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Canadian Oil Sands Network for Research and Development

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Nanoflotation – an alternative water treatment technology for the separation of clay colloids in Mining recycle process water

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CONRAD Oilsands Clay Conference

February 20-21, 2013

Today's Leading Water Treatment Technologies to remove Colloidal (Clay) Solid Particles and Organics

This is a Presentation on the leading technologies to treat recycle water at oil sands mining operations to separate clay colloidal particles and organics.

The specific application was for pre-treatment of water for Reverses Osmosis (RO) polishing

Key design parameters will be reviewed for

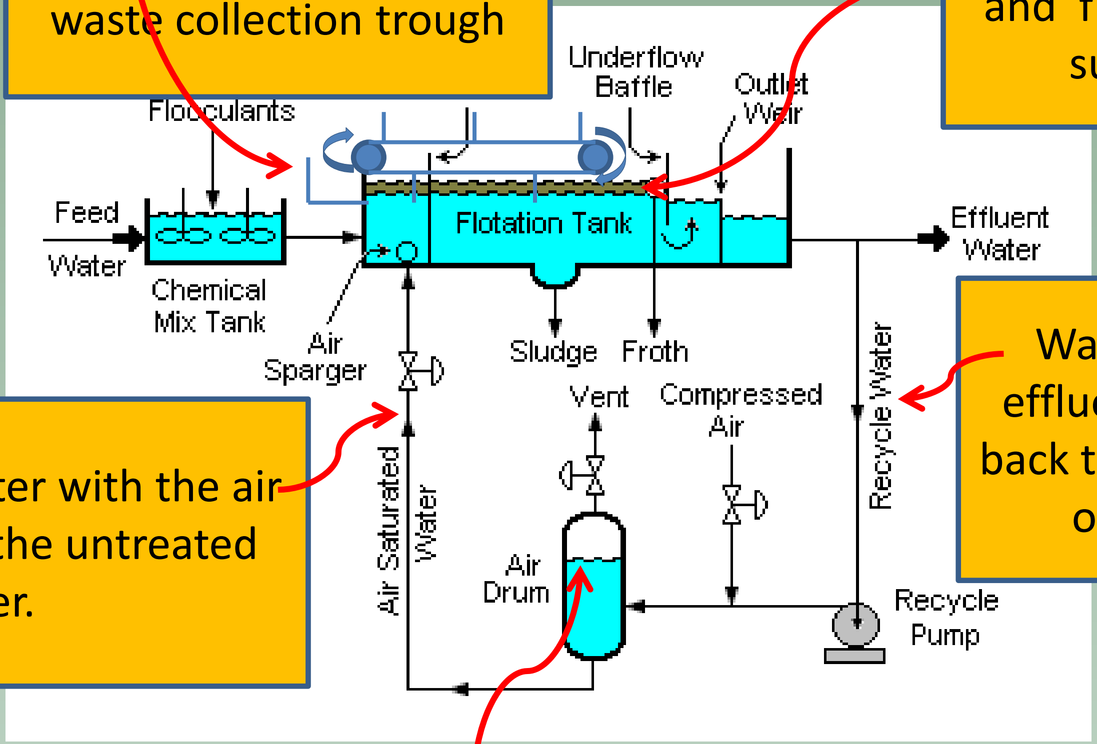
1. Dissolved Air Flotation (DAF) and Froth Flotation
2. Membranes (Polymeric and Ceramic), AND
3. **New** Nanoflotation

(a combination of DAF or Froth Flotation and Membranes)

Dissolved Air Flotation (DAF)

Skimmer pushes the solids on the surface to a waste collection trough

Solids attach to the air bubbles and float to the surface



Water from the effluent is recycled back to the head end of the plant

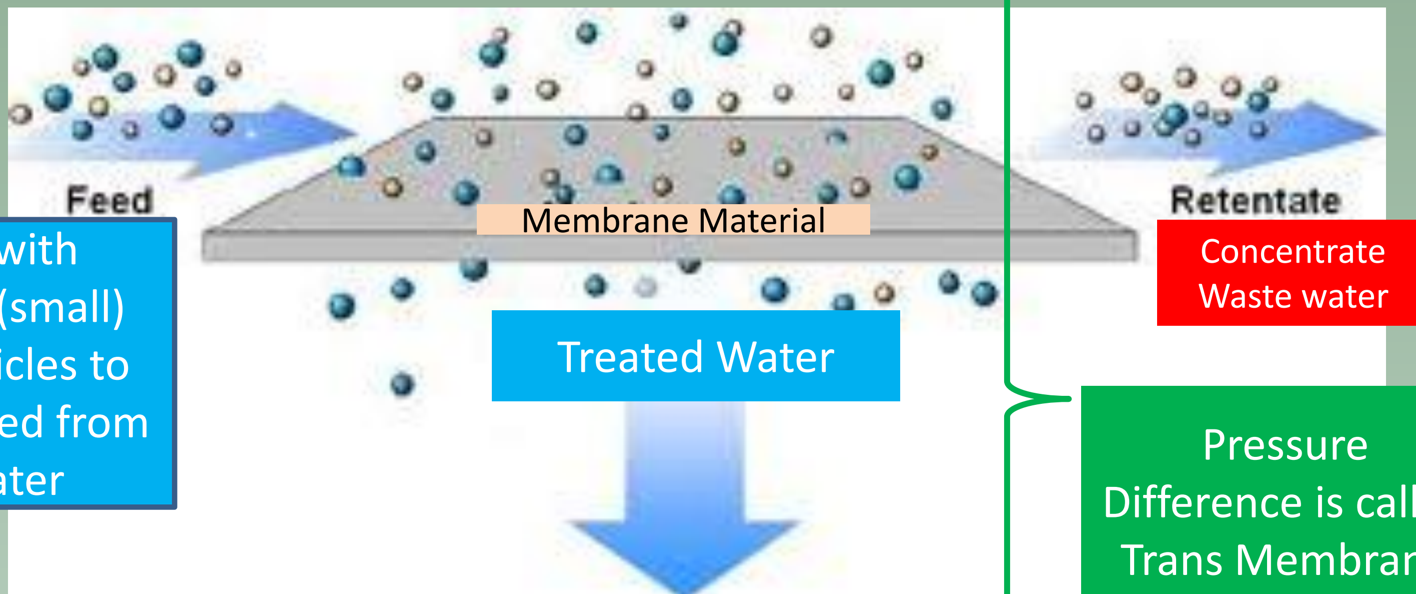
The Recycled water with the air combines with the untreated water.

Air is added under pressure (6 Bar) to the recycled water

Membranes

Pressure +++

Water with Colloidal (small) solid particles to be separated from the water

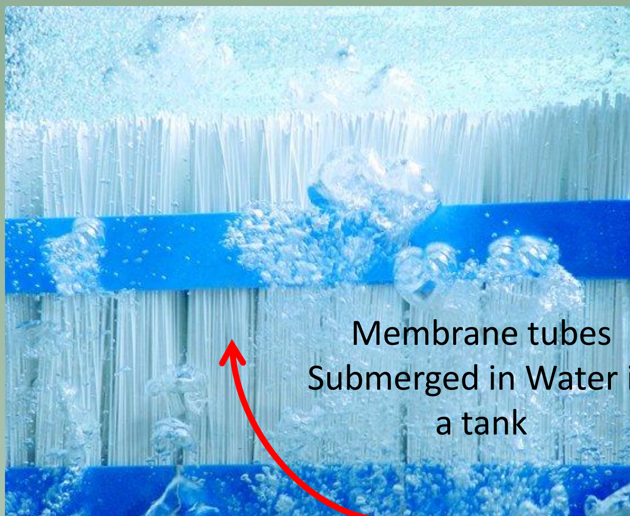


Pressure ---

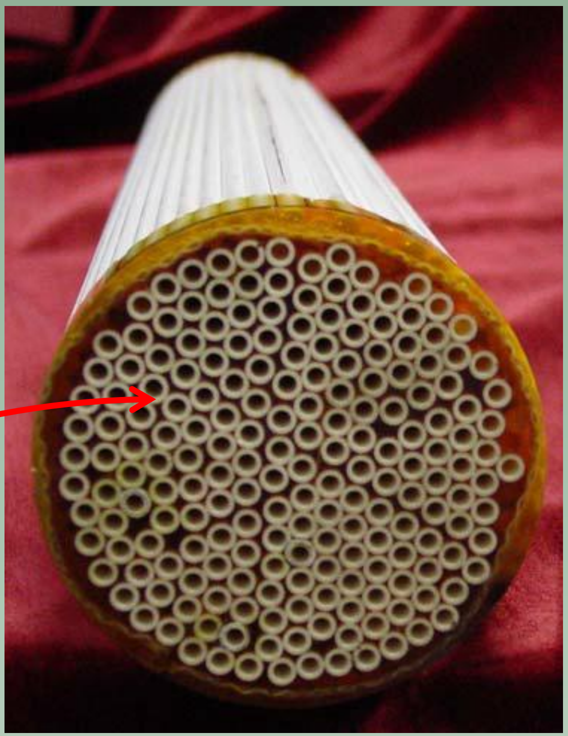
Pressure Difference is called Trans Membrane Pressure (TMP)

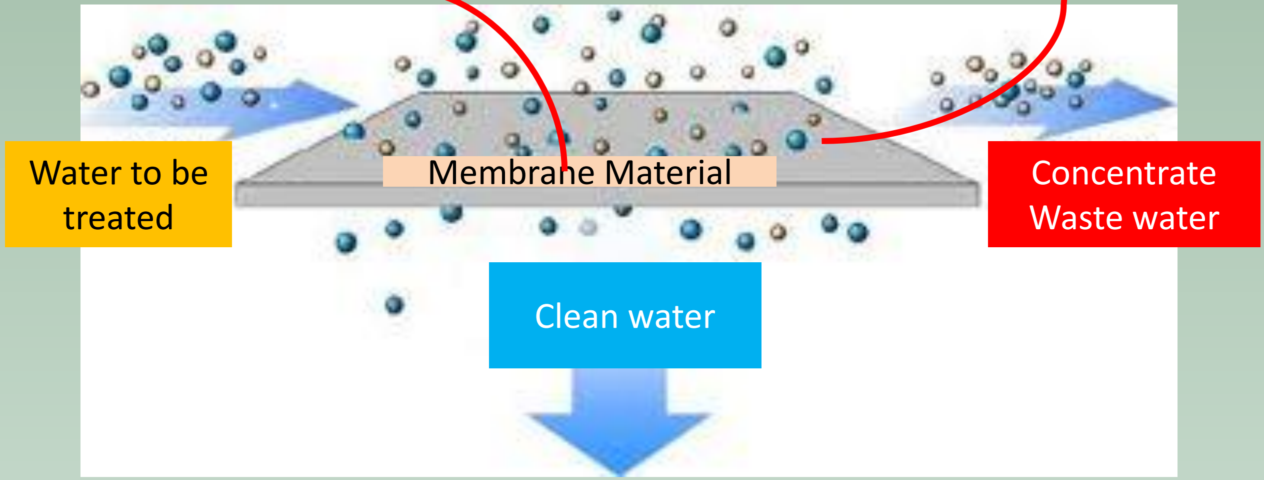
Membranes are defined as a barrier or fine screen to separate colloidal (small) particles. Membranes are not a media like sand or activated carbon

Membrane Material is rolled into Tubes

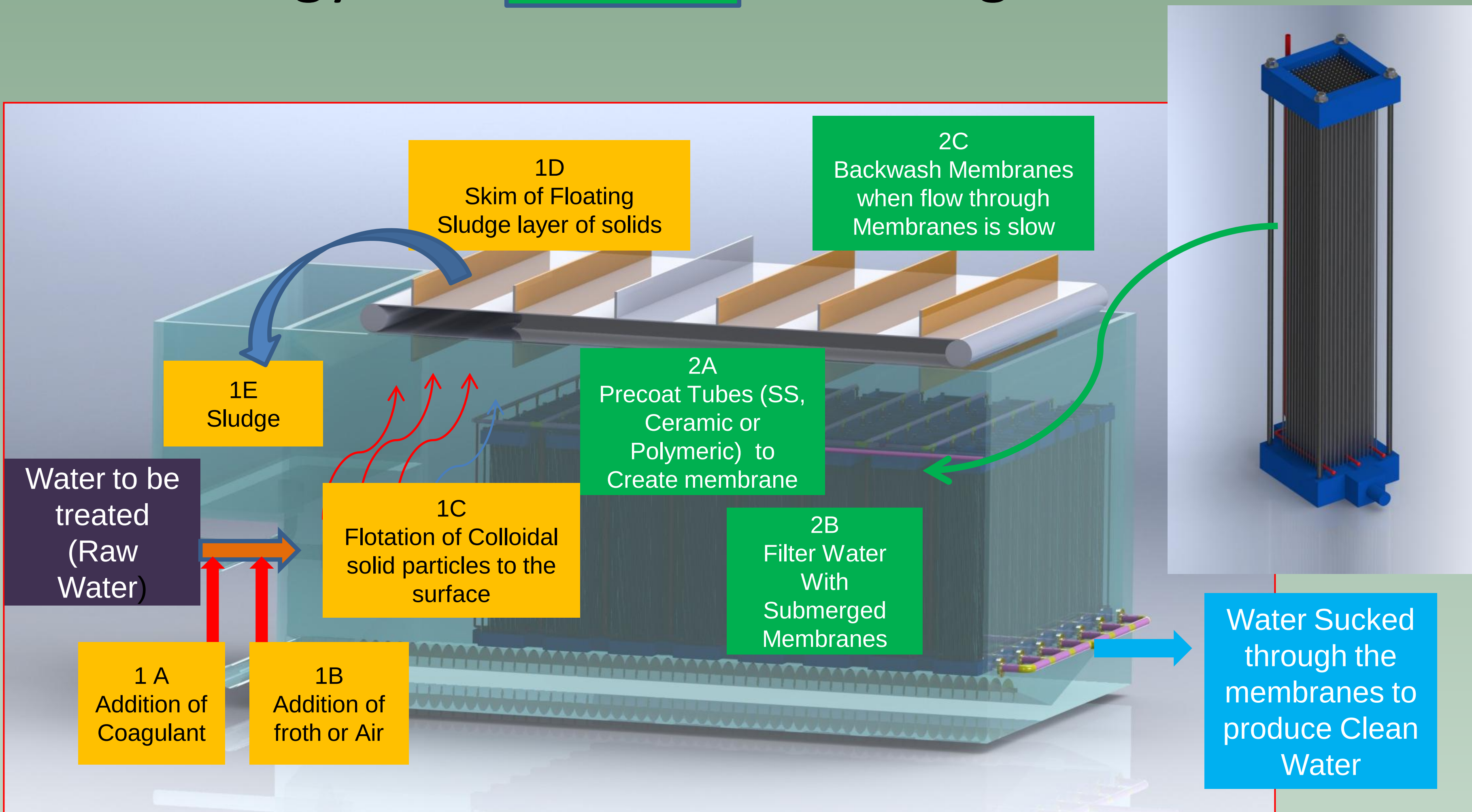


Membrane
tubes inside a
casing





Nanoflotation- Combination of Step 1 Flotation technology and Step 2 Submerged Membranes



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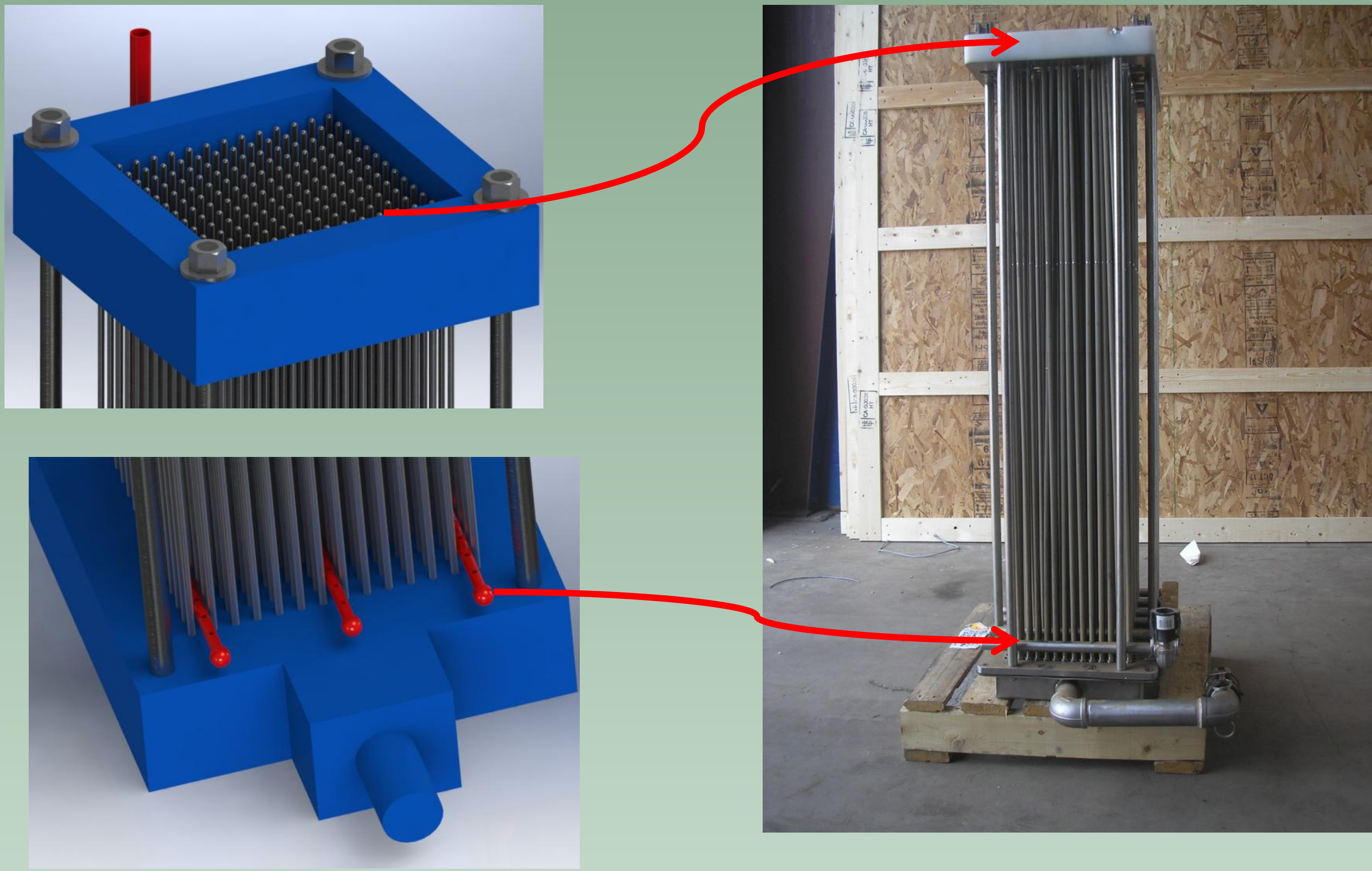
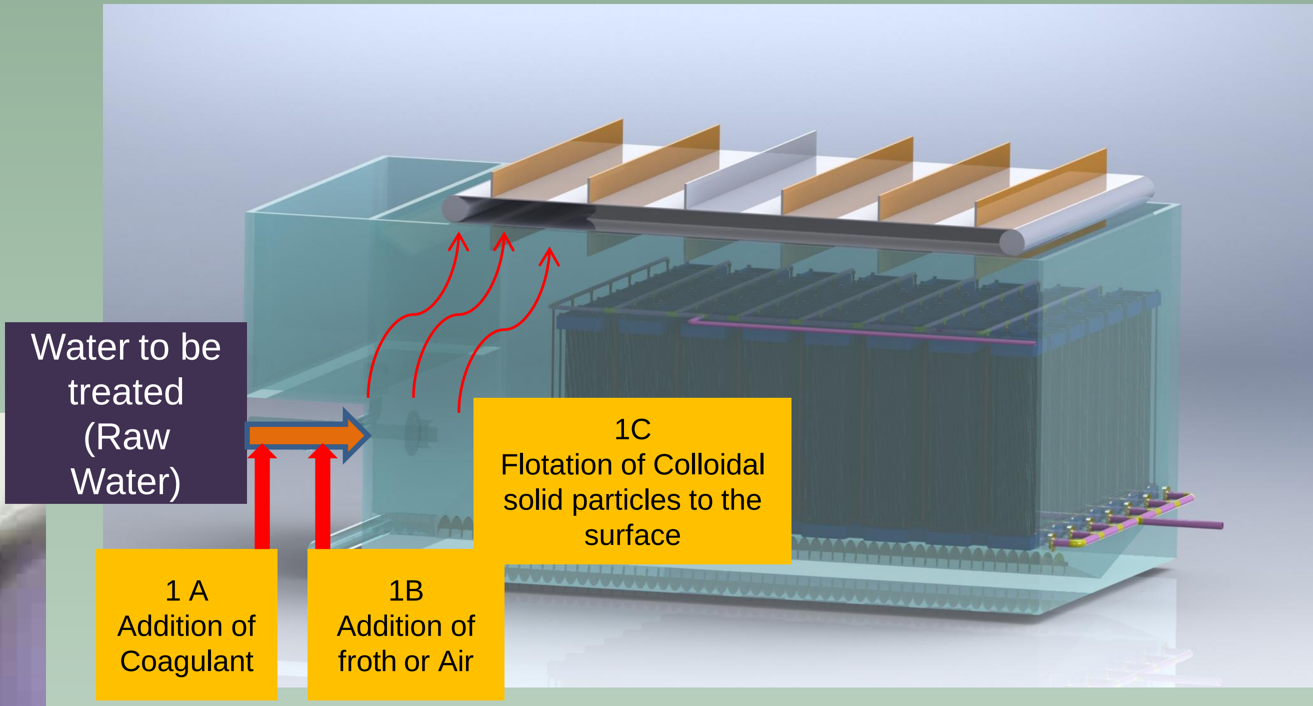
Nanoflotation Membrane Bundle



Nanoflotation Pilot Plant

Step 1 Froth Separation of Solids in water - Video



Design Loading Rates

- typical designs for Clarifiers (settling tanks) or Dissolved Air Flotation tanks rely on the flow rate (M^3 per minute) for the water being treated divided by the surface area (M^2)

- “A” times “B” = (M^2)
  of Area
- The Rate is M / hour

Typical Design Loading Rates

- Clarifiers / Settling Tanks -1 to 2 M /hour
- In the 1960's to 1980's Dissolved Air Flotation (DAF) designs for Water treatment plants were based on 5 to 10 M /hour. This is why DAF became so popular.
- In the 1990's the design rate became 10 to 15 M / hour
- In the last 10 years there are some new designs called High Rate DAF where the design loading rate is 20 to 30 M / hour.
- For Industrial Waste Water treatment, Engineers in North America still use **5 to 10** M / hour for **DAF**
- **Froth flotation** uses **20 to 30 M**/ hour for Industrial Waste Water treatment

Area requirements for Froth Flotation Versus DAF

Froth flotation Requires

50 %

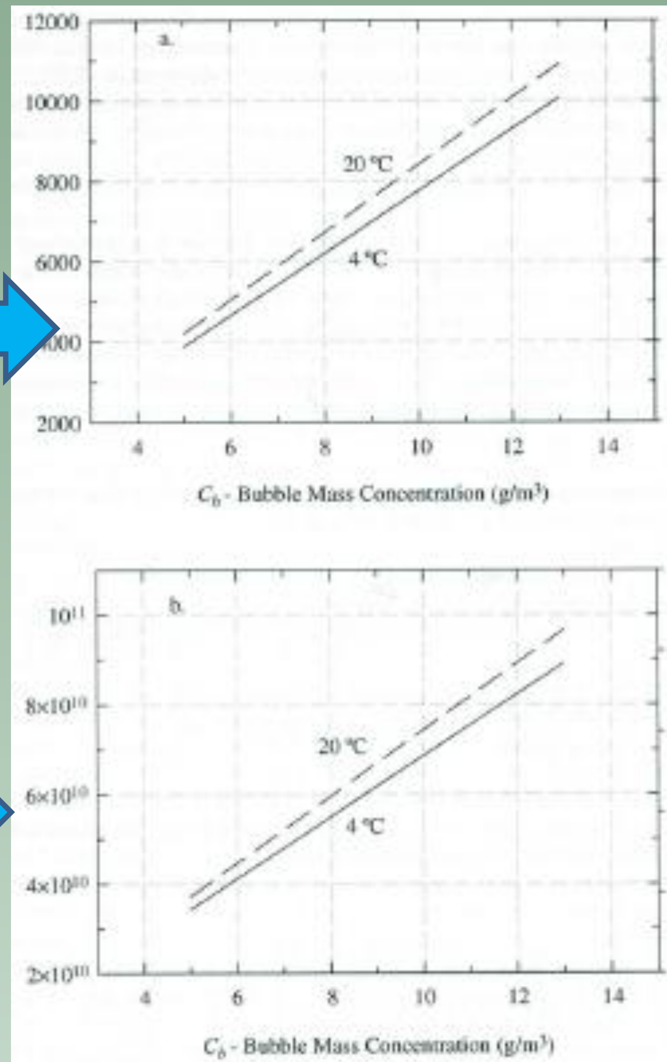
less tankage than DAF for Industrial Water treatment Projects

Typical Air Bubble Volume for DAF

Reference: Edswald, James K.; Haarhoff, Johannes; Dissolved Air Flotation for Water Clarification; American Water Works Association/McGraw Hill , 2012

Air Bubble Volume Concentration Parts per million 10000 = 1%

Air Bubble Number per M^3



Typical DAF Design is 7000 to 9000 PPM

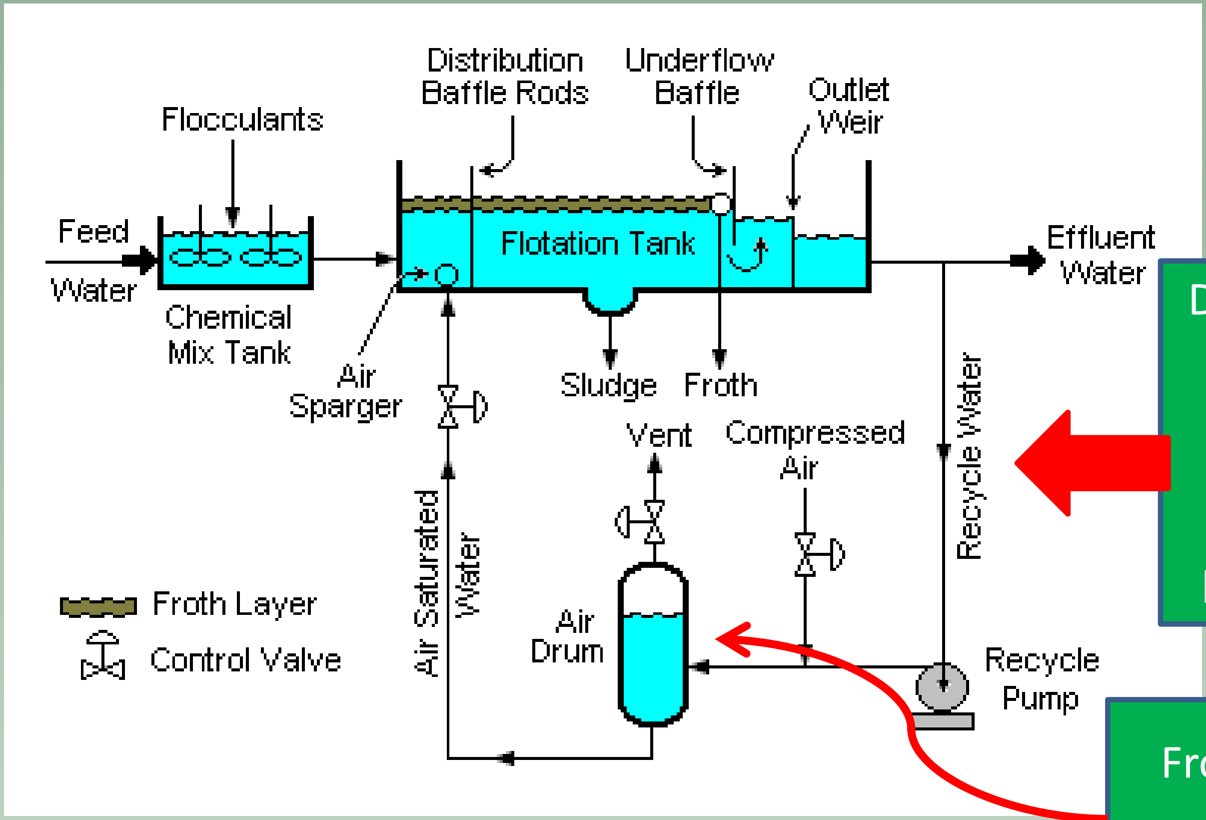
= < than 1%

Floc density in a typical water treatment application is 90 to 100 ppm. Therefore the ratio of bubbles to floc is 100 to 1

Nanoflotation is typically 3 % to 10 %

Result: Much higher number of bubbles and contact with particles

Froth Flotation- Energy Efficient with lower recycle flow and No Compressed Air requirements.



DAF requires 10 to 100 % recycle flow.
Froth Flotation requires 3 % to 10% because of the high bubble concentration

Froth Flotation does not require compressed air

Operating Costs- Froth Flotation more expensive

Froth Flotation uses Surfactant

Assuming Surfactant cost is \$2000/ M^3 the cost per M^3 of treated water is \$0.10 to \$0.20

Dissolved Air Flotation relies on Recycle water pumping and compressed air. The total amount of energy consumption is approximately 0.05 KwH per M^3. At \$0.10 per KwH the cost per M^3 is \$0.005

Air Bubbles attaching to Solid Particles in Water- the Science

Bubble and particle behavior in water is controlled by four forces

1. Van der waal Forces
2. Electrostatic
3. Hydrophobic
4. Hydrodynamic

Hydrophobic forces are the most important forces to have solid particles attach to air bubbles

Use of Coagulants in Flotation Technology

- For Flotation to perform it is important for the solid particles in the water to be neutral
- Particles are typically non polar (hydrophobic) but become negative charged because of Natural Organic Materials (NOM) and natural surfactants in the water.
- NOM and natural surfactants coat the surface of the hydrophobic particles making them negatively charged.
- To neutralize the negative charge, positive charged metal hydroxide coagulants have to be added (Alum, Ferric and Poly Aluminum Chlorides)

Coagulant Addition

- Natural Organic Materials require much more positive charged coagulants to neutralize than inorganic solid particles. (i.e. 5 to 20 times more coagulant)
- The optimum coagulant addition is to neutralize the solids.
- Over dosing will work in the opposite way where the particles will become positive charge and electrostatic forces will repel the solids.

DO NOT OVERDOSE

Impact of Hardness in Water and Total Dissolved Solids (TDS) on Coagulation

The Harder the water or the higher the TDS level the easier it will be to coagulate the solid particles in the water

Impact of Alkalinity in Water on Coagulation

High Alkalinity > 120 mg/l as $CaCO_3$

Medium Alkalinity is 60 to 120 mg/l as $CaCO_3$

Low Alkalinity is < 60 mg/l as $CaCO_3$

The higher the Alkalinity in water the greater the buffer capacity is to keep the pH stable.

- Alum provides higher positive charged particles when the pH is less than 6.5.
- PACl provides higher positive charges when the waters are in the pH 7 range.

A Closer Look At Membranes

MF and UF membranes can be made of polymeric or ceramic materials.

Ceramic

VS

Polymeric

Pressure Driven Membranes – Two formats

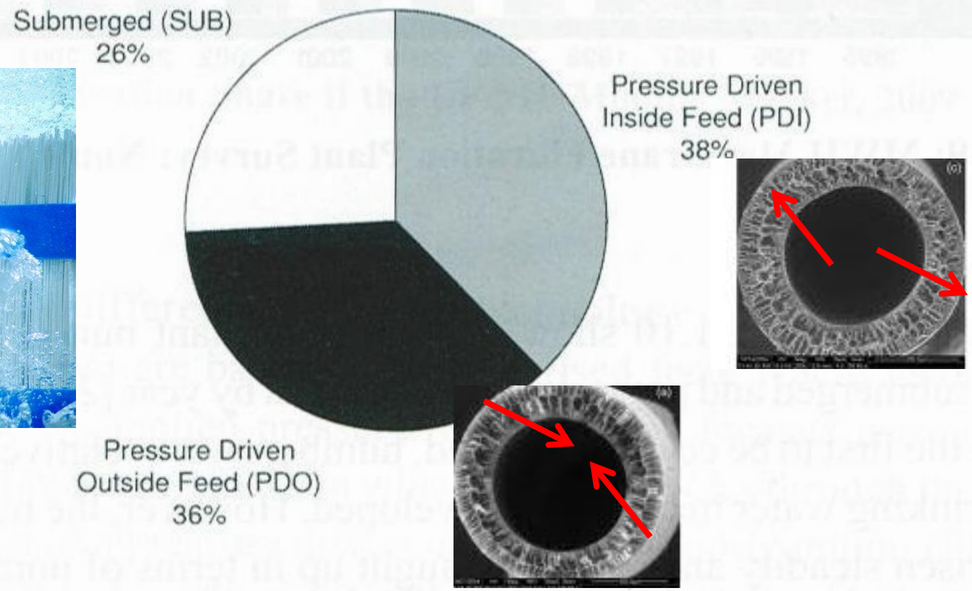


Figure 1.11: Format Share in the Water and Wastewater Market (excluding MBR), 2010

PDO membranes can handle solids in the 100 to 200 µm range
PDI membranes can handle solids in the 85 to 150 µm range
RO Membranes are limited to solids less than 5 µm

Membranes Structure and Strength

- For Membranes to have a reasonable life span, they need to have structural strength, and be able to withstand corrosive environments and high temperatures. Ceramic and stainless steel membranes are better than Polymeric membranes for durability.
- The major problem with membranes is fouling of the membrane surface.
- The surface of the membrane should be smooth, hydrophilic and neutrally charged

- **It is very difficult for all three conditions to occur at the same time**.

Membranes Structure and Ionic charge

Hydrophilic ↔ Hydrophobic

CA

PAN, PES.PS,PVDF,PE,PP

Most membrane materials are Hydrophobic and not Hydrophilic

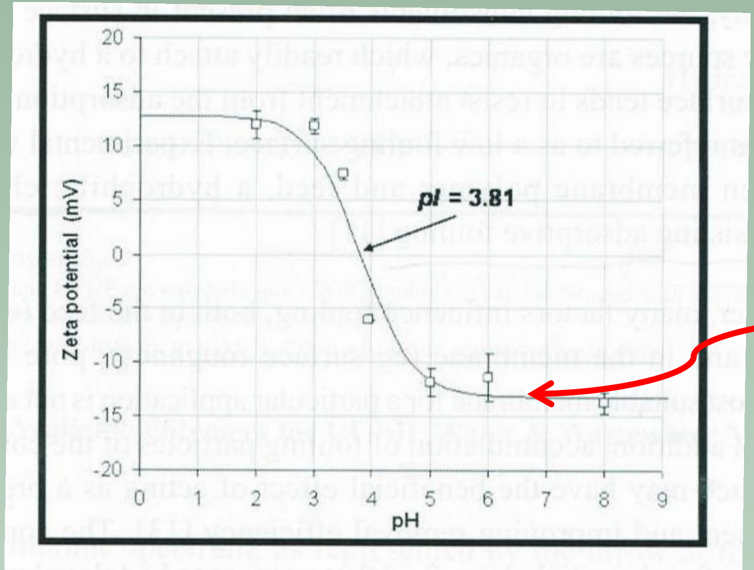


Figure 2.6: Zeta Potential curve for a typical polymer

Most membranes are negatively charged and will attract positive particles and dissolved solids causing scaling

Membranes become fouled

It is impossible to have the perfect membrane surface

- Not smooth
- Most membrane materials are Hydrophobic
- Membranes surface are typically negative charged.

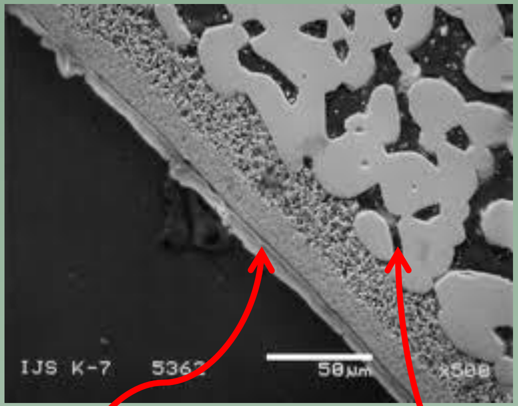
As a result membranes become fouled with the colloidal particles.

Causes of Colloidal Solid Fouling on Membranes

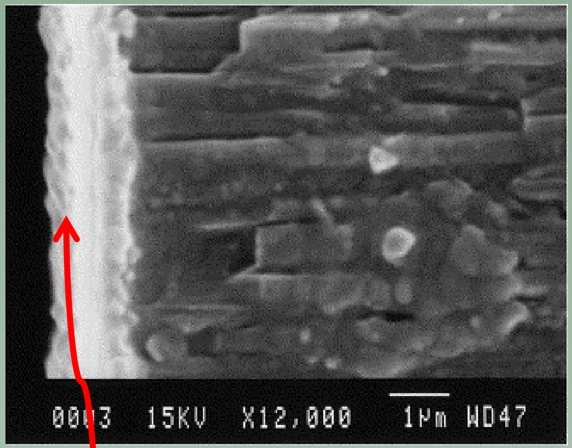
Three of the same four forces discussed earlier, regarding the attraction of bubbles to colloidal solids, are the same forces that cause the fouling on membranes

1. Van der Waal forces which are important in media filtration where colloidal particles attach to other solid particles
2. Electrostatic forces where opposites attract
3. Hydrophobic forces where the particles are driven out of the water to the Hydrophobic surfaces

Membrane layers



Fine Membrane Skin layer (Aluminum, Titanium or Zirconium Oxides) and porous sub layer in ceramic membrane



Fine Membrane Skin layer in Polymeric Membrane

The manufacturing of the membrane skin layer and the attachment of the skin layer is the membranes largest cost factor. Detachment of the skin layer during backwash is a concern

Limited Pressure and Flux (Flow Rate) for membranes

- To reduce fouling the pressure across the membrane (TMP) has to be limited to a maximum of 1 bar.
- For submerged membranes the maximum TMP is 0.7 bar
- Membranes also need to operate at a flux (flow) rate that controls fouling of the membrane. This flux rate is called the "Threshold Flux rate"
- If the flux is above the Threshold Flux rate. **Fouling of the membrane will be very fast**

Cleaning Membranes

Efficiency of the Cleaning Process depends on

1. Chemicals Used
2. Concentration
3. Contact Time
4. Temperature
5. Backwash velocity

All of this can create complications!

Nanoflotation Membranes-
The Fundamental Difference is the Precoat !!!

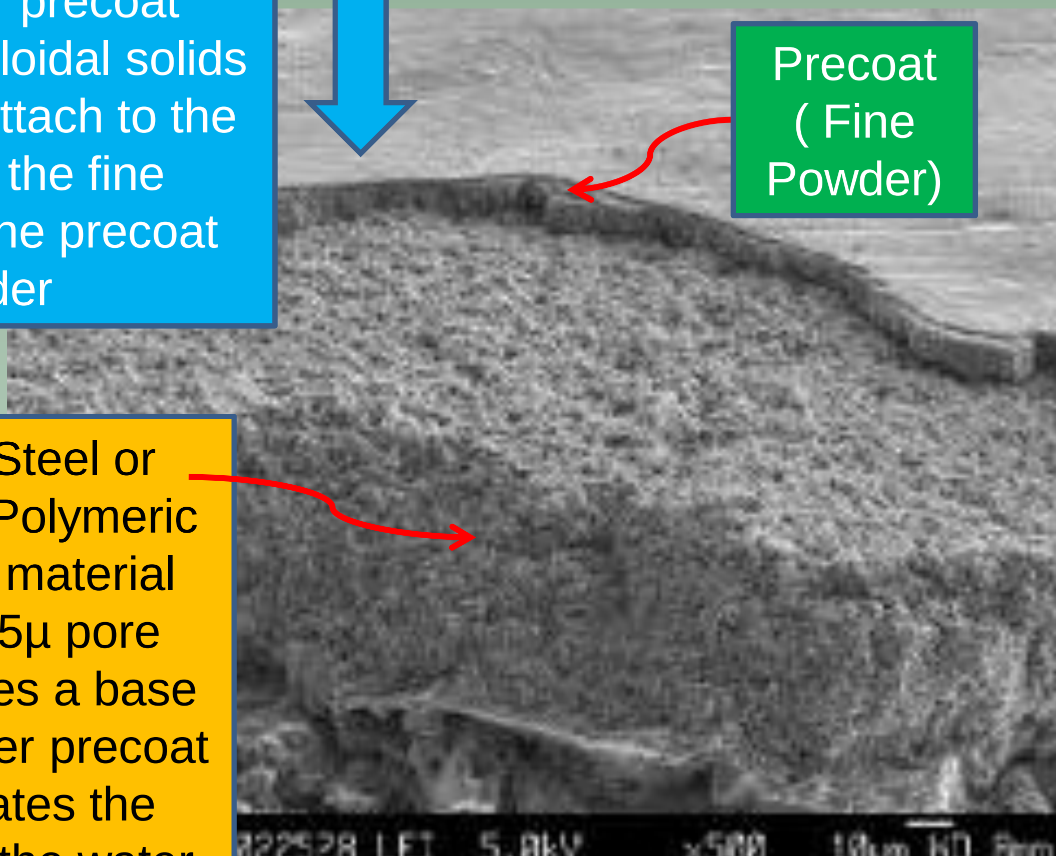
Instead of spending significant effort to stop fouling of the membrane surface, Nanoflotation encourages solid attachment to the membrane surface, because the membrane surface is a temporary precoat.

When the precoat is fouled, the precoat is removed by back washing the membrane and is replaced with a new precoat.

In addition, instead of making the membrane surface a screen or barrier for filtration, the precoat is a media. The media attracts the solids in the water to the media surface by using the three forces that typically cause fouling; Van der Waal, Electrostatic and Hydrophobicity.

Precoat to Create Temporary Membrane Skin Layer. Remove the Precoat layer When it is Fouled

As water passes through the powder precoat media, the colloidal solids in the water attach to the surface of the fine granules in the precoat powder

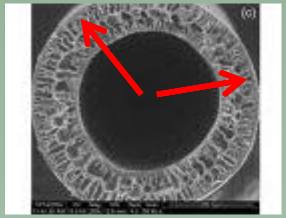


Precoat (Fine Powder)

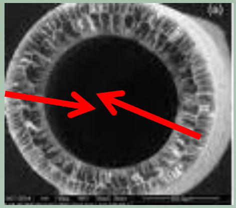
Stainless Steel or Ceramic or Polymeric membrane material with 1µ to 5µ pore size. Provides a base for the powder precoat and facilitates the drainage of the water

Typical Membrane Threshold Flux Rates

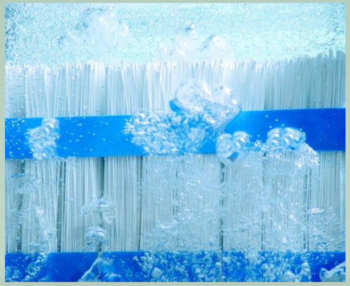
- For PDI membranes the flux rate is typically is 70 to 100 lmh (litres/m^2/hour) and turbidity of the water is < 10 NTU



- For PDO membranes the flux rate is typically is 45 to 65 lmh (litres/m^2/hour) and turbidity of the water is < 30 NTU



- For Submerged membranes, the flux rate is typically is 30 to 45 lmh (litres/m^2/hour) and turbidity of the water is < 30 NTU



Membrane Threshold Flux Rates _ Nanoflotation Pilot test

Flux rate using a precoat of metal oxide powder on Stainless Steel Membrane Tubes and water turbidity < 150 NTU in a submerged application with a TMP of approximately 0.5 bar was

375 lmh

Approximately 10 times higher than typical submerged membranes

Capital Costs

Reference :Cheryan, M; Basic Principals of Membrane Technology,Membrane/Filtration and Other Separation Technologies"Practical Short Course 22 Edition ,Texas A&M, 2012

- Costs for Polymeric membranes = $\$20$ to $\$600/ M^2$
- Cost of Ceramic membranes = $\$1500$ to $\$6000/ M^2$
- Cost of Stainless Steel (base tube only- used in Nanoflotation Pilot Test) = $\$500$ to $\$800 / M^2$

Operating Costs

Reference: Pearce, Graeme K; Uf/Mf membrane Water Pre-treatment Principals and Design, Water Treatment academy and American Water Works Association , 2011

For a polymeric membrane system treating a typical surface water source for drinking water, the typical cost breakdown for M^3 of treated water is as follows

1. Pumping - 9.2% ($0.005/$M^3$)
2. Waste Disposal - 3.6% ($0.002/$M^3$)
3. Chemicals – 14.5% ($0.008/$M^3$)
4. Membrane Replacement – 72.7% ($0.04/$M^3$)

Operating Cost of precoat for Nanoflotation Membranes

The Nanoflotation Design, where a robust membrane structure, such as stainless steel or ceramic tubes, in combination with a precoat, will allow membranes to last for many years.

The cost estimate of the precoat can vary from \$0.004 to \$0.25 per M^3 of treated water

Precoat Optimization Potential and Flexibility

The exciting benefit of the Precoat concept is the ability to customize the precoat for the water being treated and the ability to change precoats over time as the technology improves

Summary

- Nanoflotation has two component

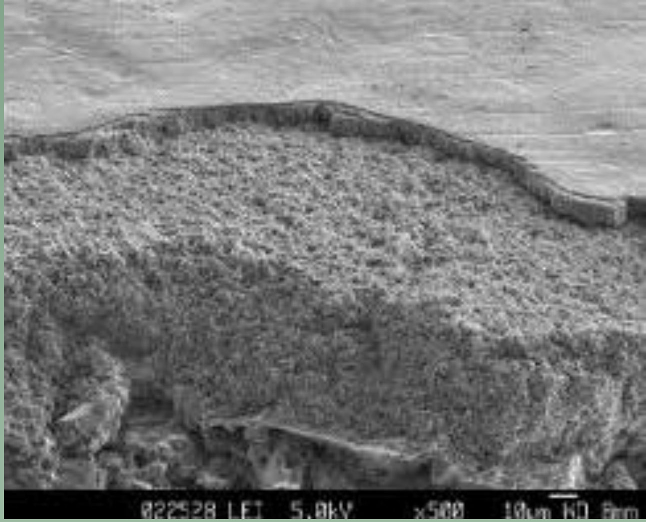
Step 1 Flotation technology

Step 2 Submerged Pre-Coat Membrane technology

Step 1 The Flotation Technology can be either Froth Flotation or Dissolved Air Flotation (DAF)

- Froth flotation is a much lower energy option but requires surfactant which makes it a more expensive operating cost
- It has a lower capital cost because hydraulic loading rates are higher than DAF technology. Tankage can be 50% smaller
- Froth flotation has much higher bubble concentration (3 to 10%) versus DAF (0.7 to 0.9%).
- Froth flotation may be a better treatment option for most Industrial Waste waters

Summary Continued

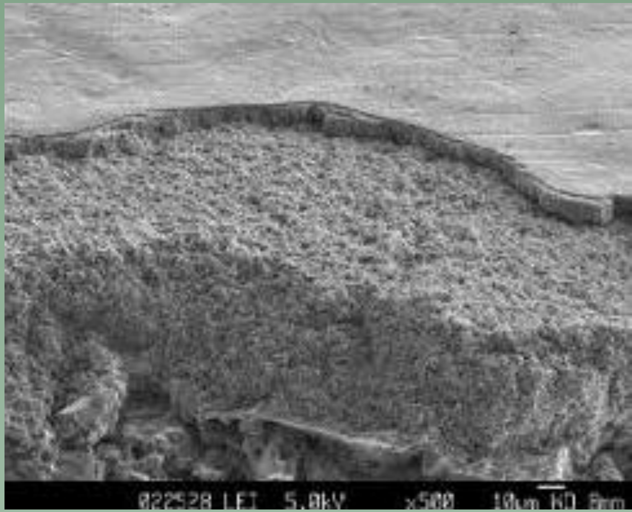


Step 2 Nanoflotation Membrane Technology is unique

It relies on a "precoat" of a fine powder to be the membrane skin layer.

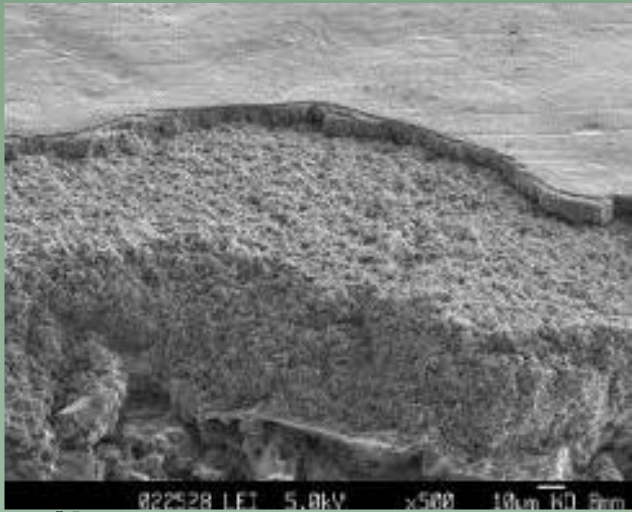
- Fouling of the membrane is not a concern.
- Colloidal particle attachment to the precoat is encouraged.
- Once the precoat is fouled with the attached colloidal particles, the precoat is backwashed, removed and replaced.
- Membrane life is longer and there is no concern about the detachment of the membrane skin layer from the membrane. The precoat is a disposable membrane skin layer.

Summary Continued



- There is a high level of flexibility customize precoat material for specific waste waters or modify over time as the precoat technology develops.
- Loading (flux) rates are significantly higher
- Pilot testing on high solid content water showed consistent colloidal particle removal (99.9% and 150 NTU to < than 0.3 NTU)
- SDI's were < than 2 and many times < 1
- Organic removals were between 20% and 40%

Summary Continued



- The Pilot testing data supports the feasibility of using a pre-coat with a coarse pored membrane to achieve water quality similar to water from a UF membrane.

  (It was a good first test!)

- Further pilot testing is essential to evaluate optimization of pre coat materials, membrane pore size , membrane materials and operation parameters.

Contact Information

Thank you

Questions ?

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