# Recycling of Process Water & Energy Saving in Surface Treatment Processes To Prevent Environmental Impact in The Twenty-First Century

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In the papers presented previously at SUR/FIN<sup>®</sup> '2000 (Chicago) and SUR/FIN<sup>®</sup> '2001 (Nashville), the different parameters for minimization in surface treatment processes were discussed. We are still working in the same line according to the European Union's 'Electrolytic Chemical Cycle Life' programme, a community project by France, Portugal and Spain participated to study the environment impact of electrolytic processes. It is aimed at minimizing existing contaminating processes and the elimination of cations and anions from surface treatment processes by the conventional system of recycling, recovery, dialysis, electrodialysis, anion-cation exchange membranes, and the complete elimination of nitrogen and phosphorus from physical-chemical and biological depurators process. It should be emphasize now the importance in achieving the total elimination of nitrogen and phosphorus, and for the year 2005 also boron. It is important that the finishing industry practices water recycling for the common good an energy savings, both of chemical and power. The EU's programme recommends that it should be possible to recover at all levels and to minimize the product in the depurators station during the physical-chemical treatment. If this is not possible during the electrochemical process, then vaporization or zero draining can be done.

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#### Industrial Wastewater Treatments

Reverse osmosis is a technology having an important development in recent years as removal technique and quality water production. It has been used in multiple applications and fields, such as making seawater and saline water potable or tertiary wastewaters recovery.

The reverse osmosis can be considered nowadays a contrasted and well-established technique. Nowadays the market offers very sophisticate, high performance membranes especially adequate for the task to be performed like high output at lesser pressure, high degree of retention, very high pressure membranes, etc. though not yet stabilized, their price has been reduced remarkably, especially for the membranes type, which is in high demand.

A general introduction of this removal technique principle it has been already explained. Now we will introduce the characteristic of the different type of membranes, together with general working parameters.

There are four basic designs of reverse osmosis units, that is

- Tubular (T)
- Plate and Frame (PF)
- Spiral coiling (SC)
- ➢ Hollow fibre (HF)

Membranes comparison							
Parameter		1	1	1	1	1	1
System Cost		T, PF		>>	PF	SC, HF	
Design flexibility	SC	>>	HF	>	SC	>	Т
Easy cleaning	PF	>	Т	>	PF	>	HF
Space saving	Т	>>	SC	>	PF	>	HF
Soiling	HF	>>	SC	>	PF	>	Т
Needed power	Т	>	PF	>	HF	>	SC

# The Four Basic Membrane Designs Classified According To Characteristics

For good performance of a reverse osmosis (nanofiltration) unit, the key parameters are the permeate flux or production rate  $(L/m^2/h)$  and salt rejection. Those two parameters are related to the following process variables:

- ➢ Pressure
- ➢ Temperature
- Conversion
- Ionic concentration of the feeding flux

Variable effects are summed below:

Variable	Effects
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Variable Increase	Permeate flux	Salts passing through
Effective pressure	+	-
Temperature	+	+
Conversion	-	+
Ionic feeding concentration	-	

+ increase- decrease

The permeate flux limitations are different according to type of waters to be treated and limitations due to contaminants and/or specific physic parameters.

# Limitations To Permeate Flux According To Global Characteristics Of Water Being Treated.

WATER TYPE	Maximum value of flux (l/m²/h) -for spiral membranes -	
Sea water	15 - 30	
Saline water	20 - 36	
Tertiary waters	13 - 24	

TURBIDNESS	<	6 NTU (UNF)
Dissolved solids (ion)	<	3000 ppm
Т	<	100 °F
SO <sub>4</sub> <sup>2-</sup>	<	400 – 500 ppm
F	<	2 ppm
Fe	<	0.1 ppm
Mn	<	0.05 ppm
SDI	<	2.0 ppm
Oxidable	<	5 ppm O <sub>2</sub>
Colour	<	20 U.C. Pt – Co
Ba <sup>2+</sup>	<	0.01 ppm
Sr <sup>2+</sup>	<	1 ppm
SiO <sub>2</sub>	<	40 ppm
рН	2 – 12 units (according to membrane type	
Temperature	5 – 50 °C (according to membrane type)	

# **Contaminants and Physic Specific Parameters For Reverse Osmosis Unit Without Pre-Treatment**

The blocking mechanism known as membrane polarization it always happens in a higher o minor degree, independently of the treated water's characteristic or the membrane's type characteristic and/or the operating conditions employed.

At the limit layer solution-membrane it is produce a high dissolvent flux through de membrane and a high rejection of solute passing through it at the same time. Consequently, a limit layer is created in this interface, which is very rich in solute and poor in dissolvent. In this area salinity and finally the water osmotic pressure will be very much higher than that of feeding water and that the mean value of water inside the permeate and which can be inferred according to the concentration cycles.

The flux needed for dragging is normally superior to that of the production and rejection flow together, both defined by calculating the flux value and the concentration cycles, respectively. This water surplus becomes the re-circulating flow and does not interfere with the system's total saline balance.

## **MEMBRANE'S BASIC PROBLEMS**

#### **Solid Incrustations:**

All type of solid (turbidness, colloid, deposit, etc.) should be eliminated from feeding water prior to entering permeate.

#### **Potential Incrustations:**

Membranes' polarization has to be reduced to minimum to avoid the probability that the rejected concentration would have values below the ions' solubility product.

#### **Fouling Deposits:**

It should be eliminated from the feeding flow all compound that could physically obstruct membranes or produce a film formation on them.

#### **Organic Deposits:**

An excess of organic matter in the feeding water could imply microbial development. At large it will result in degrading polymers forming the membrane and/or its supports and also fouling because biofilms formation. Therefore, incompatible organic compounds with manufacturing membrane's material should be avoided.

#### **Oxidation attacks:**

Resistance to oxidizing agents vary according to the type of membrane being used. Therefore, oxidizing agents should be generally avoided in the feeding water.

#### Temperature and extreme pH:

These parameters have been previously described to exceed the limit values, especially for prolonged periods of time, will result in a problem of incompatibility of temperature and pH at extreme values.

#### WATER SUPPLY FOR THE PROCESS

In case of low salinity water supply, reverse osmosis can guaranty a high quality water supply without need of ionic interchanging. Though this technique cannot compete with de-mineralise watery ionic interchange, the obtained quality is sufficient in almost all cases for general supplying or even for last rinsing water working in continues and without the inconvenience of acid and/or corrosive agents being used for regeneration.

When waters have a significant salinity, thus ionic interchange becoming necessary, changing water pretreatment by reverse osmosis can significantly reduce de-mineralised water total cost by  $m^3$ . In case of buying new equipment a more reasonable unit should be chosen with enough capacity and with cationic and anionic resin interchange

#### RINSING WATER IN THE ELECTROPAINTING INDUSTRY

The suggested reverse osmosis station will also treat rinsing water from electropainting installations. Normally, the rinsing effluents have a pH between 9 and 10 and the water's compounds are:

- Polyacrilic resins (approx. 11 % solids)
- Isopropyl alcohol (approx. 2 %)
- Cellusolve (approx. 2.5 %)
- Methanol (aproxi. 0.3 %)
- ➤ Acetone (approximate. 0.2%)
- Trietylamine (approx. 1.7 %)

In this case, both the permeate (production effluent) and the reject (concentrate) are returned to the painting line. This type of application is exceptional because it operates with a conversion indexes extremely small (7.5%).

# PRACTICAL EXAMPLES FOR METALIC CATIONS

#### Aluminium

It is been reported that a USA company from the aluminium field uses ultrafiltration followed by reverse osmosis for its laminating process.

The treated water contents 185 ppm aluminium, 80 g/L oil and grease, 207 ppm solids in suspension, and 6.4 g/ L sulphate. The ultrafiltration step reduces aluminium to 1.7 ppm (99 %) while the next step with reverse osmosis reduced aluminium residual to 0.06 ppm (an additional elimination of 96 %). The high degree of aluminium elimination in ultra filtration indicates that the metal remains mainly in particles.

In this example, the use of reverse osmosis has the advantage over an installation with ultrafiltration only, because exploitation costs are reduced due to permeate recovering from the reverse osmosis process.

## Chrome

The experience with hexavalent chromo in reverse osmosis processes is extremely limited. Further more, in some cases researchers have reached the conclusion that the technique is not satisfactory for this field of industry.

Efficiency improves when it is possible to neutralize the water with 2.6 pH. A high selective, cellulose acetated membrane achieved 92.8 % retention. This performance increased to 98.6 % when raising the pH above 7.6. Polyeteramine membranes can concentrate chromic acid solutions, if the pH is steadily maintained higher than 1.0. The pH control is necessary to avoid minimizing the membranes' hydrolysis. Polyamide membranes are especially sensitive to oxidizing agents.

## Copper

It has been contemplated reverse osmosis for rinsing water treatment from copper pyrophosphates, acid copper and copper-cyanide processes with a retention result of 99 % and higher. Theoretically, the treatment application should result in lower inversion and exploitation costs compared to other alternative processes.

But as explained in other cases, available membranes in the market are only operatives for a long period, if pH is maintained between 2.5 and 1.1 values. Moreover, the reverse osmosis process is unable

to produce high concentration rates. Special attention should be pay in the pyrophosphate process due to its probable de-composition and to avoid the adverse effects that this could have on re-circulating in the electrolytic o chemical baths.

## Iron

The table below shows retention results obtained in a field test for reverse osmosis treatment of a flux originated by acid lixiviates from mining. For the experiment, we were operating with a 75 % conversion, at 12.5 °C temperature and 28 bars (400 psig) working pressure.

ION	Affluent Concentration (ion ppm)	Retention (%)
Ca <sup>2+</sup>	111	99.3
Mg <sup>2+</sup>	83	99.2
Fe <sup>2+</sup>	70	99.1
Mn <sup>2+</sup>	14	99.1
$Al^{3+}$	8	97.4
$SO_4^{2+}$	774	99.6
SiO <sub>2</sub>	11	92.5
TDS	1319	99.1
рН	3.4	

# **Result Of Field Test for Reverse Osmosis Treatment Of A Flowing Originated By Acid Lixiviates From Mining**

In this case, the membranes life-time cannot be guaranteed mainly because the need of treating the effluent with a very low pH over a long period of time.

## Nickel

The water from the permeate is used for rinsing and the reject rich in nickel is returned to the nickel-plating bath. Using a three-steps rinsing system against flow, it is possible to achieve the conversion up to 95 % and at the same time to eliminates 92 % nickel from rinsing water. The effluent's pH is normally stabilized at 4.5.

Details in the table below show the system efficiency operating at 75% conversion, 12 °C temperature, and 28 bars (400 psig) working pressure.

# Efficiency in Nickel Salts Recovery from Rinsing Water in Nickel Plating Process

Ion	Effluent rinsing concentration (ion ppm)	Permeate concentration (ion ppm)	Retention
Ni <sup>2+</sup>	4610	230	95.0
$\mathrm{SO_4}^{2+}$	3924	53	98.6
Cľ	2580	270	89.5

It was found by comparative research that retention efficiency depends significantly on the membrane's type and modules:

# Efficiency in Nickel Recovery with Different Reverse Osmosis Systems

Membrane Type	Bath Type	Efficiency	Comments
Polyamide	Ni-Sulphamate	Good	pH > 2.5
	Ni- flourborate	Moderate	pH > 2.5
Cellulose Acetate	Ni-Sulphamate	Good	
	Ni-Flourborate	Good	

For Ni-sulphamate, the nickel retention was 84 to 98 %, while in the Ni-flour borate processes efficiency was between 70 to 95 %.

## Zinc

It has been suggested reverse osmosis for effluent treatment (both Zn-chloride and Zn-cyanide). In order to protect the membranes it is advisable to maintain feeding pH between 5 and 11 units in order to protect membranes. However, it must be emphasised that reverse osmosis on its own does not achieve completed recovery in a closed circuit.

In 1978 a reverse osmosis plant was set up In California, USA, to treat effluents from zinc-phosphate processes. The company's compromise to drastically reduce its residual effluent forced it to think how to reduce 90 % its wastewater and how to re-use effluents. For a pre-treatment prior to implementing the reverse osmosis process, it proved necessary the effluent homogenisation, multilayer dispersants addition and anti-scaling chemicals to protect membranes adequately.

The following table provides average feeding quality and reverse osmosis production data of the plant:

Parameter	Feed in Concentration	Permeate Concentration
pH	5.1	4.9
Zinc (ppm)	7.3	2.2
Iron (ppm)	0.5	< 0.2
Phosphate (ppm F)	414	109
TDS (ppm)	750	238

Reverse osmosis was also tested for various industrial effluent treatments with important zinc contain. Results are shown in the table below:

		-	
ector	Feed in Concentration	Permeate Concentration	
		( <b>T</b>	1

Average Output On Zinc Processes Separation

Industrial Sector	Feed in Concentration (Zinc ppm)	Permeate Concentration (Zinc ppm)	Retention %
Zinc plating rinse	1700	30	98
Central condensers	300	53	82
Power stations	780	3	99
Textile plants	7200	140	98
	460	250	46
	520	360	31
	7200	360	95
	1400	30	96
	4100	180	96
	1200	22	98
	24000	430	98
	9700	37	> 99

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# ATMOSPHERIC AND VACUUM EVAPORATORS

- ➢ For rinse water recovery, evaporators are atmospheric, single stage vacuum.
- Hot water and moving air flow to take out
- and transfer water from the feeding liquid to the airflow.
- Vacuum evaporators transfer heat energy to feeding power for boiling liquid at reduced temperature and pressure under controlled conditions by contact surface interchanging

# CHEMICAL SOLUBILITY IMPACT

## **Insolubles:**

- Barium sulphate
- Barium chromate
- Iron phosphate or pyrophosphate
- Iron orthophosphate

# Solubles:

- Nickel salts
  - Nickel sulphate
  - Nickel chloride
  - Etc.
- Boric acid

# VACUUM EVAPORATORS

Vacuum evaporators have been in use for more than 30 years and their cost is higher that atmospheric evaporators.

# Vacuum functioning

- 1. The boiling point temperature of the bath being concentrate, is reduced. Therefore, the potential heat harm to additives or constituents sensitive to heat, is reduced or eliminated.
- 2. The temperature differential is increase (functioning thermal power) between the heat source and the liquid being concentrate, thus resulting in more efficient and less expensive condenser and boiler designs.
- 3. When the system is switched on, the residential air is taken out, thus eliminating the possibility of propagating harmful products through a ventilation outflow.
- 4. Air is excluded from the system, thus eliminating potential oxidation in the air from recovered chemical products.
- 5. Good quality distilled water is recovered to use in the bath line.
- 6. Feeding concentration's fluctuation system, is made insensitive when programmed to work on concentrate recycling mode.
- 7. Potential harmful air emissions, are eliminated.
- 8. Working with decreased temperature, reduces the tendency to scaling formation on hot or any other type of surface.
- 9. A better control of foaming formation, is achieved.
- 10. The number of pumps required is reduced to one: a vacuum pump or an eduction circulating pump, according to the process needs.
- 11. The bath recovers an adjusted and equal concentration, hence providing a very precise control of process

# VACUUM EVAPORATORS DEFICIENCIES BY INADEQUATE MAINTENANCE

# 1) Evaporator's Capacity Decrease:

- a) Inadequate feeding or not enough vapour reaches the evaporator or vapour feeding pipes are ill designed. The results is that an important quantity of vapour becomes condensed instead of providing vapour to the evaporator. It happens more often than you can imagine!.
- b) Scales accumulation in the boil pipes.
- c) The concentration sensor is badly fit. The result is high concentration and possible solids precipitation in the evaporator.

# 1) Low Or Diminish Quantity Of Distilled Water

- a) Too high concentration and low evaporation level.
- b) Use of inadequate cooling water in the condenser scales due to an inadequate cooling harms supply; or condenser has circuit; or inadequate up keeping of cooling tower.

# 3) Contaminate Distilled Water

- a) Functioning at vacuum level for too long results in high vapour velocity and dragging to the condenser.
- b) If equipment is re-initiated too soon after manually putting off it causes a discharge in the evaporator's hot concentration. The concentration should be cooled to 10 °F at least or alternatively, it should be completely emptied and filled again prior to putting it on.
- c) If vapour works at excessively high pressure, it could produce the concentration being injected to the condenser.

# Vacuum Evaporators Advantages

- 1. The evaporation is a well known, recovery technology for bath and surface processes, conveniently tested and documented.
- 2. It provides recovery levels of more than 90 99.9 %.
- 3. It reduced waste treatment costs and substantially reducing the amount of generated sludge.
- 4. The Vacuum process minimizes lost of heat sensible components in the bath caused by thermodegradation.
- 5. There is available in the market a wide selection of single stage design equipment

## Vacuum Evaporators Disadvantages

- 1. Evaporation requires more power to work than other removal methods.
- 2. Single stage evaporators have a total working cost higher than other removal system.
- 3. Though single stage atmospheric equipments presumably have a lower to moderate cost, the recovered bath concentrations can vary.

- 4. Nowadays, vacuum equipment is designed to suit costumer's needs according to the use and applications to be performed Equipment is more sophisticated and efficient with respect to the use of power and the multiple effects or vapour compression. The initial cost of the equipment is significantly high.
- 5. For minimizing the cost of investment in whatever recovery system by evaporation, it is advisable to reduce the number of rinsing operations and water required by evaporation. Water saving techniques should be used

## CONCLUSSION

- I. Nickel, chrome and other metals should be recycled.
- II. Energetic saving in all processes should be adopted.
- III. Cost reduction by eliminating and minimizing sludge with metal content.
- IV. Saving of chemical products such as additives in the physical-chemical depurator stations.
- V. Minimization of environmental impact.
- VI. Government subventions in the European Union to sludge minimization.

#### References

- 1. Baker, R.A., Corning Glass Works (1987) 'Evaporative Recovery of Hazardous Materials', HAZTECH International Conference, August 26-28, 1987, St. Louis, Mo.
- 2. Veit, P.L., 'The evaporator: A Great Tool, But No Free Lunch', Metal Finishing, November 1989, pp 31-34.
- 3. McLay, W. J., 'Evaporative Recovery', from 1980 AES Sponsored Environmental Compliance & Control Course.
- 4. Prutton & Maron, 'Fundamental Principles of Physical 'Chemistry', Revised Edition,
- 5. The MacMillan Co., New York, 1952, pp 184-185.
- 6. Pollution Prevention: EPA Statement of the definition, Polllution Prevention News, June 1992
- 7. Pollution Prevention For the Metal Finishing Industry, The Northweast Waste
- 8. Management Officials Association, Boston, MA, February 1997.
- 9. The Nalco Water Handbook, 2nd Edition Kramer, Frank, N., Ed. MacGaw-Hill, New York, N.Y., pp 20.1-20.3, 1988.
- 10. Rinsewater Water Contamination of Hadallerg., Boeing Co, MDR 2-36070, 25 June, 1974.
- 11. Rinse Water Reyde Design 1 Operations, Gregory, R. Allan, Advanced Chemical Technologies & Charles M. Babb, Hytech Finishers, January 2000.
- 12. USEPA, Handbook For Constructed Westland Receiving and Mine Drainage, EPA / 540 / SR 95/523, 1993

# **Filtration Ranges**







## WATER EVAPORATORS

Series	400	500	600	700	800
Evaporation Rate	8 – 10 GPH	15– 18GPH	33 – 39 GPH	63 – 68 GPH	126–144 GPH
Footprint	65" x 23"	86" x 23"	85" x 43"	98x 43"	128" x 58"
Tank Capacity	118 Gallons	174 Gallons	333 Gallons	296 Gallons	517 Gallons
Heat Sources	Se	eries available for 1	natural gas, liquid j	propane, steam or e	lectricity
Construction	Various	s alloys to suit appl	lication, including	super austenitic, hi	gh nickel, etc.

#### WATER EVAPORATORS

Series	400	500	600	700	800
Evaporation Rate	8 – 10 GPH	15– 18GPH	33 – 39 GPH	63 – 68 GPH	126–144 GPH
24 Hour Rate	192 Gals	360 Gals	792 Gals	1,512 Gals	3,024 Gals
Footprint	65" x 23"	86" x 23"	85" x 43"	98x 43"	128" x 58"
Tank Capacity	118 Gallons	174 Gallons	333 Gallons	296 Gallons	517 Gallons
Heat Source		All series available fo	r natural gas, liquid pi	opane, steam or electric	city
Construction	Var	ious alloys to suit app	lication, including su	per austenitic, high nick	xel, etc.



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Parameters	M.U.	Feed	Destillate	Concentrate
pН		12.6	9.8	> 13
Density	g/ml	1.021		1.1
Colour		Green-yellow	Colourless	
Odour		Odourless	Odourless	
Conductivity	⊮S/cm	35500	25	
Sedimentable solids 2 h	ml/l	< 0.1		
Suspended solids	mg/l	86		
Fixed solid at 105°C	%	3.4		OMPLE SUBJECT
Fixed solid at 600 °C	%	1.8		
COD	mg/l	5100	45	
Chlorides	mg/l	3800	1.7	
Ammonium	mg/l	1.5	0.6	
Mineral Oils	mg/l	121	5	
Anionic surfactants	mg/l	< 0.5	< 0.5	
Non ionic surfactants	mg/l	270	0.2	
Total surfactants	mg/l	270	< 0.25	
Waste typology: Distillation Yield: Note:	> Mixture water of > 90% > The des	of softner eluates a stainless steel pro stillate and concent	and rinsing water an oducts. rate have been obta	nd alcaline degreasi ained by vacuum

Parameters	M.U.	Feed	Destillate	Concentrate
pH		12.1	3,1	4
Density	g/ml	1.015		1.22
Colour		Light brown	Colourless	
Odour		Odourless	Odourless	
Conductivity	/~S/cm	18300	310	
Sedimentable solids 2 h	ml/l	< 0.1		
Suspended solids	mg/l	2500		
Fixed solid at 105°C	%	1.7		
Fixed solid at 600 °C	%	1.4		
COD	mg/l	1600	270	
Chrome III	mg/l	235	< 0.01	
Iron	mg/l	74.4		
Nickel	mg/l	196	< 0.01	
Zinc	mg/l	706	0.09	
Sulphates	mg/l	1420	<2	
Chlorides	mg/l	3350	<1	
Fluorides	mg/l	1.2		
Ammonium	mg/l	24.1	1.2	
Nitric nitrogen	mg/l	< 50	<1	
Anionic surfactants	mg/l	7	< 0.2	
Non ionic surfactants	mg/l	24	< 0.3	
Total surfactants	mg/l	31		
Waste typology:	> Rinsing	water from nickel	-chromium and zinc	plating.
Distillation Yield:	> 85%			
Note:	> The dis	tillate and the con	centrate have been	obtained by

0H Densisty		0.0		
Densisty		2.3	3.7	2.5
al and a second s	g/ml	1.007		1.09
lolour		Green-blue	Colourless	Green-blue
Ddour		Perfumed	Odourless	Perfumed
Conductivity	/KS/cm	11.240	205	> 145000
Fixed solid at 105 °C	%	2.9		38.2
Fixed solids at 600 °C	%	0.5		6,6
Suspended solids	mg/l	215		
Sedimentable solids 2 h	mi/i	0.5		
COD	mg/l	38000	480	500740
Numinium	mg/l	2.7	< 0.05	35.6
ron	mg/l	10.5	0.07	137.6
Zinc	mg/l	4.4	0.03	57.6
Sulphates	mg/l	< 100		
Chlorides	mg/l	1950	26	25400
fotal phosporus	mg/l	41	< 0.05	541
Ammonium	mg/l	< 10	<2	
fotal oils	mg/l	N.D.	10	
Anionic surfactants	mg/l	6300	< 0.1	83160
Non ionic surfactants	mg/l	1400	< 0.2	18480
otal surfactants	mg/l	7700	< 0.3	101640
(KN	mg/l	48	12	475
Natar tunology:	> Rigina w	atar from enane :	thoro strepreteb hos	uction
istillation Yield	> 85%	ater nom soaps i	and detergents produ	
Note:	> to % > The dist evaporation of the dist ev	illate and the conv ation of the waste eoretically calcula	centrate have been of Data concerning the ted according to the	obtained by vacuu e concentrate, hav obtained distillation