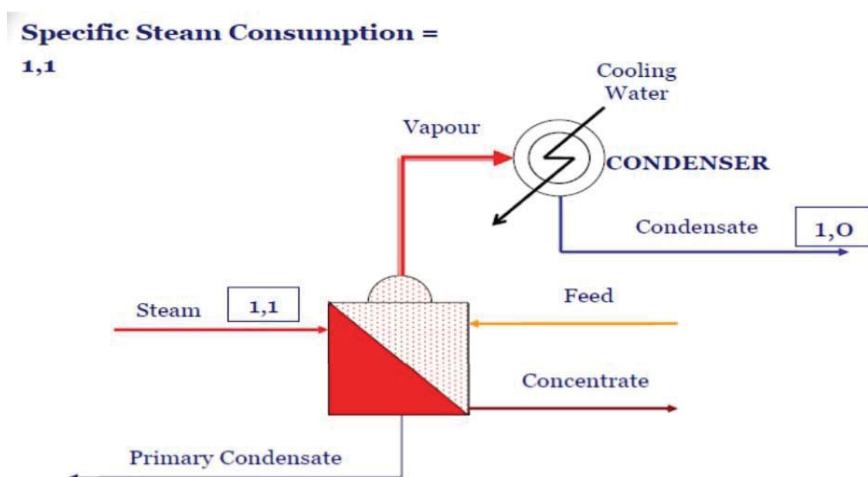
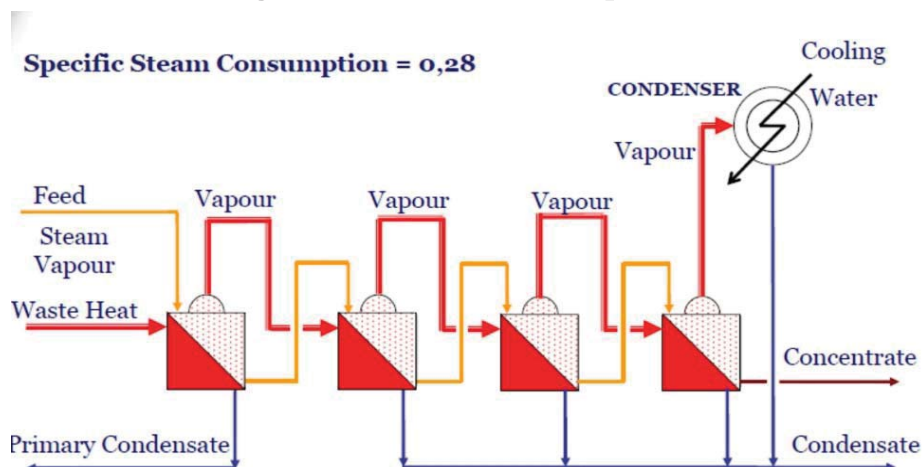
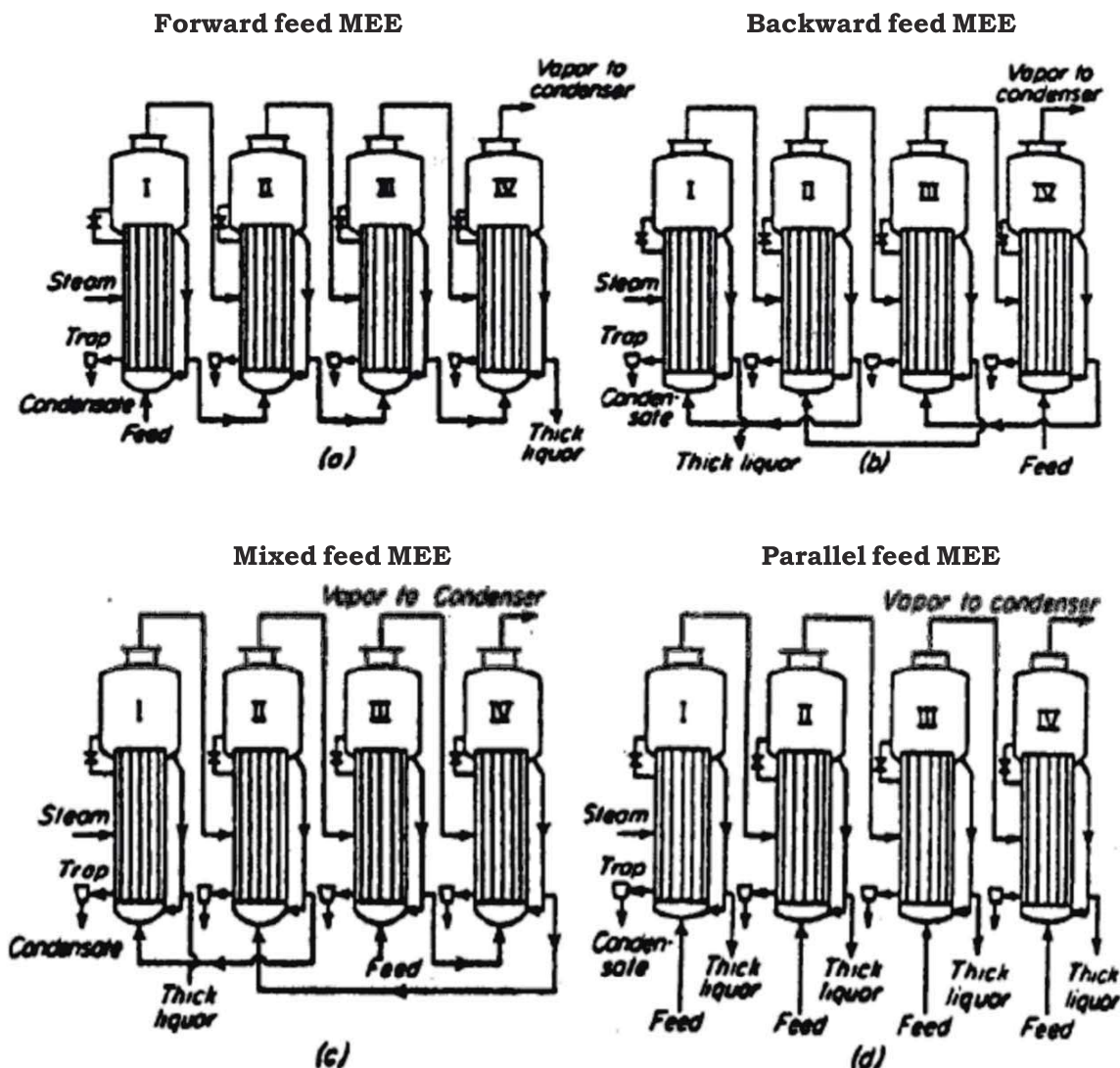


Fig. 2.34: Multi Effect Evaporator



There are 4 types of configurations of MEE: (see fig. 2.35)

Fig. 2.35: Various configurations of MEE



MEE Configuration is selected as per temperature and concentration of feed. The purpose of an evaporator system is to produce the required amount of specified product at the lowest total cost. The designer of an evaporator system must consider a wide range of variables in selecting the system which provides the best balance between operating cost and capital investment. The evaporator type, the number of effects, and the type of compression system are the most important variables.

Operational problems in MEE technology is scaling and fouling of heating surface. Fouling may be defined as the formation of deposits on heat transfer surfaces which impede the transfer of heat and increase the resistance to fluid flow. The growth of deposits causes the thermal and hydrodynamic performance of heat transfer equipment to decline with time. Fouling is of various types, e.g. precipitation, particulate, Chemical reaction, corrosion, biological fouling. Corrosion fouling can be reduced by using Titanium material for construction. Other fouling are eliminated by frequent cleaning.

Guidelines for design of MEE are as follows

- the number of effects increases as the steam costs increase or plants become larger
- mechanical vapour compression looks attractive if electrical power is available at reasonable costs and boiling point rises are low
- thermal compression looks attractive when electrical power is costly and boiling point rises are low
- when boiling point rises are large, combinations of vapour compression and pre-concentrators followed by multiple-effect systems look attractive
- larger plants enable heat recovery systems to be more easily justified
- mechanical vacuum pumps are generally more energy efficient than steam jets.

Number of effects that can be practically installed depends on pressure of the steam, Boiling Point Rise (BPR) of the process fluid and Temperature of cooling water

It is also necessary to consider other factors besides the evaporator design. Steam generation, electrical power, and cooling water distribution and supply costs may be sufficiently reduced to justify particular system designs.

Sometimes evaporator efficiency can be sacrificed in order to utilize all of the heat available in a waste heat stream. Final operating pressure may be determined by the ability to recover the heat of condensation in some other part of the plant.

Energy Optimization in Evaporators

Staging: Often in MEEs the concentration of the liquid being evaporated changes drastically from effect to effect especially in the latter stages. In such cases, this factor can be used to advantage by “staging” one or more of the latter stages. Staging is the operation of an effect by maintaining two or more sections in which liquids at different concentrations are all being evaporated at the same pressure. The liquid from one stage is fed to the next stage. The heating medium is the same for all stages in a single effect, usually the vapour from the previous effect. Staging can substantially reduce the cost of an evaporator system.

- Multi-staging reduces thermal energy requirement
- Suitable with high pressure steam pressure
- Reduces cooling tower power requirement
- Reduces cooling water makeup required in cooling tower.

Pre-heating: Pre-heating the feed reduces size of main heat exchange. If forward feed is required and the feed is cold, energy economy can be improved by preheating the feed in stages with vapour from intermediate evaporator effects. Steam economy improves with pre-heating and also minimizes thermal losses. If excess heat is available then this option is suitable.

Compression Evaporation:

Compression evaporation could be defined as a process in which part or all of the evaporated vapour is compressed by means of a suitable compressor to a higher pressure level and then condenses. The compressed vapour provides part or all of the heat required for evaporation.

Compression evaporation is frequently called recompression evaporation. The compression method uses the vapours from the evaporator and recycle them to the heating side of the evaporator.

Compression can be achieved with mechanical compressors or with thermal compressors. Thermal compression uses a steam jet to compress a fraction of the overhead vapours with high pressure steam. Mechanical compression uses a compressor driven by a mechanical drive (electric motor or steam turbine) to compress all the overhead vapours.

Energy economy obtained by multiple-effect evaporation can often be equaled in a single-effect compression evaporation system.

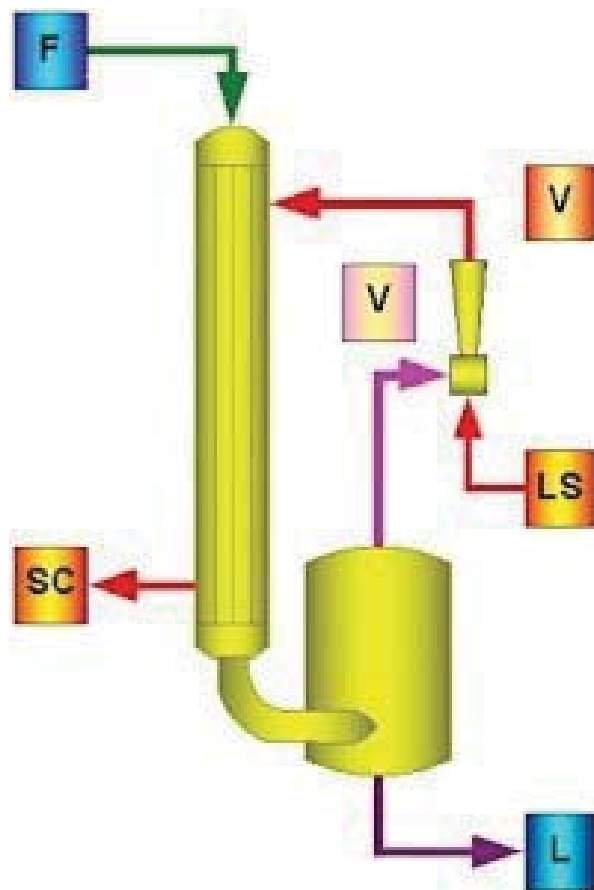
To achieve reasonable compressor costs and energy requirements, compression evaporator systems must operate with fairly low temperature differences, usually from 5 to 10°C. As a result, large heat transfer surfaces are needed partially offsetting the potential energy economy.

Thermal Vapour Re-compressor (TVR) or Thermo-Compressors:

Thermal compression is the term used to describe the application of a steam jet ejector or thermo-compressor to an evaporator in order to increase the steam economy.

Thermal compression evaporators are well suited for single or double effect systems where low operating temperatures and improved economy are desired. They also find application where space is limited. For practical application the temperature difference across the thermo-compressor should be less than 15%.

The application of thermo-compressors is limited when the boiling point rise is high. Thermal Compressors improve steam economy by lowering the operating temperature of evaporation plant. It is suitable for almost all kinds of evaporation plants and liquids excluding high boiling point liquids. See fig. 2.36

Fig. 2.36: Thermal Vapour Re-compressor (TVR)

F = Feed
LS = Steam

V = Vapour
SC = Steam Condensate

L = Liquid concentrate

Mechanical Vapour Re-compressor (MVR)

Mechanical vapor compression evaporator technology has been used for over 100 years and is a proven means to significantly reduce energy required for evaporation. Water vapour generated in the evaporator is compressed to higher pressure. Compressed vapour acts as heat source for evaporation process and gets condensed in the evaporator heat exchanger.

It is similar to a conventional single-effect evaporator, except the vapour released from the boiling solution is compressed in a mechanical compressor. The compressor adds energy to the vapour to raise the saturation temperature of the vapour above the boiling temperature of the solution by whatever net temperature difference is desired.

Compressor power is proportional to the increase in saturation temperature (ΔT) produced by the compressor. An evaporator designer must optimize power consumption and heat transfer surface. Mechanical vapour compression achieves the highest possible energy savings. See fig. 2.37 & 2.38

Fig. 2.37: Mechanical Vapour Re-compressor (MVR)

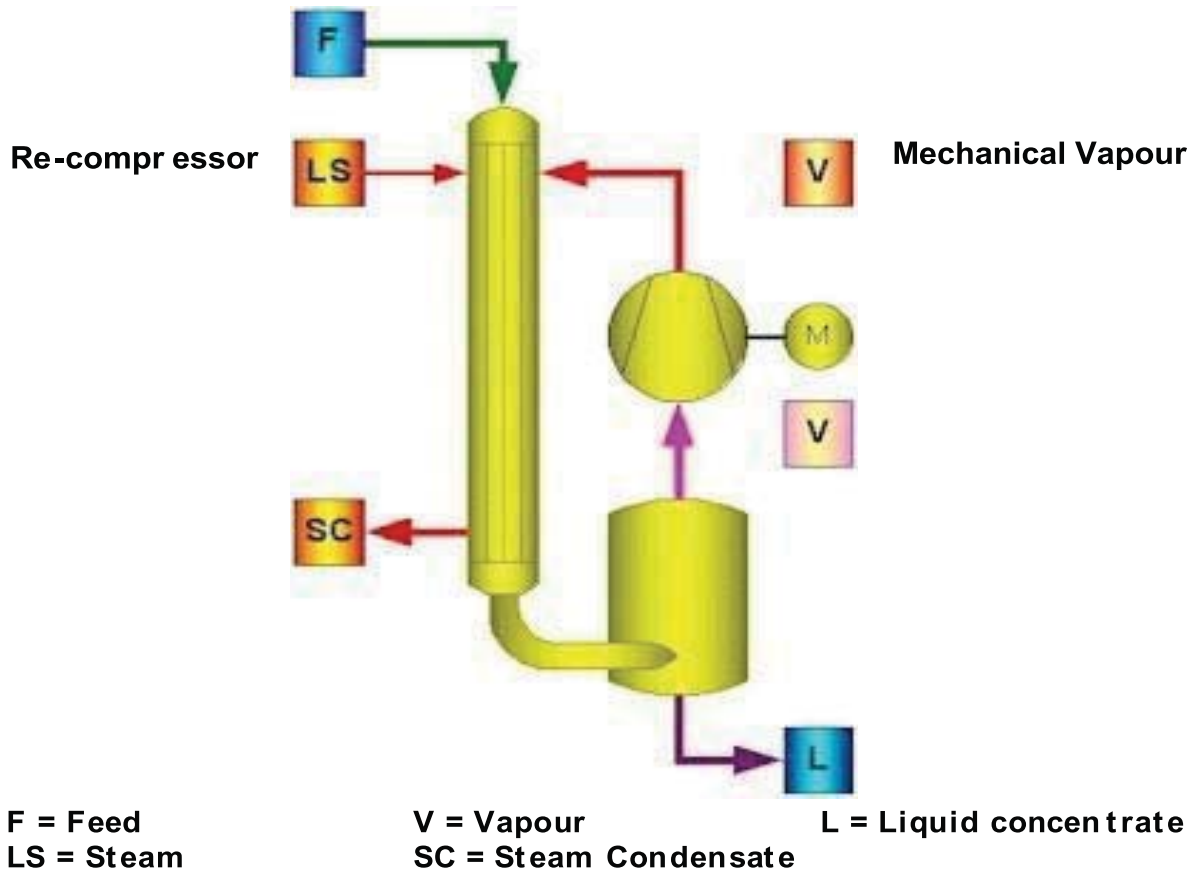
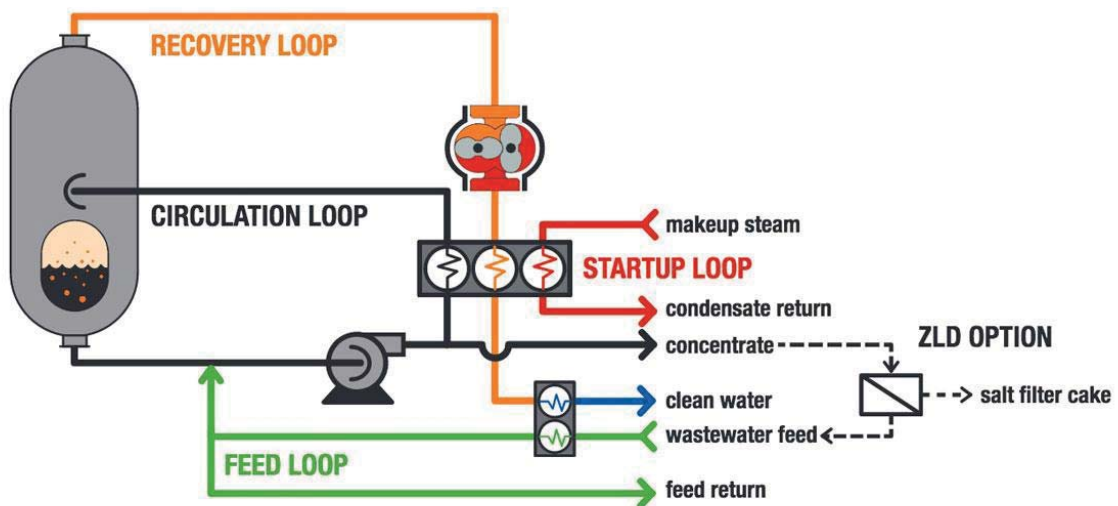


Fig. 2.38 : Configuration of MVR



MVR eliminates thermal energy requirement. The system has high efficiency and low operating cost due to low energy consumption. MVR is suitable for liquid with narrow BPR. MVR is not suitable when steam is readily available in plant.

Selecting the most economical method of evaporation requires knowledge of the costs of energy, capital, operating labor, spare parts, and maintenance over the life of the system. Energy and capital costs dominate and show the greatest variance among evaporator types. It is often difficult to assign true costs to energy sources. Each case must be considered individually. The economics can be calculated only if accurate costs are known; approximations and educated guesses will not provide the correct answer.

Compressor is heart of the system. The major factors to consider in selecting a compressor are the flow rate, compression ratios, and variability of evaporator flow rates, operating conditions, vapour temperature, expected maintenance, and installed cost. Generally, the costs for all mechanical compressors limit their application to situations in which the compression ratio is less than 2, since multistage or a series of single stage compressors would be required for higher compression ratios. Compressors applied to evaporator systems include positive displacement, and radial-flow turbo and axial-flow centrifugal. Each has advantages for certain applications.

The solution for the processing and project requirements is a system of mechanical vapour recompression unit (for initial concentration where acceptable to remove large quantities of water) followed by multiple-effect, steam heated units to finish evaporation process. Another key factor is that the site should have availability of necessary electrical capacity to meet the requirements of the MVR system.

Advantages of MVR technology

- ✓ Steam and overall energy consumption significantly reduces compared to conventional steam heated evaporator systems with the same capacity.
- ✓ Substantially lower operational cost than MEE
- ✓ Reduction in Cooling water requirements
- ✓ The main vacuum pump for evaporator system is reduced in horse power, capacity & size compared to one required without use of a MVR
- ✓ Higher condensate temperatures provide additional steam savings.

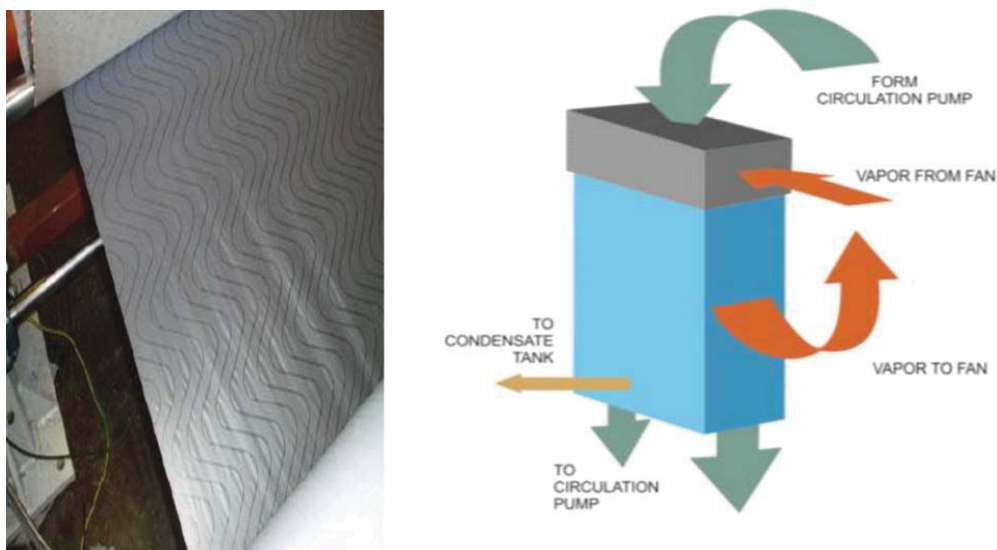
Limitations of MVR technology

- ❖ Very high capital cost
- ❖ MVR alone cannot be used for all streams due to its limitation of temperature difference
- ❖ Energy consumption is more than conventional evaporation due to high capacity compressor
- ❖ MVR is not suitable when steam is available readily

Innovations in Mechanical Vapour Compression (MVR)

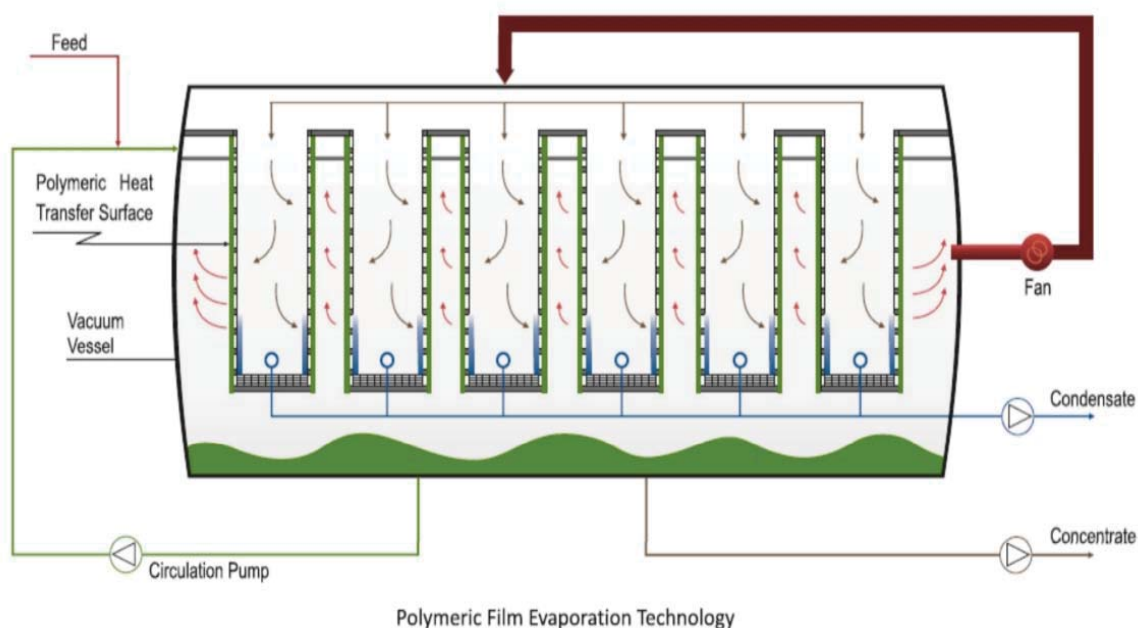
Conventional MVR uses Stainless Steel material (SS316), or its alloy or titanium for heat transfer. Advanced polymer membranes have now been developed, which have several benefits. See fig. 2.39

Fig. 2.39: Polymeric film sheets in MVR



These polymeric film sheets have larger heat transfer surface area and require less foot pint area. Polymeric film evaporation technology works on the same principle as conventional mechanical vapour compressor with lower temperature difference. Energy requirement is typically 10to15 kWh per m³ of purified water.

Fig. 2.40: Polymeric film evaporation technology



Preheated effluent is pumped in horizontal cylindrical vessel and uniformly distributed on the heat transfer element (made up of polymer). These polymeric heat transfer modules are placed one after other along the length of the vessel. As water flows down, evaporation takes place. The vapour is drawn by a high speed centrifugal fan, which compresses the vapour and increases pressure and saturation temperature. The saturated vapour condenses on the inner surface of the modules at the bottom. The concentrated effluent is pumped out for further treatment to crystallizer or disposal.

Advantages of Polymer MVR

- ✓ Works on lower temperature difference, therefore less steam consumption than conventional evaporation
- ✓ Higher surface area
- ✓ No scaling and corrosion problems
- ✓ Lower operating cost

Disadvantages of Polymer MVR

- ❖ High capital cost
- ❖ Replacement of polymers required every year which adds to operational cost
- ❖ Since it works on lower temperature difference, fluctuations in design parameters are not accepted by the system.
- ❖ Technology is not suitable if steam is readily available

Table 2.7 presents a comparative operational costs of various evaporation technologies

**Table 2.7: Operational Cost of various evaporation technologies
(Excl. Replacement cost)**

Technology	Electricity required (KWH/ m ³)	Steam required (kg/ m ³)	Cost Rs/ m ³ (@6Rs/ KWH, 1RS/ kg steam)
MVR Polymer technology	12-15	10-15	82-115
Conventional MVR	25	20	170
Conventional MEE - 1 effect	2	1100	1112
Conventional MEE - 4 effects	3	280	298

Combinations of MVR, MEE and crystallizer are used depending on waste water characteristics, availability of steam and operational cost.

Improvements in Evaporation Technologies: Many improvements have been made in evaporator technology. The improvements have taken many forms but have served to effect the following:

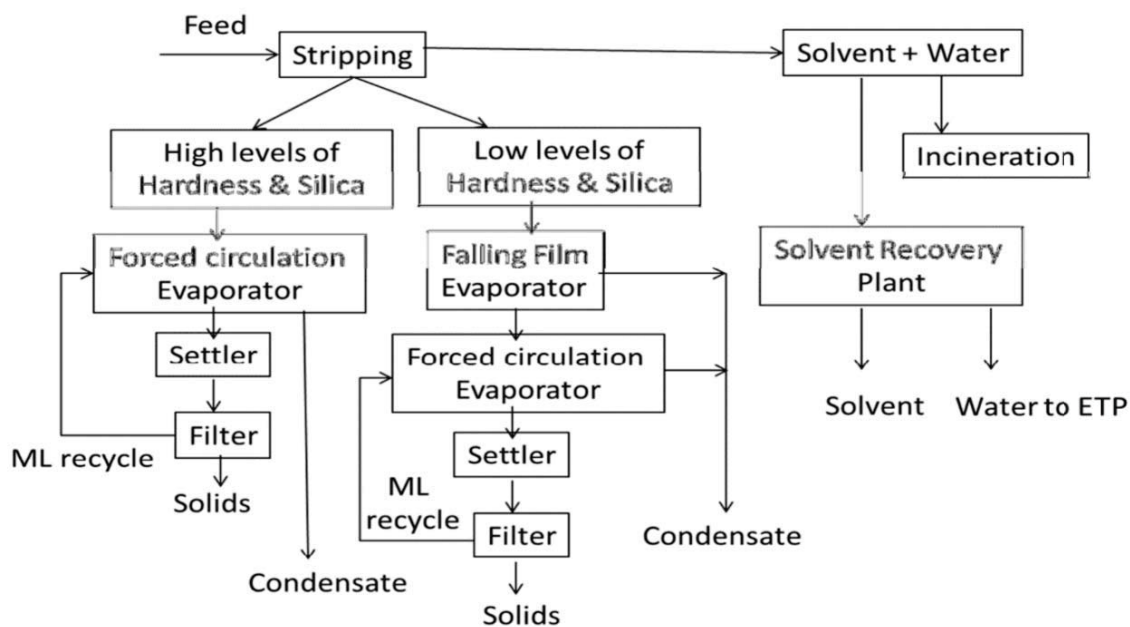
- Greater evaporation capacity through better understanding of the heat transfer mechanisms.
- Better economy through more efficient use of evaporator types
- Longer cycles between cleaning because of better understanding of salting, scaling, and fouling.
- Cheaper unit costs by modern fabrication techniques and larger unit size.
- Lower maintenance costs and improved product quality by use of better materials of construction as a result of better understanding of corrosion.
- More logical application of evaporator types for specific services.
- Better understanding and application of control techniques and instrumentation has resulted in improved product quality and reduced energy consumption.
- Greater efficiency resulting from enhanced heat transfer surfaces and better energy economy.
- Compressor technology availability has permitted the application of mechanical vapour compression.

Selection of Evaporation Technology

Fig. 2.41, 2.42, & 2.43 presents four options of configurations of various evaporation technologies for different applications

Fig. 2.41

Waste Water with High Volatile + High Boilers + Inorganic Solids- Option 1
(For API, Bulk Drug Pharmaceutical, Chemical & Dye Industries)

**Fig. 2.42**

Waste Water with High Volatile + High Boilers + Inorganic Solids – Option 2
(For API, Bulk Drug Pharmaceutical, Chemical & Dye Industries)

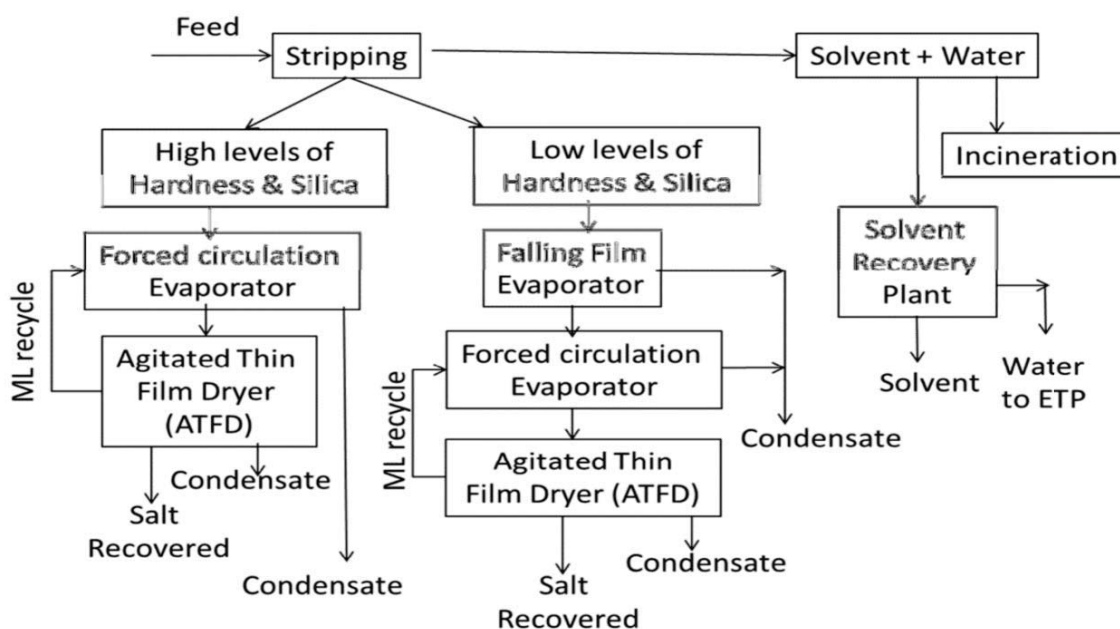
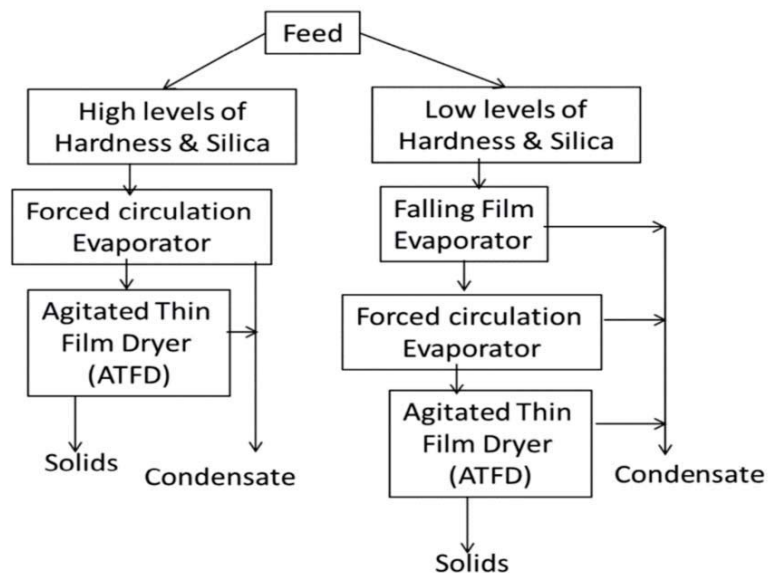
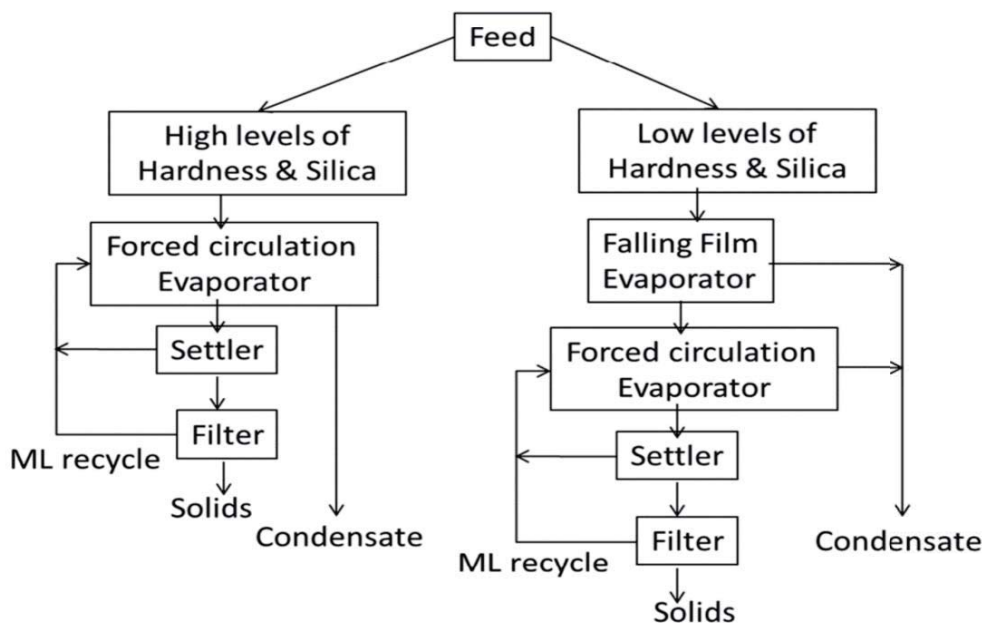


Fig. 2.43: Option 3 & Option-4

Waste Water with High Boilers + Inorganic Solids
(For Pesticides, chemical & Dye Industries)



Waste Water with Crystalline Inorganic Solids
(For Dairy, Textile, Oil refinery Industries)



2.2.5 Agitated Thin Film Dryer

Agitated Thin Film Dryer (ATFD) is used for drying a solution of high TDS water or recovery of products. The outcome of ATFD is in the powder form having 10-15% moisture. This system evaporates the solution by thin layer formation on the Surface. ATFD is evaporation of water/solvents to make concentrated liquid to dry powder or flakes. The system often includes other dewatering systems nutsche / vacuum nutsche; centrifuge / pusher type centrifuge to optimize the costs of operations.

ATFD is the ideal apparatus for continuous processing of concentrated material to dry solids. A typical ATFD consists of a tubular heat transfer area with an external heating jacket and a fast-revolving, inner rotor with flexible or rigid wiper elements. Inside of the shell which is equipped with rows and pendulum blades all over the length of the dryer. The hinged blades spread the wet feed product in a thin film over the heated wall. The driving speed is adapted to the product being handled, its specifications and task.

The feed product is evenly distributed by the rotor and its wipers over the heating surface, forming a thin liquid film of uniform thickness. Highly turbulent swirls are produced at the tip of the rotor blades and wipers with intensive mixing and agitation of the product, as it comes into contact with the heating surface. This assures excellent heat transfer combined with constant renewal of the product film and provides an even heating and short residence time of the product through the heated zone.

The turbulence increases as the product passes through the clearance before entering calming zone situated behind the blades as the heat is transferred from jacket to main shell. The smooth agitation water/solvent evaporates and liquid gets converted to slurry/cake / dry power or flex. The vapours produced rise upward, counter-currently to the liquid and pass through Cyclone separator mounted on vapour outlet of ATFD.

These vapours are further condensed in condenser and recovered as condensate. System operates under vacuum for temperature sensitive products and atmospheric condition for normal drying. Due to its inherent design features, it is ideal for thermal treatment of solutions and heat sensitive products, where reduced operating temperatures and vacuum operating pressures are desirable.

Key Advantages of ATFD

- ❖ Good heat conductivity (k-value), even when working with highly viscous and contaminated products
- ❖ Minimal thermal stress, thanks to low operating capacity, and a short dwell time (10-20 seconds of mean dwell time)
- ❖ No dead zone, preventing overheating and high product quality guaranteed
- ❖ Continuous mechanical cleaning of the heating surface prevents incrustations
- ❖ High evaporation rates, due to highly turbulent film and large difference in temperature
- ❖ Gentle evaporation, due to short residence time, rapid conveyance in the heated zone
- ❖ Constant product film renewal, combined with suppressed boiling points due to operation under vacuum
- ❖ Reduced need for maintenance because of sophisticated bearings and shaft sealing parts
- ❖ Shorter downtime and assembly time for maintenance and inspection
- ❖ No corrosion as outside surface is usually made of stainless steel
- ❖ Evaporation in one pass, no circulation
- ❖ Small film thickness, no hydrostatic height
- ❖ High turndown ratio and high flexibility for variation in requirements
- ❖ Low operating pressure down to 1 micron to reduced boiling temperature
- ❖ Single step drying because of unique designed combination of vertical and horizontal dryers
- ❖ Effective evaporation of concentrated slurries, heat sensitive products, viscous and fouling fluids up to 99% in a single pass
- ❖ Simple installation as the equipment is supplied skid mounted with all inter connecting piping, condensers and vacuum system
- ❖ Single source responsibility for all project stages because of combined expertise in vacuum technology, heat transfer, evaporation, crystallization and drying – a design mix which gives optimal results

Applications of ATFD

Mainly used for difficult vaporization and heat exchange processes, especially where products to be handled are highly viscous (as conventional plants cannot meet user demands because heat transfer is insufficient). Due to the liquid film, mechanically generated on the heating surfaces, thin film equipment achieve much better heat transfer rates, even with highly viscous products containing solids.

- To concentrate highly viscous products, polluted liquids, salt solutions, oils, resins, etc.
- As a sump evaporator for vacuum rectification columns
- Sludge drainage
- To continuously dry powdery residues
- Distillation of high-boiling substances under high vacuum
- Degassing and/or removal of volatile components of highly viscous products
- Heating or cooling of viscous solutions
- Improve product quality by removing colour bodies, minimizing impurities and eliminating thermal degradation
- Increase product recovery by reclaiming additional bottoms product from overhead and distillate products from bottoms
- Separation of close-boiling compounds
- Enhanced product recovery

Crystallization

Forced-circulation crystallizers are used to evaporate the water past the crystallization point. Crystals are dewatered and the resulting filtrate is returned to the crystallizer. Crystallization can be achieved by spray driers to overcome high solubility of certain salts. The clean condensate is returned to the process for reuse and the dewatered crystals are transported off-site for reuse or disposal.

Spray Drier: An evaporator combined with a spray dryer is an ideal solution for small quantities of waste water. The waste water is typically (but not necessarily) concentrated in a vapour recompression evaporator. The concentrated brine is fed directly into a spray dryer. During spray drying, an enormous heat and mass transfer takes place within a fraction of time.

Spray drier starts with the atomization of a liquid feedstock into a spray of droplets. The small droplets are created by an atomizer - either a rotary wheel or a high pressure nozzle, rotating atomizer is selected for ZLD applications due to the often viscous, crystalline, harsh and corrosive nature of the feed.

The droplets are introduced into a hot airstream, which is cooled down due to the evaporation of the water from the concentrate. This now colder and humid air is discharged from the dryer through a cyclone, bag filter or a combination of the two. After separation of the now dry particles, the air is discharged into the atmosphere and the dry particles (solids) can be cooled and suitably disposed.

Although the spray drier is low in cost as compared to MEE /incinerator, it has disadvantage of possible release of dioxins and furans due to lower operating temperatures.

Liquid-Liquid Extraction (LLE)

Liquid-liquid extraction (LLE) is an important separation technology, with a wide range of applications in the modern process industry. LLE also known as solvent extraction and partitioning, is a method to separate compounds based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent.

The extraction process is based on different solubilities of components in two immiscible, or partially miscible, liquids. The components that need to be recovered are extracted from the feed stream with the help of an extractant (often called solvent). Both liquids have to be thoroughly contacted and subsequently separated from each other again. To achieve high purities and yields, it is necessary to operate with multiple stages and with the liquids flowing counter-currently.

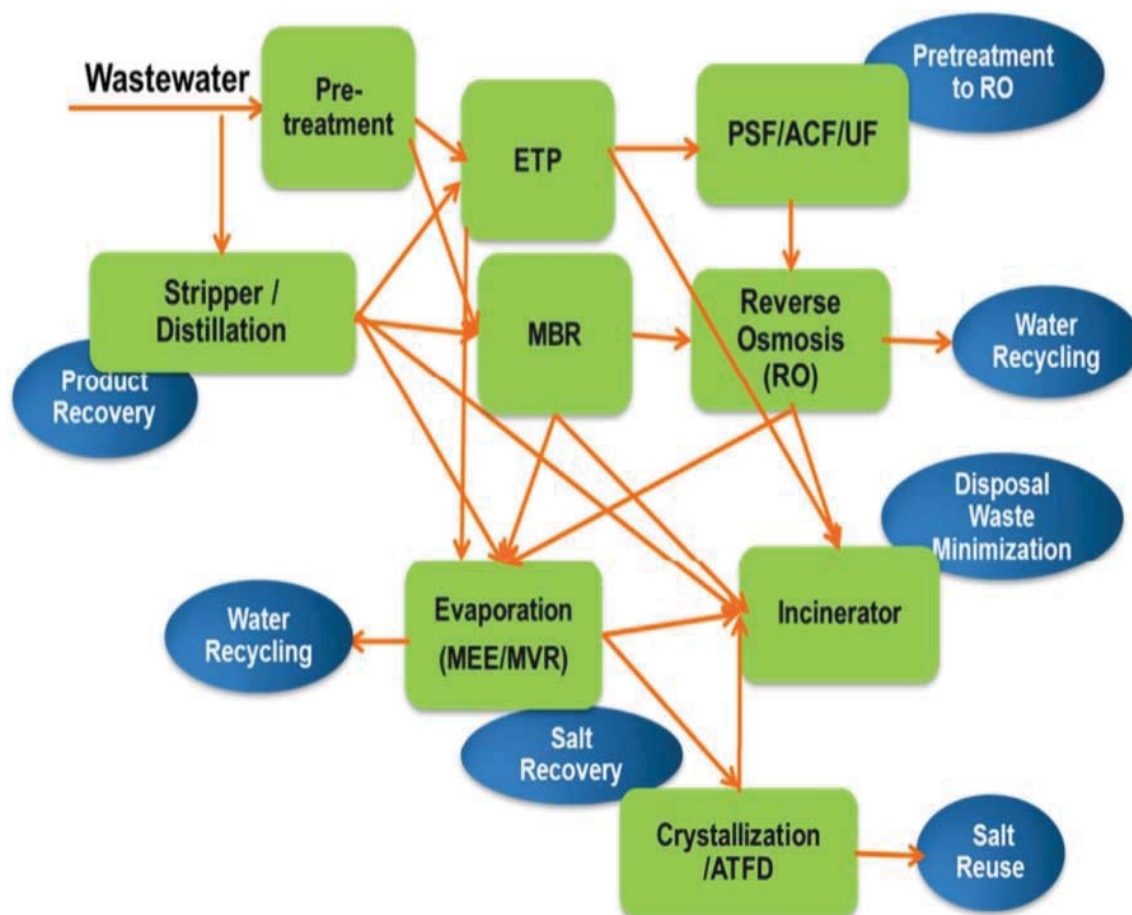
2.3 Configuration & Comparative Assessment of ZLD Technologies

ZLD technologies can be applied to various sectors of industries depending on the quantity of waste water, characteristics of waste water streams and sources of generation, recycle and reuse potential for water and salt, etc. ZLD technologies can be used in variety of combinations with ultimate objective of:

- 1) Recovering useful material,
- 2) Recovering and recycling maximum water and
- 3) Management of reject by evaporation and drying methods.

An optimal ZLD system needs to be developed according to type of waste water to be treated. A decision matrix shown in fig. 2.44 is developed as a guideline for applicability of ZLD technologies in various sectors of industries as well as to assess the economic feasibility with various combinations of ZLD technologies and their interconnectivity.

Fig. 2.44: Various combinations of ZLD Technologies for different application



Detailed Technology evaluation sheet is included in this manual.

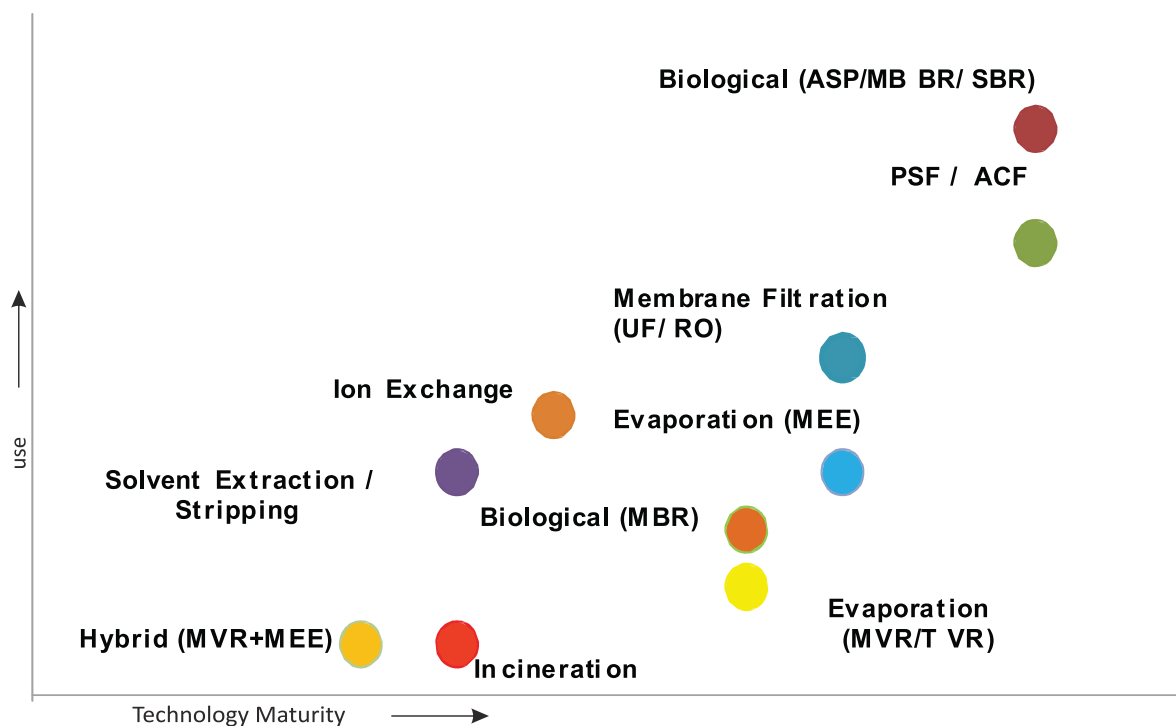
ZLD Technologies Matrix for selection:**Table 2.8**

ZLD Technology	Used for	Advantages	Disadvantages	Type/M OC/ Components	Applicable for
Membrane Bio Reactor (MBR)	Used as biological secondary treatment for reduction of organic load (COD/BOD)	Secondary clarifier not required Treated water quality is better than conventional ASP, MBBR and SBR Post treatment of sand filtration not required	Capital cost is more than other aerobic biological technologies (ASP, SBR, MBBR) Membrane replacement after five years	hollow fiber Membranes Pore size 50-10,000nm Pressure < 2 bar Flux-50-500LMH	Textile industry CETPs Oil Refineries Fertilizer industry
Solvent Recovery-Air Stripper	Used for recovering solvents / Ammonia recovery by providing air	Conventional proven method for removal of solvents Economical when solvents with low solubility in water are present in waste water	Applicable only when large quantity of solvent with low solubility in water is present in waste water Difficult to capture solvent when in low concentration	Packed bed column air blowers	Recovery of useful solvents, ammonia in pharmaceutical industry pesticide industry Chemical industry.
Solvent Recovery-Steam Stripper	Used for recovering solvents by using steam Solvents can be reused or are saleable	Solvent recovery is more compared to air stripping Useful even less quantity of solvent present in wastewater	Not suitable for water miscible, high boiling solvents Scaling occurs in column which is to be cleaned periodically	Packed bed or grid trays in column Steam used	Recovery of useful solvents, ammonia in pharmaceutical industry pesticide industry Chemical Industry.
Ultra Filtration (UF)	Used for removal of colloidal matter and bacteria and viruses Used as pre-treatment to RO	Removes suspended, colloidal particles, bacteria, viruses. Best pre-treatment for RO	Does not filter dissolved solids, gases and organics. Frequent Backwash, membrane cleaning Replacement of membranes after 5 years required	Hollow fibre membranes MOC : PVDF, PP, PAN Pore size:1-100 Pressure: 1-10 bar Flux: 10-200LMH	pre- treatment to RO in all ZLD plants
Reverse Osmosis (RO)	Used for removal of salinity (TDS) and residual organics by passing wastewater through semipermeable membrane by applying high pressure	Most Effective treatment for removal of salinity (TDS) with more than 99% salt rejection Clean technology and no handling of chemicals like acid/alkali like ion exchange technology Permeate water is free of ions and can be used in industrial processes	Very high capital cost High energy consumption due to high pressure pumps Membrane replacement required after app. 3 years Cleaning of membrane frequently due to Membrane fouling Reject water	Polyamide with a polysulphone support layer Pore size : < 1nm Pressure: 10-80 bar Flux: 5- 100LMH	Used in all industrial sectors for TDS removal and recycling the water

Multiple Effect Evaporator (MEE)	Used to evaporate wastewater to separate water and salt by using heat of steam in sequence of vessels	Proven method for recovery of water from saline water and separation of salt	Very high Operating cost due to steam requirement	MOC: SS 304, SS316, SS 316L, SS316TI, Titanium	Pharmaceutical Industry, Textile Industry, Pesticide industry, Dyes & Dye intermediates, Steel Industry, Fertilizer industry
Mechanical Vacuum Compressor (MVR)	Water vapour generated in the evaporator is compressed to higher pressure which acts as heat source for evaporation	Eliminates thermal energy requirement Useful when steam not available Low operating cost	Suitable only for liquid with narrow boiling point rise (BPR) Suitable when ready steam is not available in the industry	Conventional :SS 316/Titanium Advance d: Polymer	Textile industry
Crystallizer	Used to dry high TDS water or products using heat	Used for recovery of salts like Sodium Sulphate, Sodium Chloride, Sodium Thio-Sulphate, Zinc Sulphate etc.. Simple evaporation method of single effect evaporation	Scaling and corrosion of unit is a problem Requires frequent cleaning	SS 304 / SS 316	All industrial sectors
Agitated Thin Film Dryer (ATFD)	Used to dry high TDS water or products using fast revolving rotor in a heating jacket.	Good heat conductivity, so can be applied for highly viscous fluids Gentle evaporation and high evaporation rate Continuous cleaning of heating surface One pass evaporation	Scaling and corrosion of unit is a problem	SS 304 / SS 316	Applicable for Salt recovery in Dye & Dyes intermediates Textile industry Pharmaceutical industry for final drying before disposal
Incinerator	Used for burning the concentrated effluent by thermal energy	Useful method for very high strength (High COD) effluent which is difficult to biodegrade No further treatment is required	Requires very high energy Operational cost is high Capital cost is high Viable for only small quantities of effluent	SS3016 incinerator with air pollution control system	Pharmaceutical industry Dye and Dye intermediates Pesticide industry

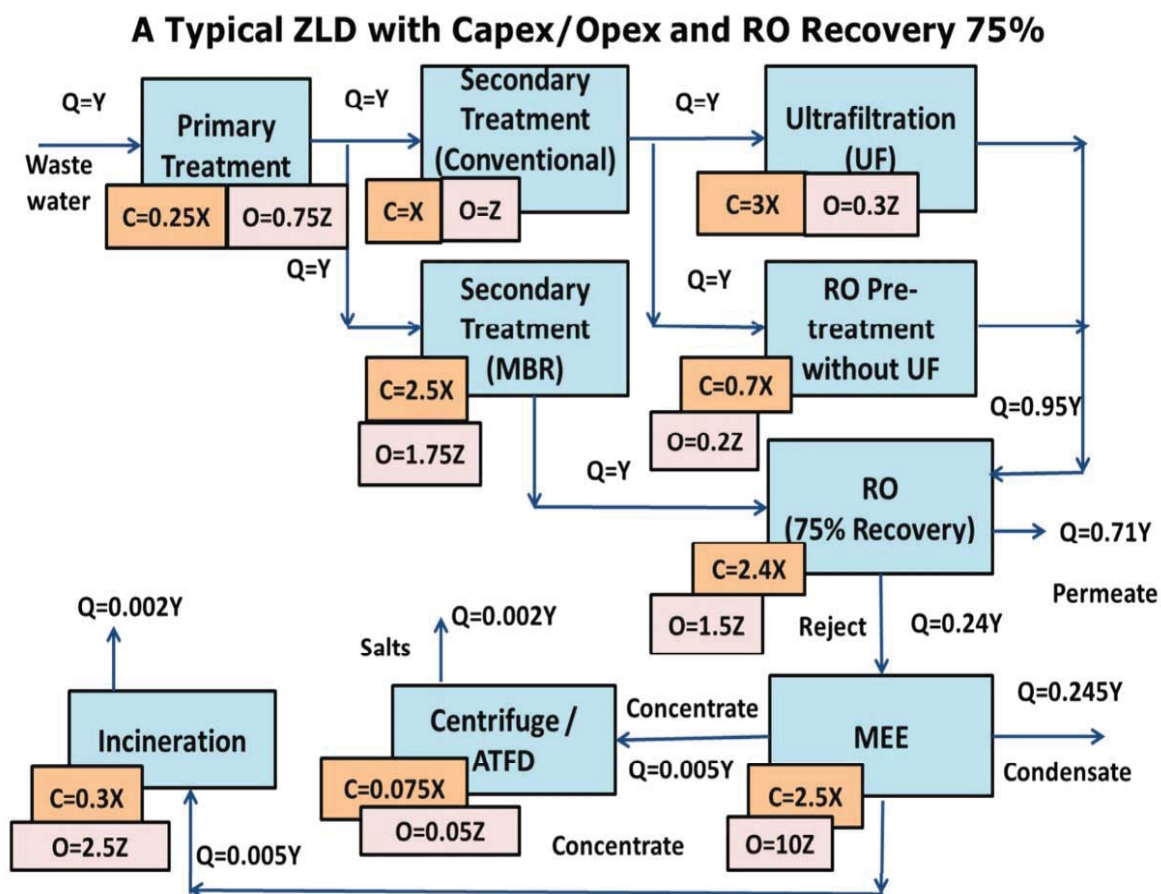
Fig. 2.45 provides a complete assessment of ZLD technologies, based on maturity, depending on the extent of recovery desired.

Fig. 2.45: Technology Maturity Graph



Note: Technology Maturity is based on the application experience.

Fig. 2.46: ZLD with 75% RO recovery



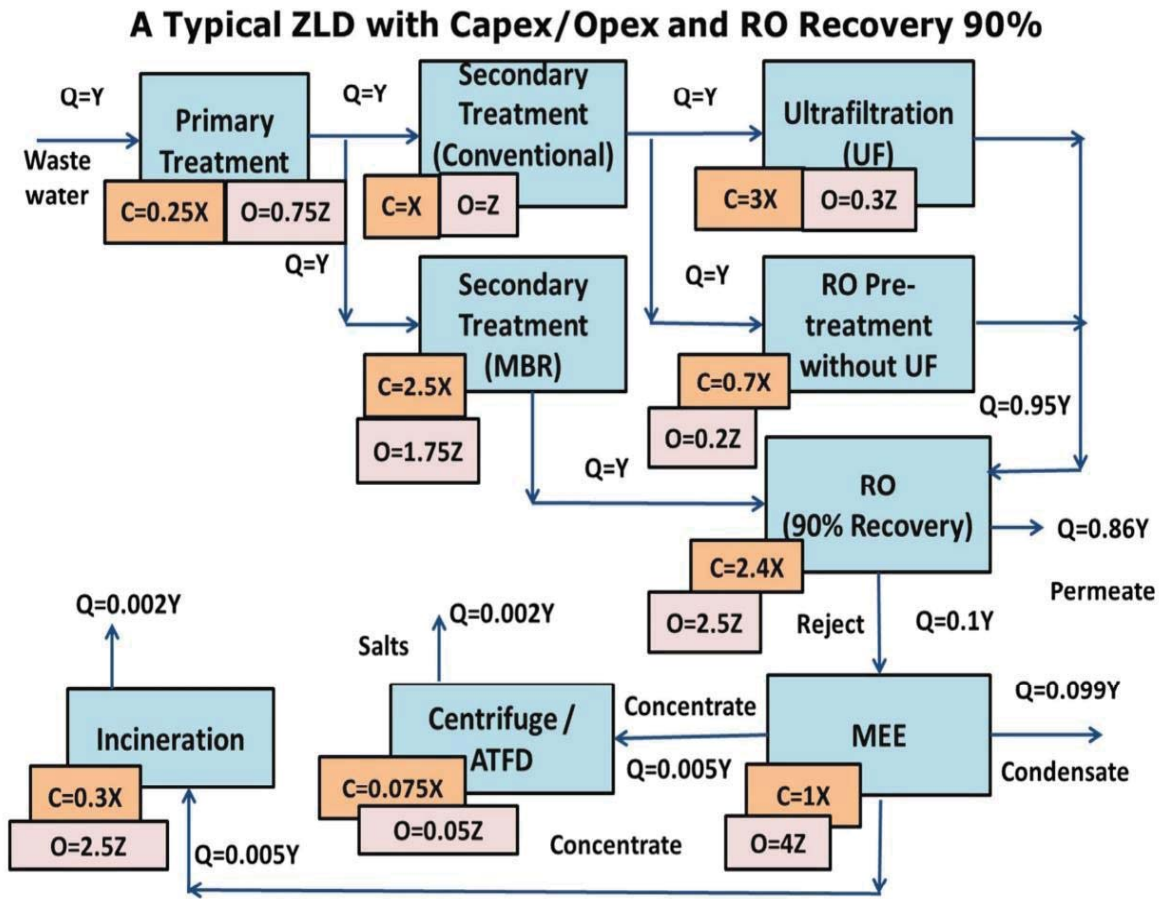
Note : Q = Flow (KLD/MT); C & O =Capex & Opex costs are proportionate to respective Q to unit

C = Capital Cost represented as 'X'

O = Operating Cost represented as 'Z'

Q = Flow represented as 'Y'

Fig. 2.47: ZLD with 90% RO recovery



Note : Q = Flow (KLD/MT); C & O =Capex & Opex costs are proportionate to respective Q to unit

C = Capital Cost represented as 'X'

O = Operating Cost represented as 'Z'

Q = Flow represented as 'Y'

INDUSTRIAL APPLICATION OF ZLD

3.1 Pharmaceutical Industry

The pharmaceutical industry can be divided into two major segments – Bulk drug and formulations. Bulk drugs are the active pharmaceutical ingredients (APIs) with medicinal properties, which are used to manufacture formulations. The Indian pharmaceutical industry manufactures about 400 bulk drugs belonging to various therapeutic segments. Formulations are the end-products of the medicine manufacturing process, and can take the form of tablets, capsules, injectable or syrups.

Major sources and characteristics of effluent

ZLD technologies are mostly applied to API manufacturing industries. The production of special niche API brings with it the problem of specific type of pollutant in the effluent. The effluent parameters vary with the niche of product and hence there is no single solution common for all. Pollution control boards are being very strict on the API industry for effluent release outside the premises and are being pushed to adopt ZLD regime. Active Pharmaceutical Ingredients from waste water streams are the emerging contaminants in the aquatic environment, because of their adverse effect on aquatic life and humans. The waste from API industries contains high COD, high TSS, other harmful chemicals and high amount of salt along with various nascent chemicals such as bromine & chromium. The chemicals present in the effluent is dependent on the product being processed at the manufacturing facility and hence a tailor made solution is required for making each API manufacturing facility ZLD compliant.

Major sources of generation of waste water from API industry are:

1. Lean Stream (Low COD-Low TDS)
 - a) Process Plant - From reactor washings (second washing onward)
 - b) Waste water from utilities such as – From DM plant regeneration, RO reject, cooling tower blow down, Boiler Blow down, etc.
 - c) Floor washings
2. Mother Liquor Streams (High COD-High TDS, High TDS- low COD, High COD-low TDS)- From Process plant – product separation, First washings of reactors
3. Mother Liquor Stream (high Solvents) - From process plant comprising solvent reactions
4. Mother Liquor Stream (high Ammonia) - From Process plant comprising ammoniacal nitrogen reactions

Note: High COD >5000 mg/l, High TDS >5000mg/l, Low COD <5000mg/l, Low TDS <5000mg/l. Lean flow is usually 100 to 300KLD depending on size of industry. Mother liquor stream flow is very small (10 to 30KLD).

Treatment of Waste water

Since there are various sources of effluent generation with varying characteristics, the first objective is to segregate the streams at source.

A typical treatment of segregated streams is as follows:

- Low COD-Low TDS streams: Taken to Effluent Treatment Plant (ETP) for primary, secondary biological treatment (ASP/MBR/SBR) and then to tertiary treatment of sand filtration/UF and RO.
- ML-1: Mother Liquor Stream: (High COD-High TDS, High TDS-low COD, High COD-low TDS): Taken to evaporator (MEE) for concentration of the stream. Distillate from MEE is routed to ETP, if not of recyclable quality.
- ML-2: Mother Liquor Stream (with solvents): Taken to Solvent Stripper for recovering solvent
- ML-3: Mother Liquor Stream (high NH₃): Taken to NH₃ Stripper for removal of ammonia. Or it is treated with high grade (>95% lime) and Calcium sulphate is isolated and sent to cement industry.
- It is observed that while effluent with high NH₃-N content owing to inorganic ammonia may be treated as above but the effluent containing NH₃-N owing to organic content may require incinerations or its segregation for further purification.
- RO permeate is recycled back in process, cooling tower, boiler make up water.
- RO rejects are concentrated in MEE, dried by crystallizer / ATFD and mixed salt sent to TSDF.
- Sludge from ETP is dewatered and sent to TSDF

ZLD treatment options:

Figures 3.1.1, 3.1.2 & 3.1.3 present various options for the configuring ZLD systems for the pharmaceutical industry.

Fig. 3.1.1: Option 1 - ZLD for Pharmaceutical Industry

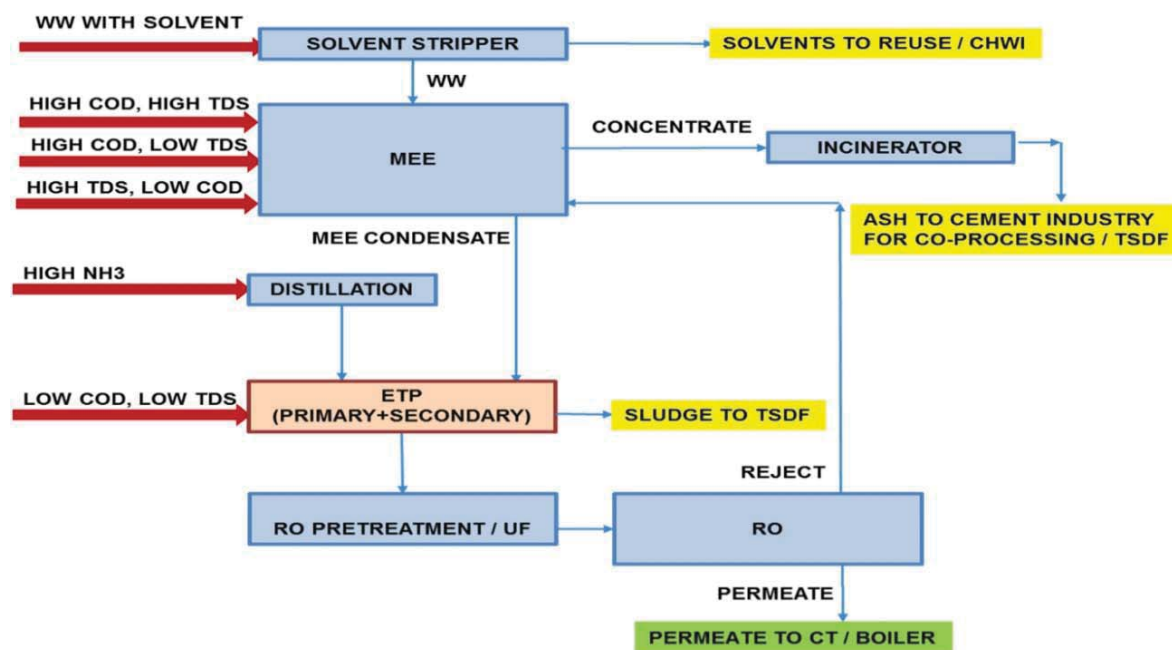
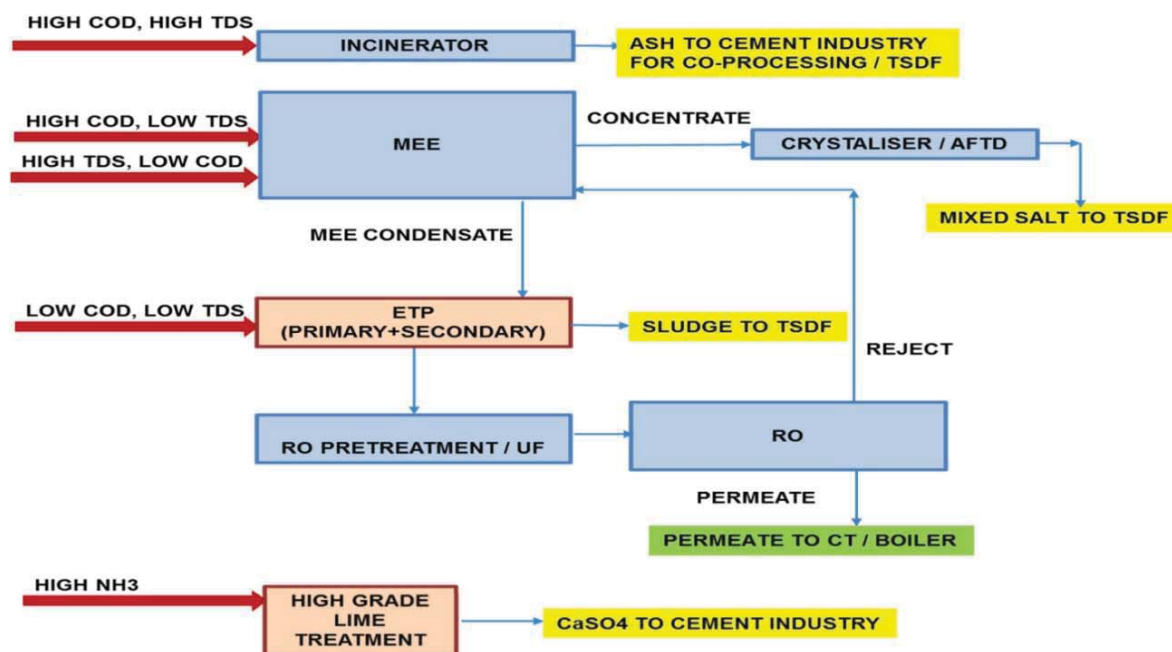


Fig. 3.1.2: Option 2 - ZLD for Pharmaceutical Industry

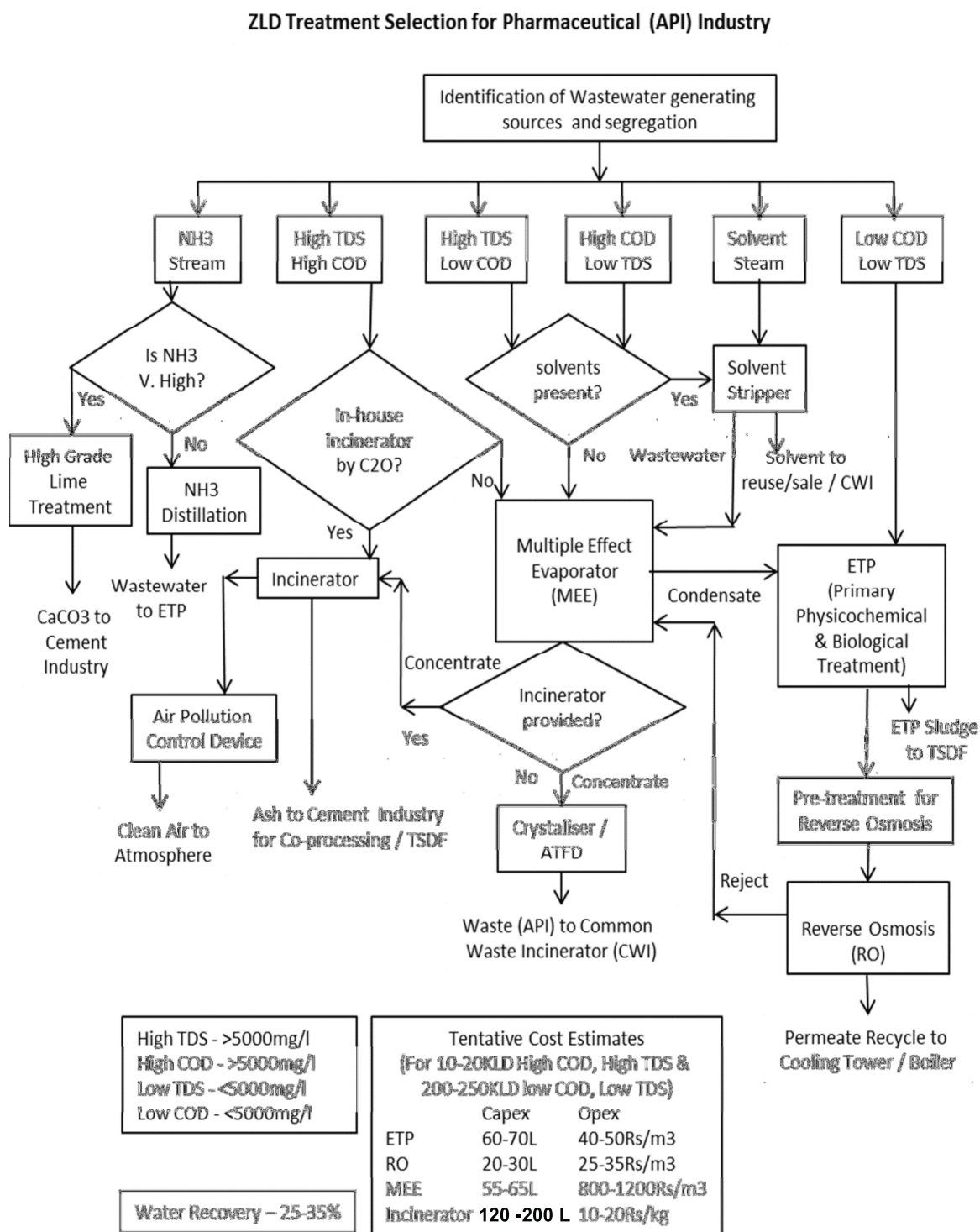


68



Figure 3.1.4 provides decision tree for arriving at optimum ZLD configuration for pharmaceutical industry

Fig. 3.1.4: Selection of ZLD Treatment for Pharmaceutical Industry



3.2 Textile Industry

Textile industry can be classified into three categories: Cotton, woolen and synthetic based on raw material used. The textile dyeing industry consumes large quantities of water and produces large volumes of waste water from different steps in the dyeing and finishing processes. Textile units use a number of dyes, chemicals and other materials to impart desired quality to the fabrics.

These units generates a substantial quantity of effluents, the quality of which in most of the cases is unsuitable for further use and can cause environmental problems, if disposed without proper treatment. Due to the increasing resource constraints and the environmental requirements, these textile units need to adopt a sustainable approach, while waste need to be viewed as unutilized resources. Ways and means must be found to recover water and chemicals from these “waste” resources.

Advanced treatment methods, like membrane filtration, not only help in reducing the pollution but also provide a scope for recovery and recycling of water and chemicals. Waste water from printing and dyeing unit is always rich in colour, reactive dyes, chemicals and refractive organic matter. It is a complex mixture of inorganic and organic compounds. In synthetic fiber mills use of cooling water is quite high. Final rinse water after mercerizing, bleaching and dyeing is slightly contaminated and can be recycled for further rinsing.

Major Sources of wastewater generation: Following are the processes generating wastewater

Table 3.1

Process	Effluent composition	Characterstics
Sizing	Starch, waxes, carboxy methyl cellulose (CMC), polyvinyl alcohol (PVA), wetting agents.	High in BOD, COD
De-sizing	Starch, CMC, PVA, fats, waxes, pectin	High in BOD, COD, TSS, Total dissolved solids (TDS)
Bleaching	Sodium hypochlorite, Cl ₂ , NaOH, H ₂ O ₂ , acids, surfactants, NaSiO ₃ , sodium phosphate, short cotton fiber	High alkalinity, high TSS
Mercerizing	Sodium hydroxide, cotton wax	High pH, low BOD, high TDS
Dyeing	Dyestuffs urea, reducing agents, oxidizing agents, acetic acid, detergents, wetting agents.	Strongly coloured, high BOD, TDS, low TSS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, thickeners, cross-linkers, reducing agents, alkali	Highly coloured, high COD, oily appearance, TSS slightly alkaline,

Treatment of waste water

Waste water from dyeing and printing processes is rich in colours which are many times not bio-degradable and difficult to treat. Mercerizing waste water has high concentration of salts in waste water. It is necessary to segregate the streams. Initial dye bath stream shall be separated from other streams. The dye bath stream is 10-15% of total waste water. Dye bath after primary treatment can be directly treated in evaporation technology for reduction of volume. Condensate is recycled in process.

Other waste water is treated with primary physic-chemical treatment followed by biological treatment. After biological treatment waste water is processed through pressure sand and activated carbon filters. Then water is subjected to UF/ RO system for recovery of water for recycling in process. Rejects from RO system are subjected to MEE process. Concentrated slurry from MEE is subjected to crystallizer/ATFD for further drying of salts. Glauber salt is recovered by chilling and then crystallizer. Glauber salt is reused in process again. Mixed salt is either reused or suitably disposed-off.

Proper selection and application of individual or combination of the advance treatment methods in textile industry can effectively make recovery of water and salts from effluent streams for their reuse in production process. Along with the recovery and reuse of water and salt, the advance methods can also be applied to meet stringent environmental or regulatory requirements such as zero effluent discharge. Membrane filtrations can produce treated water with high purity. The evaporator and crystallizer combination can recover salt.

The effluent stream bearing high salt i.e. the spent dye bath is segregated and treated for recovery of salt. This effluent stream has low volume and can be treated using a chemical treatment followed by multi-effect evaporation and crystallization. Glauber salt (Sodium Sulphate decahydrate) based dyeing enables recovery of the salt. The other effluent stream i.e. wash water can be treated separately by primary/secondary treatment methods followed by RO system to recover water.

Recovery

Water recovery is achievable up to 98% by using multistage RO system and proper operation of pre- treatment and evaporation technologies. Glauber salt is recovered from the system and is reused in the process

Following are ZLD treatment options for textile wastewater:

Fig. 3.2.1, 3.2.2 & 3.2.3 present various options for configuring ZLD system for textile industry

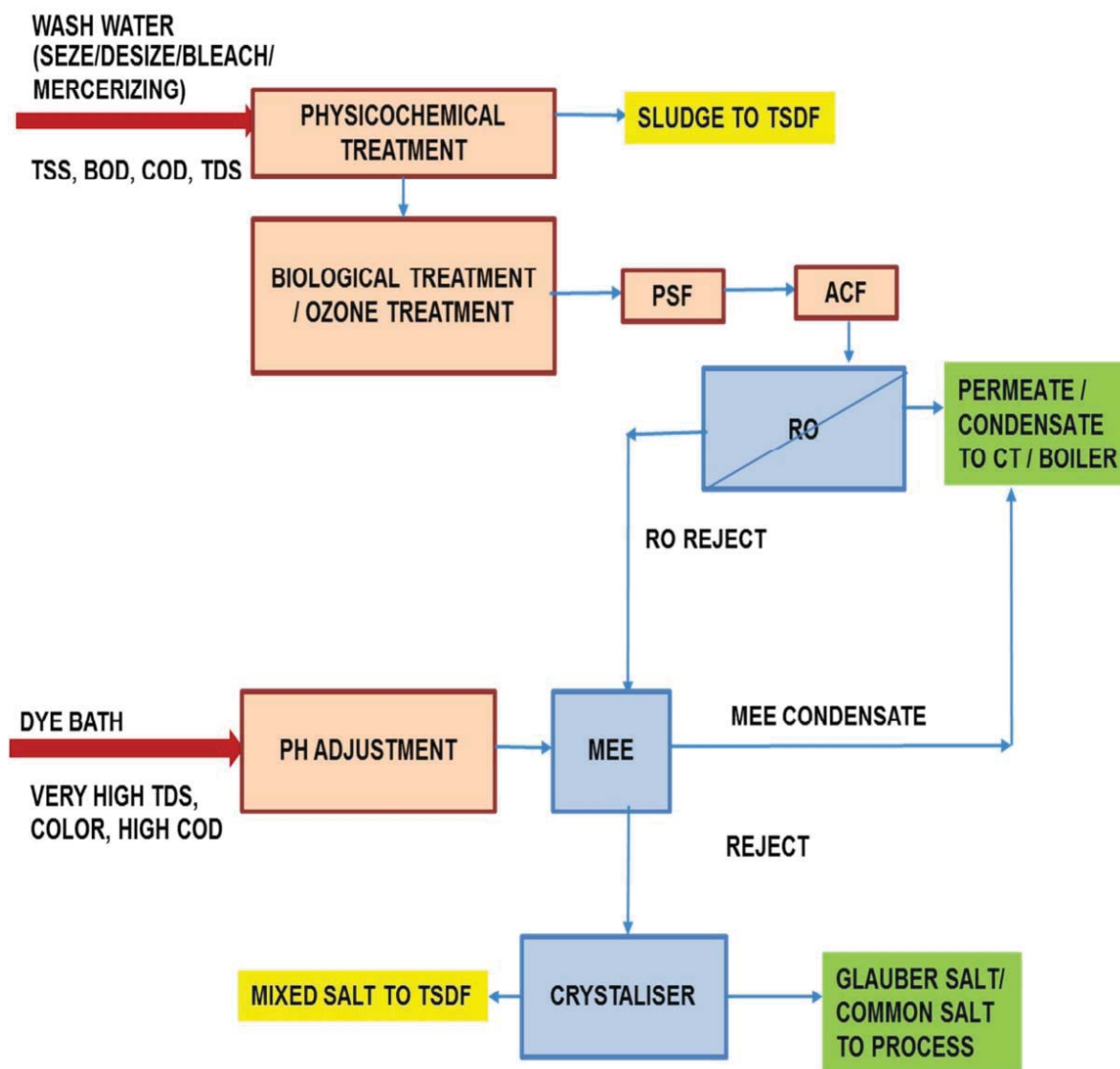
Fig. 3.2.1: Option 1: Textile ZLD system

Fig. 3.2.2: Option 2: Textile ZLD system

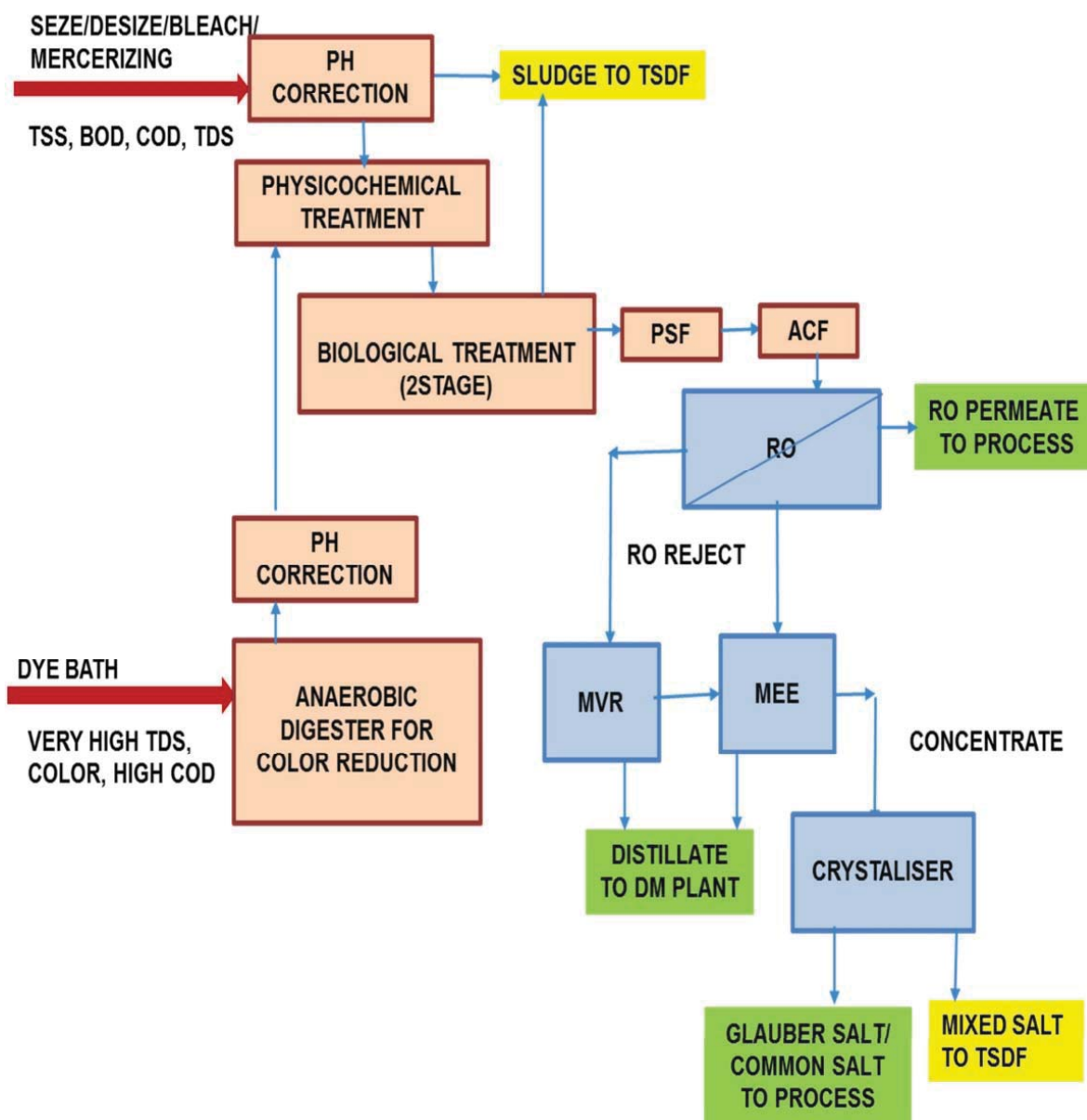


Fig. 3.2.3: Option 3: Textile ZLD system

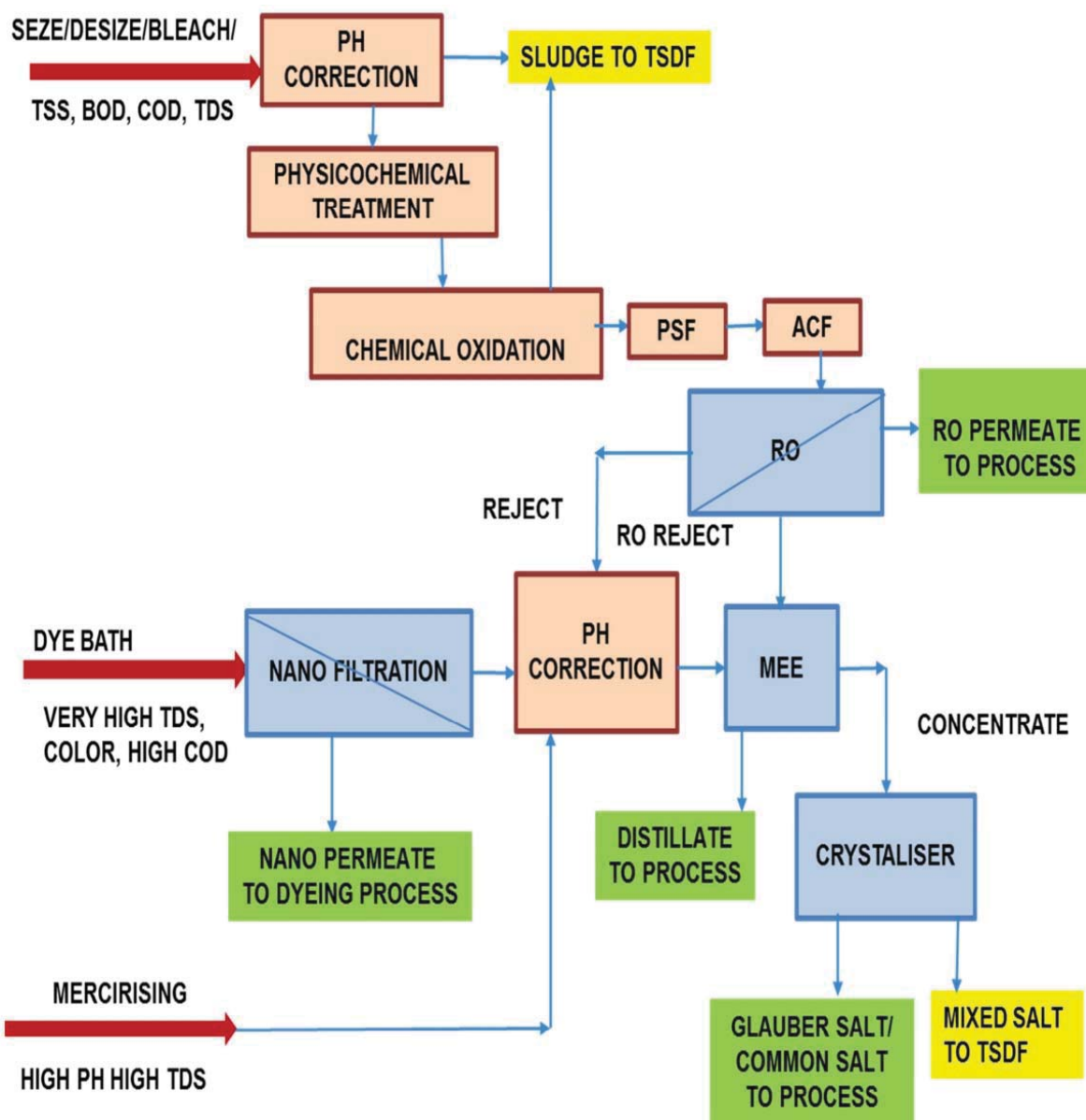


Figure 3.2.4 presents a typical material balance for ZLD system

Fig. 3.2.4

TYPICAL MASS BALANCE FOR 500 KLD TEXTILE ZLD

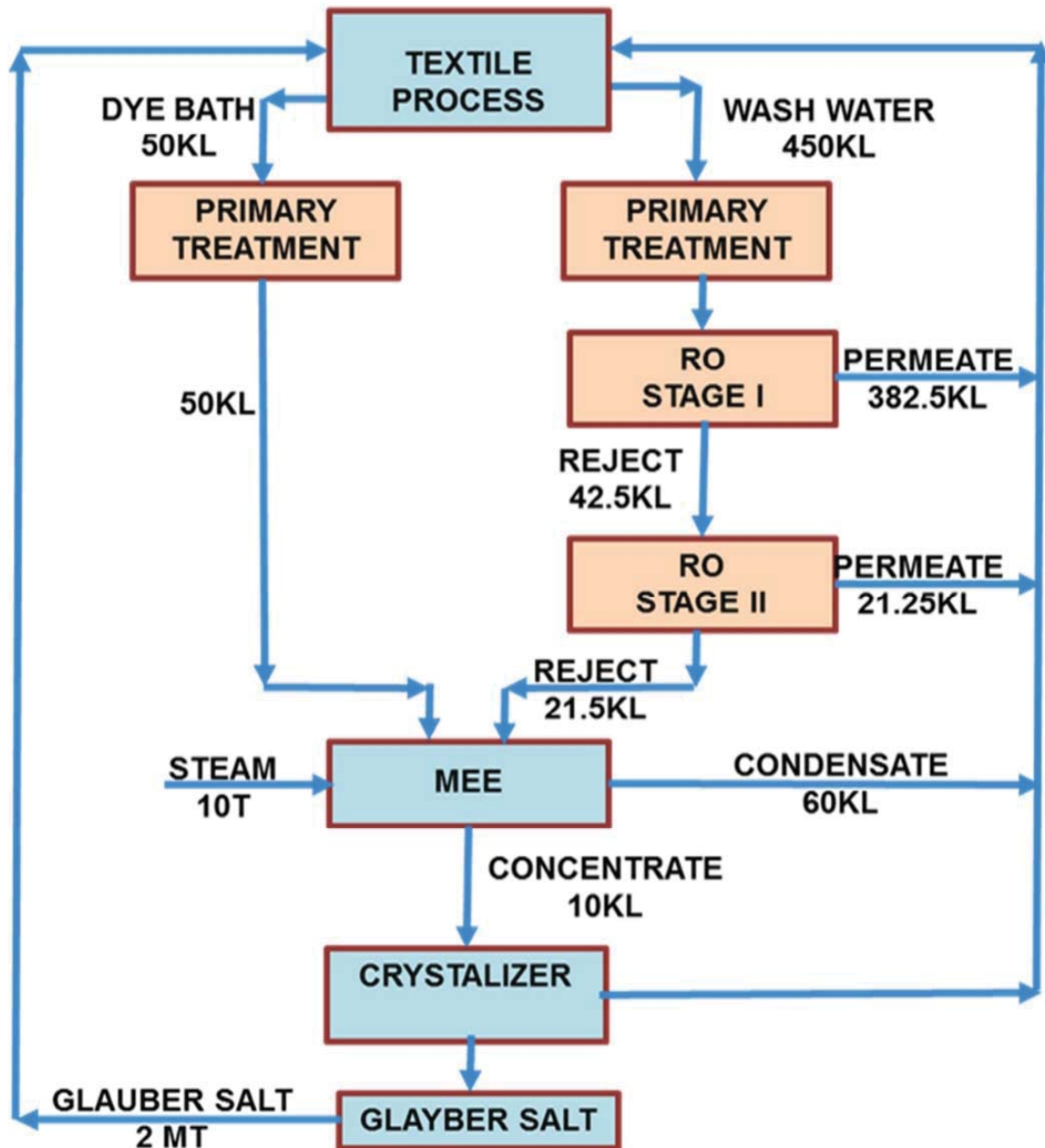
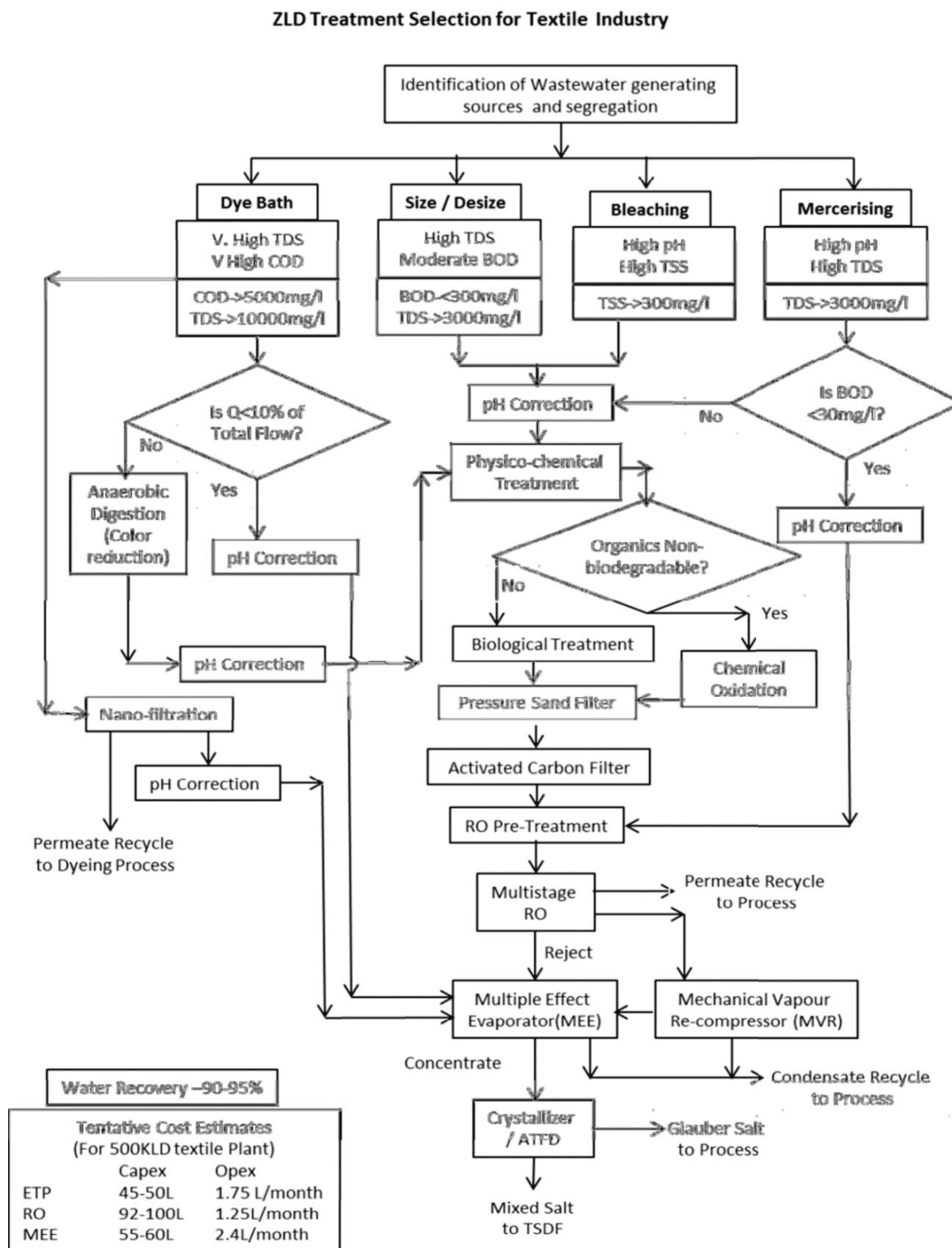


Figure 3.2.5 provides decision tree for arriving at optimum ZLD configuration for textile industry

Fig. 3.2.5: Selection of ZLD Treatment for Textile Industry



3.3 Dyes and Dye Intermediates

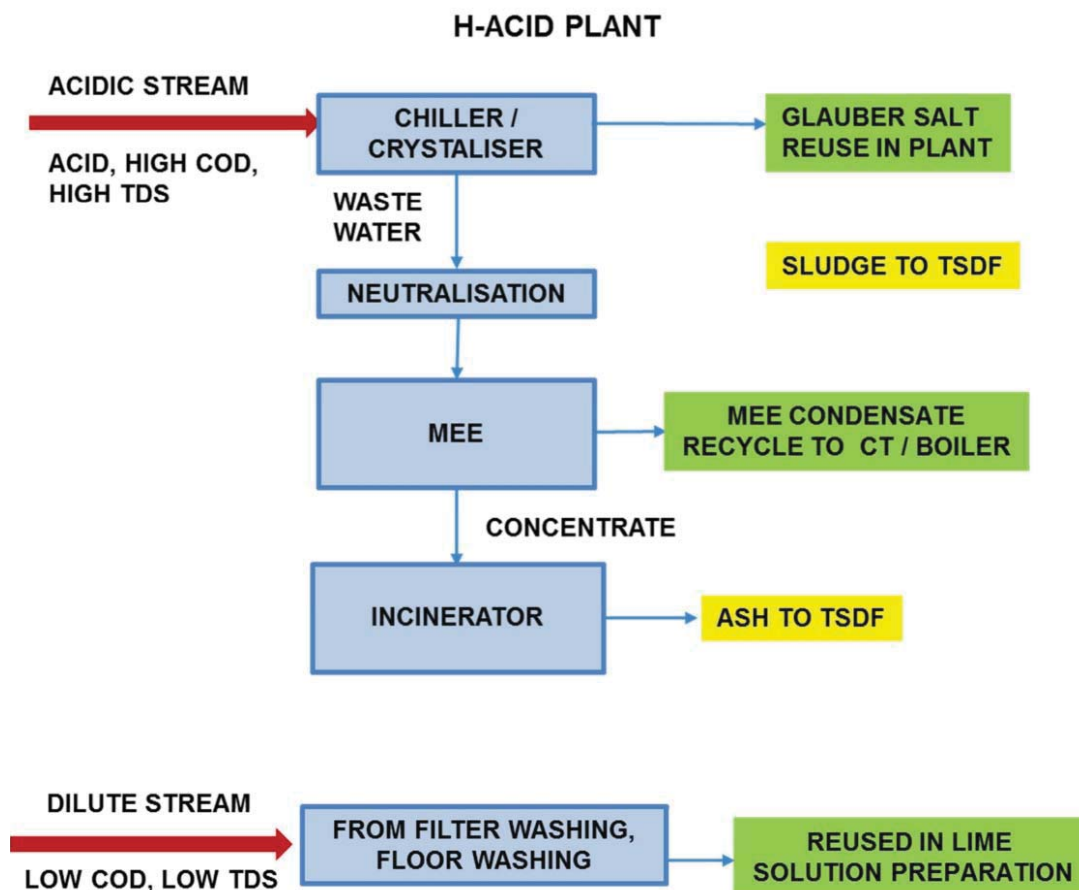
In dyes and Dye intermediates industry, H acid production and Vinyl Sulphone manufacturing are two major units.

H- Acid Plant: Manufacturing of H-acid involves various processes and generates two types of effluent. See fig. 3.10

Acidic Stream: This stream is generated from isolation stage of H-acid during Filtration and centrifugation process. Effluent generation is 15-18 ltrs /kg of product, having High COD and TDS values as Mother Liquor. This waste water is passed through crystallizer, where mother liquor is chilled to recover Glauber salt. The recovered Glauber salt is reused in H-acid manufacturing plant. Acidic waste water is then neutralized. The neutralized effluent is passed through the Multiple Effect Evaporator. Condensate generated is reused back in the process for hot water wash /cooling tower make up, and the concentrate having specific gravity 1.3-1.35 (high in organics), is incinerated or spray dried. Thus in above treatment there is recovery of Glauber salt which is reused in H acid manufacturing, reduction of salt in waste water for better MEE operation, reuse of condensate water from MEE. Concentrate from MEE is incinerated.

Dilute stream: This stream is mainly generated during gypsum cloth, filter washing and floor washings. This dilute stream is reused in lime solution preparation, gypsum washing, etc.

Fig. 3.3.1

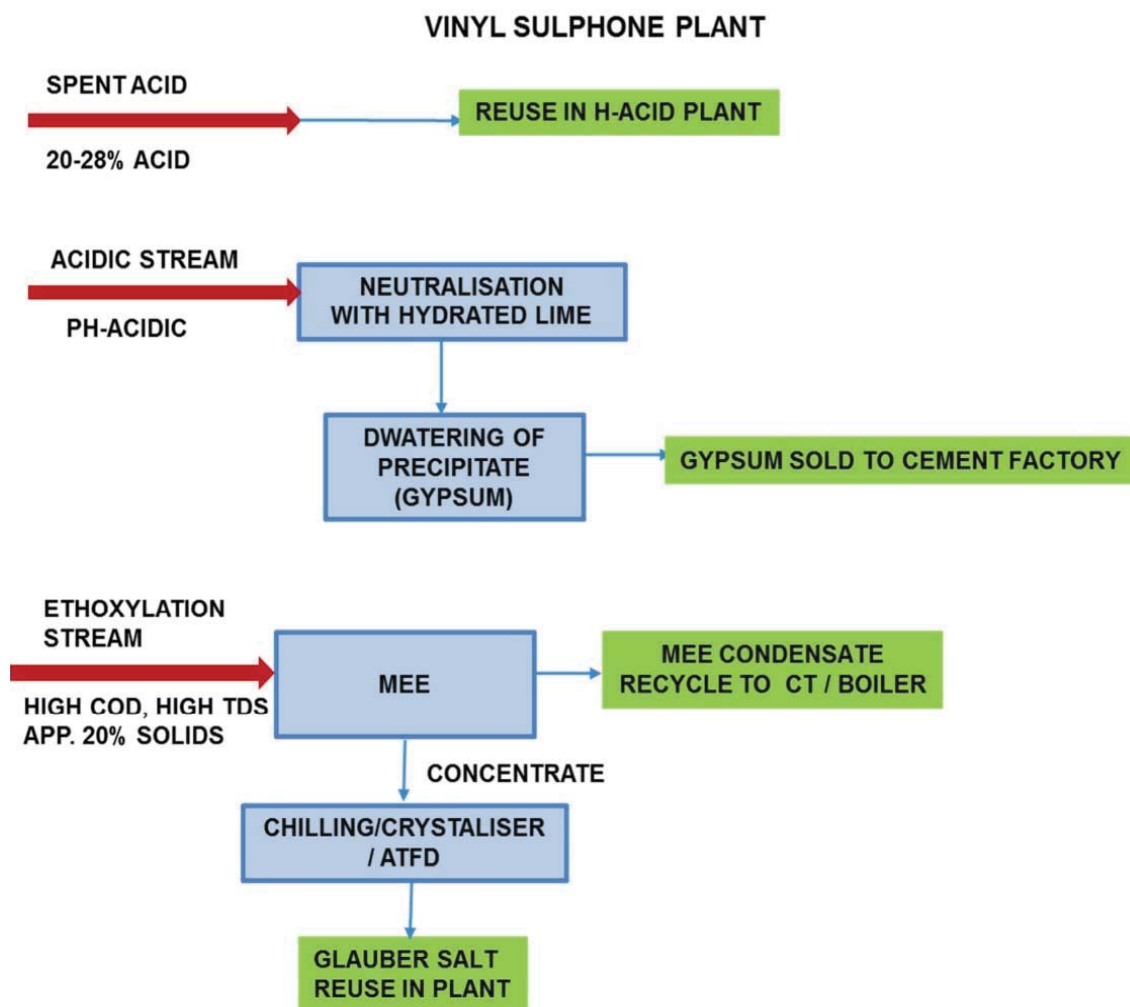


Vinyl Sulphone Plant: In the manufacturing of Vinyl Sulphone, effluent is generated at two stages. The stage one is of acidic effluent of Acetyl Sulphonyl Chloride (ASC) and stage two is neutral ethoxylation effluent. See fig. 3.11

Acidic Stream: Acidic waste water of 20-28% acidity sulfuric acid (6 ltrs/kg) is generated from drowning of sulpho mass in ice chilled water in ASC manufacturing. This spent acid effluent is reused in H-acid plant at isolation stage. Washings of ASC are neutralized with hydrated lime. The neutralized sludge is dewatered resulting in Calcium sulphate (Gypsum), which is sold to cement industry.

Ethoxylation Stream: The other stream is Ethoxylation waste water generated during the condensation stage of reduction mass with Ethylene oxide. The Ethoxylation waste water generated @ 6-6.5 ltrs/kg has high COD/TDS. The Ethoxylation waste water (20% solids) is passed through the Multiple Effect Evaporator to recover sodium sulphate (Glauber Salt) after chilling. Glauber salt is reused in dyes manufacturing. Condensate water from MEE is recycled back in cooling tower makeup.

Fig. 3.3.2



3.4 Chemical Industry

The chemical industry produces various industrial chemicals. Basic chemicals or "commodity chemicals" are a broad chemical category including polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic/organic chemicals, and fertilizers. The chemical industry is of importance in terms of its impact on the environment. Chemical industrial waste water usually contain organic and inorganic matter in varying concentrations. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or almost not bio-degradable. This means that the waste water also contains a wide range of substances that cannot be easily degraded.

There are various chemical processes carried out in manufacturing of chemicals depending on the type of chemical produced. Generally for pesticide, aromatic chemicals manufacturing industry wastewater is broadly divided into high strength and low strength wastewater streams.

High strength wastewater streams:

- a) High TDS (>10,000 mg/L) with High COD (non-volatile organics >10,000mg/l)
- b) High TDS (>10,000 mg/L) with High COD (volatile organics > 10,000mg/l)
- c) High TDS (>10,000 mg/L) with low COD (volatile organics <10,000mg/l)
- d) High COD (volatile organics or mixed organics >10,000 mg/L) with low TDS (<10,000mg/l)
- e) High COD (non-volatile non-biodegradable organics >10,000 mg/L)
- f) Very High COD (>10% volatile organics, 1,00,000mg/l) low TDS (<10,000mg/l)
- g) Very High COD (>10% non-volatile organics) with Very high TDS (>1,00,000mg/l)

Low strength wastewater streams:

- a) Low TDS (<10,000 mg/L) without organics
- b) Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) without volatile organics
- c) Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) with volatile organics (solvents)

ZLD Treatment Scheme:

It is necessary to identify, characterize and segregate the streams before treating. High strength streams are usually from various chemical processes, first washings of reactors, etc. Lean or low strength streams are generally utility streams such as cooling tower and boiler blow-downs, DM water plant regeneration, rejects from RO, and process plant reactor washings and floor washings, etc. Treatment of each stream is given below.

High strength waste water treatment:

- ❖ High TDS (>10,000 mg/L) with High COD (non-volatile organics >10,000mg/l): Multiple-effect Evaporator with dewatering of residual salt; this stream can be mixed with RO Reject
- ❖ High TDS (>10,000 mg/L) with High COD (volatile organics > 10,000mg/l): Single effect Evaporator with dewatering of residual salt and thermal oxidation of vapours (for air pollution control). Heat can be recovered by pre-heating the vapours using exhaust gases.
- ❖ High TDS (>10,000 mg/L) with low COD (volatile organics- <10,000mg/l): Multiple-effect Evaporator with dewatering of residue and treatment of condensate in bio-treatment system.
- ❖ High COD (volatile organics or mixed organics >10,000 mg/L) with low TDS (<10,000mg/l): Single-effect Evaporator with dewatering & incineration of residual salt and thermal oxidation of vapours (for air pollution control). Heat can be recovered by pre-heating the vapours using exhaust gases.
- ❖ High COD (non-volatile non-biodegradable organics >10,000 mg/L): Multiple-effect Evaporator with incineration of residue
- ❖ Very High COD (>10% organics, 1,00,000mg/l) low TDS (<10,000mg/l): Incineration, followed by heat recovery
- ❖ Very High COD (>10% non-volatile organics) with Very high TDS (>1,00,000mg/l): Multiple-effect evaporator with incineration of residue

Single-effect evaporator with thermal oxidation of vapours and dewatering of residual salts.

Low strength waste water treatment:

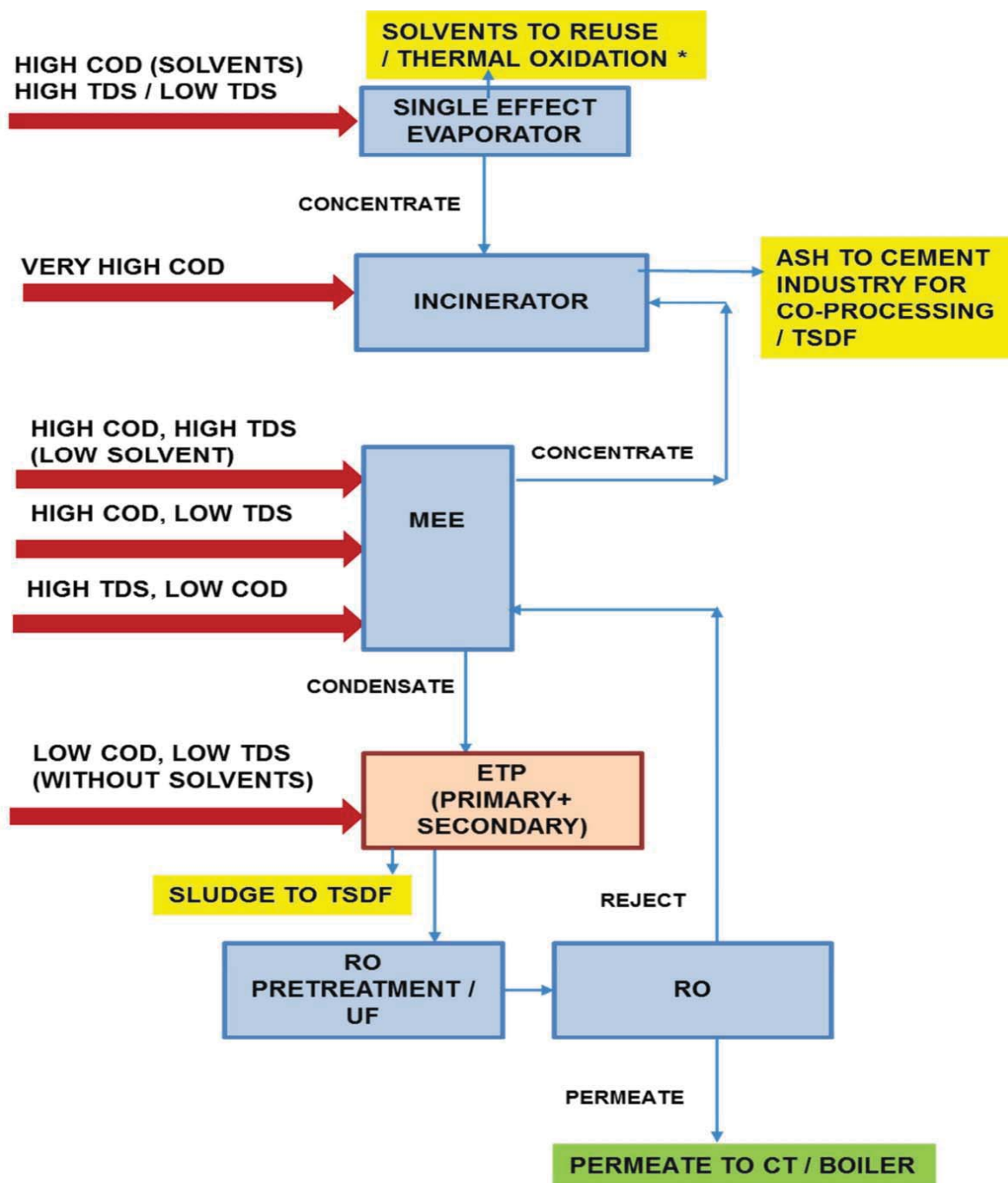
Low strength wastewater is first treated by primary and secondary treatment for removal of suspended particles and biodegradable organics. Further water is treated in tertiary treatment to remove TDS for recycling the permeate water is reused in the process. Rejects are treated by MEE and salt is dewatered by centrifuge / ATFD.

- ❖ Low TDS (<10,000 mg/L) without organics: Primary treatment for removal of TSS, metals and hardness, followed by ultrafiltration (UF) and Reverse Osmosis (RO). Reject from RO to MEE.
- ❖ Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) without volatile organics: Primary treatment for removal of TSS, metals and hardness, followed by MBR and RO. Reject from RO to MEE.
- ❖ Low TDS (<10,000 mg/L) with low COD (<10,000 mg/L) with volatile organics (solvents): Solvent stripper followed by Primary treatment for removal of TSS, metals and hardness, followed by membrane bio reactor (MBR) and Reverse Osmosis (RO). Reject from RO to MEE.

Primary treatment for removal of TSS, metals and hardness, followed by high rate bioreactor followed by membrane bio reactor (MBR) and Reverse Osmosis (RO). Reject from RO to MEE.

Figures 3.4.1, 3.4.2 & 3.4.3 present various options for configuring ZLD system for chemical industry

Fig. 3.4.1: Option 1: ZLD system for Chemical Industry



NOTE: * - THERMAL OXIDATION WITH STIPULATED AIR POLLUTION CONTROL NORMS

Fig. 3.4.2: Option 2: ZLD system for Chemical Industry

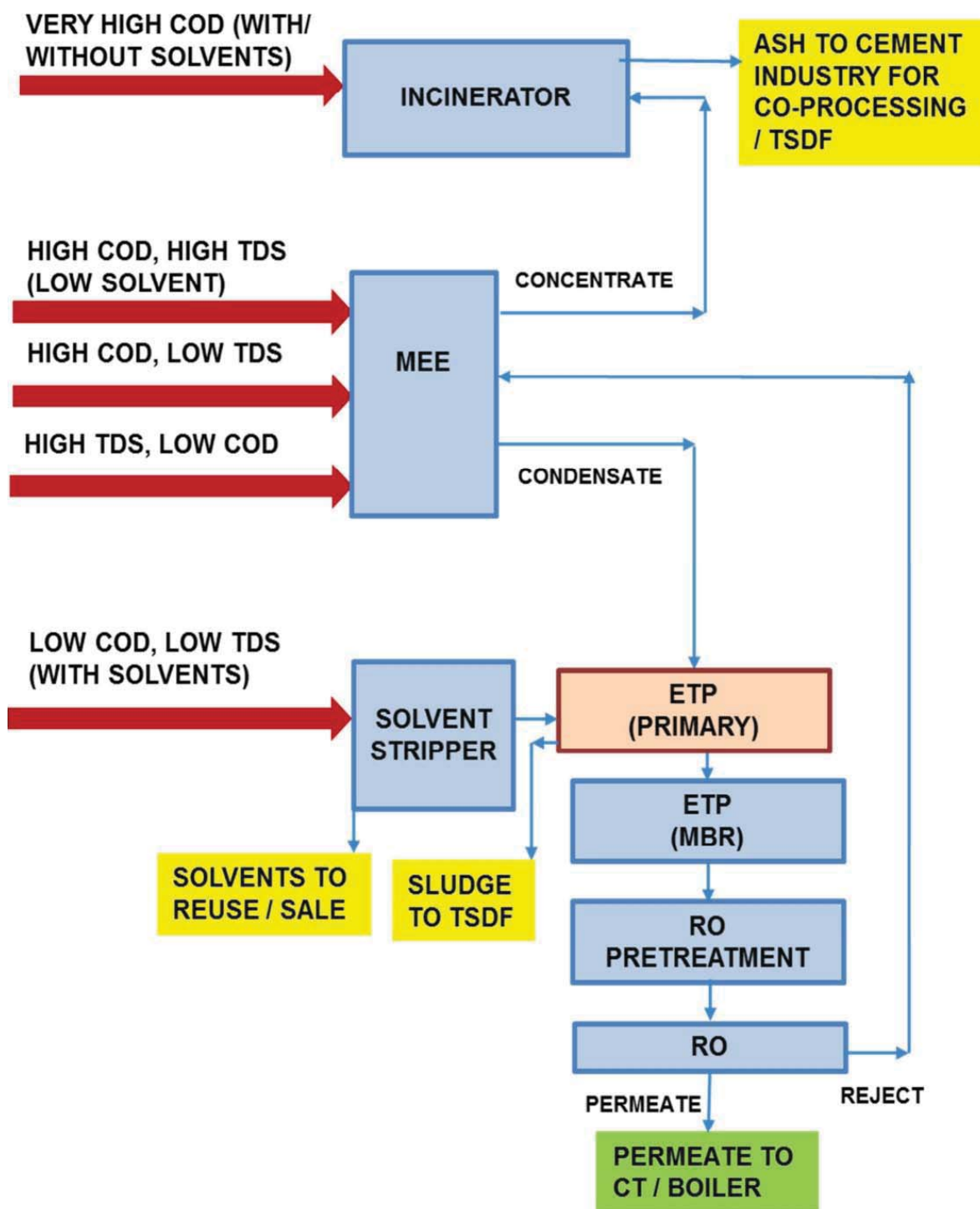


Fig. 3.4.3: Option 3: ZLD system for Chemical Industry

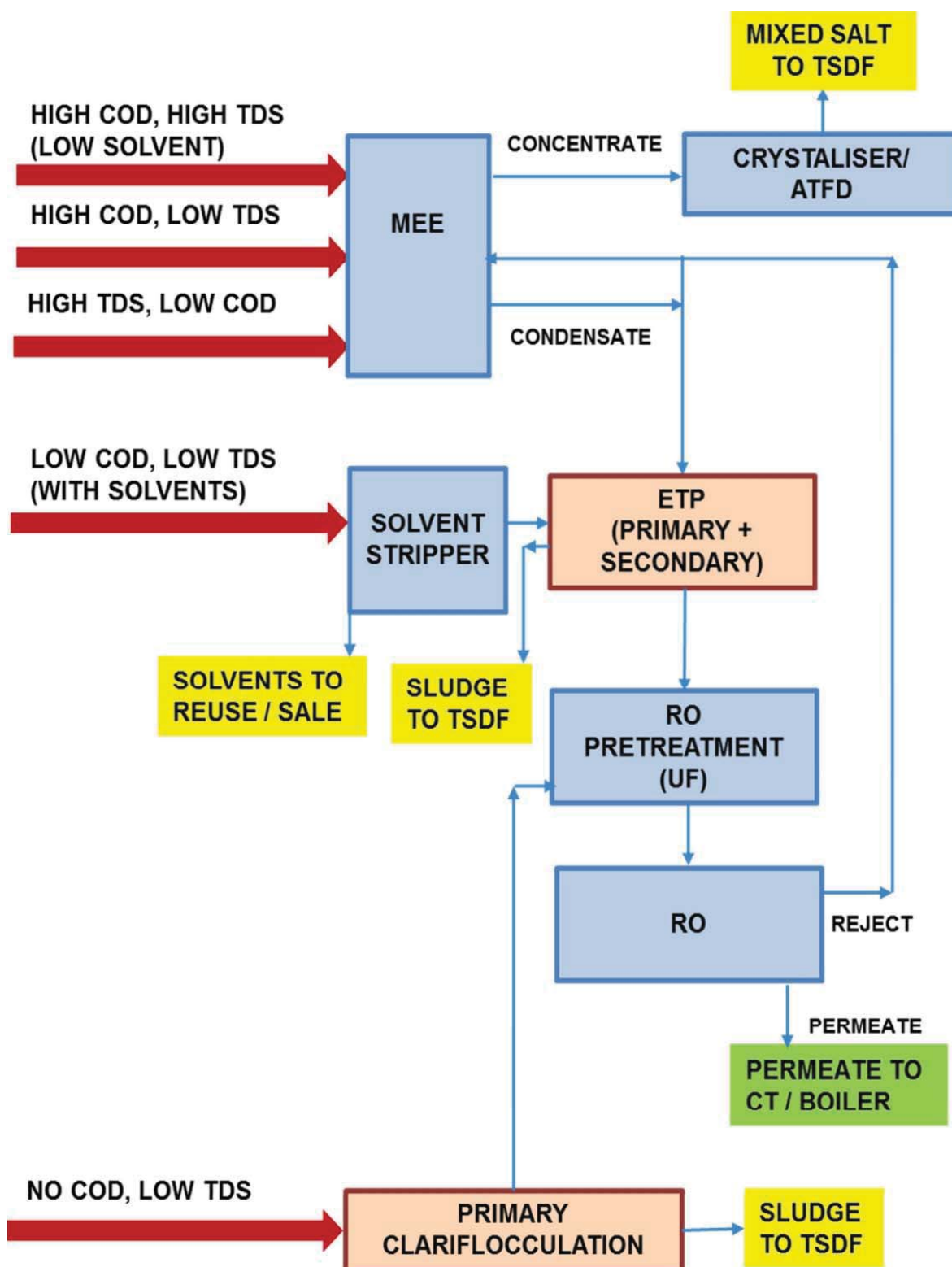
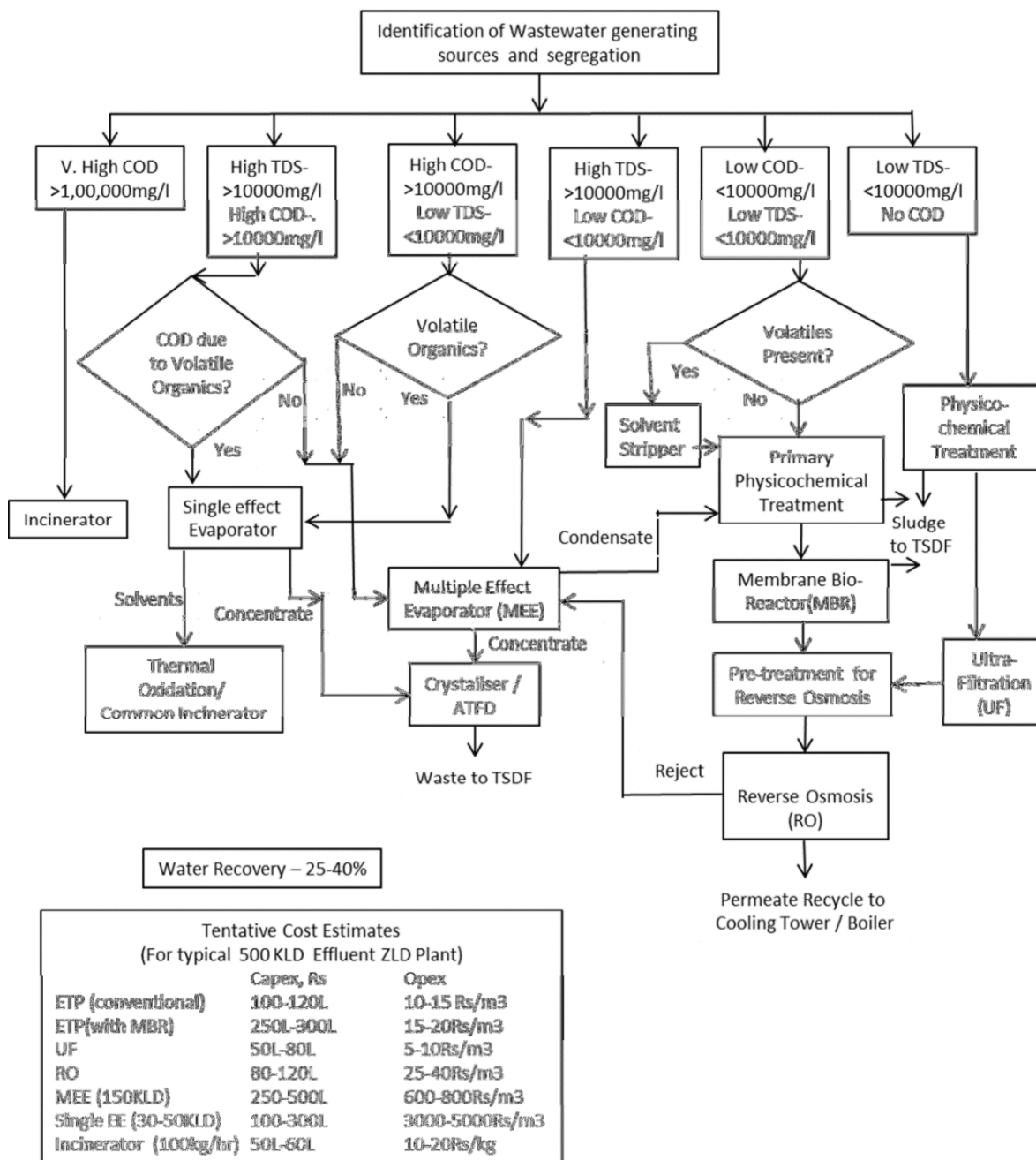


Figure 3.4.4 provides decision tree for arriving at optimum ZLD configuration for chemical industry

3.4.4 Selection of ZLD Treatment for Chemical Industry

Fig. 3.4.4

ZLD Treatment Selection for Chemical Industry



WAY FORWARD

Zero Liquid Discharge (ZLD) systems in the industry have become a mandatory requirement due to indiscriminate pollution and its devastating impact on water bodies. Due to water scarcity, river and ground water pollution and landlocked locations for discharge of effluents, Zero Liquid Discharge (ZLD) framework is being imposed.

5.1 Challenges:

High CAPEX and OPEX: Major challenge for installing ZLD system is that the Capital cost (CAPEX) and operational cost (OPEX) are very high. To address these technical and financial challenges assistance is required.

- 1. Financing Models** Feasible and attractive financial models need to be developed to promote ZLD successfully. Financial institutions can come up with a more amenable solutions like BOOT model whereby the investment into implementing a ZLD unit would be made by a third-party investor who would recover their return on investment by charging a tariff over a long concession period, typically 10-15 years. There are two risks involved for investor. One Technology & Operations Risk and other credit risk. Once these parameters are well identified and the risks quantified, a risk premium can be priced, which then can be built into the financial model. The risk premium is the return on investment the investor would seek.
- 2. Incentives** Government should come up with suitable incentives to promote ZLD schemes. These incentives could either be Tax exemptions, accelerated depreciation or operational subsidies based on performance to the industry that is installing ZLD system and operating it successfully.
- 3. Financial support** Need to be extended by Central and State government modelled on the support provided to Common Effluent Treatment Plants (CETPs) in the past.

Technology Selection: Technology selection is a big challenge. Effluent from every industry are unique and to resolve the challenge, ZLD scheme varies from case to case basis.

1. Every ZLD system is unique. A proper technology selection and customized ZLD system for the specific industry need to be developed. It is necessary to involve technical experts for customizing the design of ZLD scheme.
2. There are many developments and innovations in ZLD technologies. It is essential to select a technology innovation according to nature of effluent and economics of operation on long term basis.

Training/capacity building for awareness and guidance of ZLD scheme need to be conducted. Seminars/workshops need to be organized for sharing technology innovations, experiences and guidance to industries.

Technology Innovations: Operational cost of ZLD technologies is very high owing to energy and replacement cost, in order to meet these challenges, efforts are needed for -

1. Focused R&D in new products, energy efficiency, replacement cost, cleaning frequency, etc. needs to be carried out.
2. Efforts to develop ZLD technology products to handle specific complex effluents in waste waters e.g. pharmaceutical & dyes industry need to be promoted.
3. Energy efficient technologies need to be developed for effective waste water treatment.
4. Material of construction for ZLD technology products need to be long lasting with minimum maintenance requirement.

5.2 Process Change

It is necessary to revisit manufacturing processes which are generating waste waters. By making changes in process technologies, by changing raw material and/or catalysts and by adopting advanced energy efficient methods, it is possible to minimize generation of waste water. It is also possible to recover maximum useful material from waste. This will reduce the cost of ZLD scheme.

By judicious combination of advanced technologies, by adopting technology/process change and facilitating finance Zero Liquid Discharge systems can be implemented on a large scale across sectors and manufacturing capabilities on systemic basis.

It is hoped that this Technology Guidance Manual provides support to Regulators, Financial institutions, Technology providers and Industry.

References

1. Cumulative ZLD Reference Facilities based on reference plant data from Aquatech, GE Water and Veolia. URL: <http://www.bluetechresearch.com/streams/themes/zeroliquiddischarge/> accessed on 5.05.2015
2. Gujarat Pollution Control Board, Annual report 2013-14, Green Gujarat- Ecological and Industrial Balance
3. Vivek V. Ranade, Vinay M Bhandari, Industrial Wastewater Treatment, Recycling and Reuse; URL: <https://books.google.co.in/books?id=XiETAgAAOBAJ&pg=PA500&ing=PA500&dq=wastewater+fromapi+and+bulk+drugs&source=bl&ots=XkgbKvmk8o&sig=klntLVez0roWelxeGdRYI3GO6I&hl=en&sa=X&ei=ev4YVYGMMHeU9aogZAP&ved=OCDSO6AEwBg#v=onepage&q=wastewater%20from%20api%20and%20bulk%20drugs&f=false>
4. Data compilation by Marmara University, Turkey
5. Michael Pilutti, PE, Julia E. Nemeth, PE, Julia E. Nemeth, PE ; Technical and Cost Review of Commercially Available MF/UF membrane Products.
6. A study by University of BATH, UK; Improvements in membrane technologies
7. Kali Peng Lee, Tom C Arnot, Davide Mattia; University of Bath publications
8. Paul E. Minton, Union Carbide Corporation; Handbook on Evaporators
9. APV Handbook on evaporators
10. Guidelines on Techno-economic feasibility of implementation of Zero Liquid Discharge (ZLD) for Water Polluting Industries; Central Pollution Control Board, January, 2015
11. Michael E. Williams, Ph.D., P.E; Review of Wastewater Treatment by Reverse Osmosis, Williams Engineering Services Company, Inc
12. Manivanan, R.; Recycling of Industrial Effluents
13. Central Pollution Control Board, MoEF, April, 2007; Advance Methods for Treatment of Textile Effluent
14. Anand P. Dhanwani, Srinivasarao Meka, Shrey B. Patel; "Selection of Technology to Treat Waste Water Generated from Dye Intermediate Manufacturing Industry"; International Journal of Innovative Research in Science, Engineering and Technology, Vol 3, 201.
15. Naik D. J., Desai H.H.* 1 and Desai T. N.; "Characterisation and treatment of untreated wastewater generated from dyes and dye intermediates manufacturing industrial area, Gujarat", Journal of Environmental Research And Development Vol. 7 No. 4A, April-June 2013
16. S. Mehta, "Zero Liquid Discharge Technologies and economics", Envirovision, 2011
17. POPE, JAMES D., and HUDE, JEFFREY M., LURGI; PSI Industrial performance of the mechanical vapor recompression and multiple effect evaporator system: successful operation and significant reduction in steam usage.
18. "Combination Thermal Process with Zero Liquid Discharge"; SOUTHERN CALIFORNIA REGIONAL BRINE-CONCENTRATE MANAGEMENT STUDY- PHASE I, October 2009
19. Solvent Recovery Handbook; URL: <https://books.google.co.in/books?id=GcjMEOWiMV5C&pg=PA38&lpg=PA38&dq=solvent+recovery+stripper&source=bl&ots=2OSF32YFO&sig=yEEWbr3ogL6bTAEalfTPyOclgwI&hl=en&sa=X&ei=MDYrVbngPIKdugT13oHgDw&ved=OCE8O6AEwBO#v=onepage&q=solvent%20recovery%20strippers&f=false>
20. Craig R. Bartels, PhD; "Reverse Osmosis Membranes for Wastewater Reclamation"
21. Lee, K. P., Arnot, T. C. and Mattia, D. (2011); "A review of reverse osmosis membrane materials for desalination-development to date and future potential. Journal of Membrane Science, 370 (1-2). pp. 1-22. ISSN 0376-7388; University of BATH
22. Richard L. Stover Desalitech, Inc. "A Primer on Reverse Osmosis Technology"; Chemical Engineering, July, 2014
23. Michael Pilutti, PE, Julia E. Nemeth, PE, "TECHNICAL AND COST REVIEW OF COMMERCIALY AVAILABLE MF/UF MEMBRANE PRODUCTS"; International Desalination Association BAH03-029
24. Amos Bick, Leonid Gillerman , Yossi Manor and Gideon Oron, "Economic Assessment of an Integrated Membrane System for Secondary Effluent Polishing for Unrestricted Reuse", Water 2012, ISSN 2073-4441
25. Guidelines for design of RO System, Lanxess
26. I. Sajid Hussain, "Case Study of a Zero Liquid Discharge Facility in Textile Dyeing Effluents at Tirupur", One Day National Workshop on CETPs - Hyderabad-23rd November 2012
27. Kader Gaid Technical Department, Veolia water France; A Large Review of the Pre Treatment
28. "Evaluation and Selection of Available Processes for aZero-Liquid Discharge System for the Perris, California", Ground Water BasinReclamation, managing Water in the West, Desalination and Water Purification Research and Development Program Report No. 149
29. "Survey of high recovery and Zero Liquid Discharge Technologies for water utility", Water Reuse Foundation

